Proceedings of the 3rd International Circular Packaging Conference

3 CIRCULAR PACKAGING CONFERENCE

Ljubljana and online
19th and 20th October 2023

PROCEEDINGS OF THE 3RD INTERNATIONAL CIRCULAR PACKAGING CONFERENCE

3RD CPC 2023

The Proceedings contain peer reviewed scientific and professional papers.

Publishers

Pulp and Paper Institute, Bogišićeva 8, 1000 Ljubljana, Slovenia
Faculty of Polymer Technology, Ozare 19, Slovenj Gradec, Slovenia

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Place and date

Ljubljana, 2023

Kataložni zapis o publikaciji (CIP) pripravili v Narodni in univerzitetni knjižnici v Ljubljani
COBISS.SI-ID **168715779**
ISBN 978-961-90424-9-6 (Inštitut za celulozo in papir, PDF)

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FOREWORD

Dear Readers,

The first time we organized the conference we had luck, the second time it became a pattern and the third time, it became a habit. All people involved already are aligned to organize this conference every second year, and even if it becomes a habit, we still feel lucky to be able to talk and collaborate with amazing companies, authors, researchers, speakers, and stakeholders. In this mutual journey, we must all align and collaborate towards eliminating littering and damage to Nature either through raw material depletion or by the intended or unintended release of toxic components in soil, water, or air.

The only constant on Planet Earth is change. The climate is changing, the world as we know it has changed more dramatically in the last few years and months and the policy on packaging waste at least in Europe is expected to be changed. This will also have a great impact on the packaging landscape, from materials producers, and production companies to the recycling stakeholders which need to fulfil the demand for recycled content ratio. But we must not forget that the circularity hierarchy starts with reducing and rethinking the processes and the whole supply chain and product lifecycle. So we must all also change, to see the big picture, not the small conveniences.

This conference is also changing as new young forces will carry the torch and organization of this conference further to expand this community and enlarge the circle of collaborators. The new generations will hopefully make their habit of coming to Slovenia every second year to the Circular Packaging Conference.

In the name of all involved in the organization, I want to thank the sponsors, authors, companies, and reviewers for their efforts and dedicated work to make this event happen again. I want to personally thank the organizing team and especially Urška and Gregor who put great effort into organizing and elevating this conference to new heights through all these changes.

In Ljubljana, 19th October 2023 *PhD Igor Karlovits*

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ENZYMES AS INNOVATION FOR BIOBASED PACKAGING AT THE FOOD VALUE CHAIN

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Original scientific paper
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Abstract: *Despite the ultimate and global goal should be reducing the amount of packaging used and/or substituting the plastic by biobased ones, some goods will require to be packed. For instance, small fruits such as berries have to be sold together, certain fresh products need to be protected with a case to prevent damages, and others need to be packaged to extend their shelf-life and maintain adequate organoleptic properties. For this reason, an outstanding advance in packaging material, with consistent features and appropriate cost-benefit, will lead to a decrease in food waste and less use of plastics, which causes so much damage to the environment. Thinner plastic films and containers contaminated with food usually can´t be recycled or used for food contact applications, limiting their reuse. Compostability can be a preferred end of life for such type of packaging. Several commercial materials are available, being polylactic acid one of the most used biopolymers due to their characteristics and price. However, PLA is industrial compostable but not home compostable. In this study, biobased matrices based on PLA and Biodolomer® and an enzymated Master Batch providing enhanced compostable properties to the final packaging, have been used. The enzymated masterbatch can increase the compostability in a 20%-30% (to be labelled as home compostable) together with an increase of compostability of packaging with a thickness above 2 mm.*

Keywords: biodegradability, compostability, enzymated masterbatch, PLA matrix, packaging.

1 INTRODUCTION

Currently, there are no cost-effective, home-compostable materials with high bio-content rate that complies with food packaging requirements (resistance, transparency, compostability and food safety requirements). 86% of plastics that are used for packaging are bio-based but non-biodegradable, such as bio-based PET. In the case of rigid packaging, according to TÜV Austria database, only 32 rigid packaging products have been certified "OK Compost Home". For instance, the EU project FRESH developed and upscaled performant cellulose-based trays. Other products include trays made of sugarcane pulp, natural fibres, or paper but none of these solutions combine home-compostability & transparency.

Materials with high PLA content are difficult to process. Their low viscosity and melt strength cause problems during extrusion such as bubble instabilities or excessive neck-in during extrusion. Also, PLAs brittle nature makes it hard to process as thin film and requires blending with other cheaper & less environmental-friendly polymers (Robertson GL, 2012). All those issues impend scaling up and a lot of effort is set towards optimisation of blends and extrusion processes. Also, Biodolomer®, a high-quality mineral filled biomaterial is in a validating phase although is opaque, so it is useful in non transparent applications.

These options present several advantages, including low environmental impact and maintained properties. While both, PLA and Biodolomer, are ready for industrial scale production, very few food packaging applications currently rely on these raw materials. Indeed, it is mostly used in the cosmetic sector or for cups.

Furthermore, the various possible end-of-life for these packaging solutions includes the usual recycling (mechanical and chemical), incineration and composting/biodegradation options. Mechanical recycling and home-compostability of packaging biobased materials are poorly developed in Europe and have limitations for subsequent reuses.

Even if chemical recycling is virtuous for single-layer packaging, recycling in a broader sense is currently not suitable in Europe for multi-layer packaging, which is mostly incinerated or landfilled. Some approaches are available to tackle this challenge but are still at an early stage of industrial development, such as the solvent based CreaSolv® technology or the use of removable barrier layers. In the case of multi-layer packaging, which is widely used in the food sector, the development of compostable solutions, would enable to address this lack of suitable and sustainable end of life options.

In this sense, enzymes can help to manufacture fully biodegradable compostable plastics especially for PLA-based products. It is then of high interest the combination of transparency and home compostability for film products, so the customers can see the product inside but also high thickness packaging (although non transparent) with home compostability features for rigid packaging as trays, as unique selling points which cannot be achieved by any other biopolymer available as of today.

2 MATERIAL AND METHODS

2. 1 Materials

Compostable bioplastics were obtained by mixing selected biopolymers, an enzymatic masterbatch, which is a *compound made with PLA base and protected enzymes to have enough enzymatic activity,* and other additives to improve material final performance in a conventional extrusion compounding process (Coperion ZSK26 co-rotating twin-screw extruder, semi-industrial) at AITIIP facilities (Zaragoza, Spain). The compounded materials were afterwards dried (Mini dryers Moretto X DRY AIR T) to ensure a low water level content that could negatively affect to the product properties.

The compostable materials selected were PLA (Natureplast, France) and Biodolomer (Gaia, Sweden). Films were based on Natureplast PLE 005-A and Biodolomer I for injection moulding. The enzymated masterbatch was added at a 5% for film packaging and at a 10% for rigid packaging (thickness above 2 mm). Due to industrial secret is not possible to indicate the exact percentages used and other additives used.

Table 1. Samples references, description, and main composition.

Reference	***Description***	***Matrix***	***Enzymated mastebatch***
SSTF5-23	*Stretch film*	*PLA*	*5%*
SFSF6-23	*Flow pack film*	*PLA*	*5%*
SRP2-23	*Injection moulding*	*BIODOLOMER*	*10%*

2. 2 Production of demonstrators

The materials compounded were transformed into final products films and cosmetic jars, the extrusion blow moulding machine (LABTECH LBM 125, semi-industrial) equipped with a Laboratory Extruder Types LE25-30/C and LE30-30/C Manufactured by: Labtech Engineering Co., Ltd. Was used to obtain the compostable films. Stretch films were produced with different thicknesses

between 15-50 microns and a width of 23 cm, samples for flow pack were produced with thickness between 50-70 microns and width of 31 cm.

The injection moulding machine with an 800 kN clamping force (KraussMaffei 80/380 CX) for processing of thermoplasts, was used enabling fast and cost-effective prototype jars production (Lid: ± 4.3 mm (edge) and ± 5.9 mm (top) – Outer cup: ± 6.3 mm (sidewall), ± 4.9 mm (bottom) – Inner cup: ± 1.0 mm (sidewall), ± 0.9 mm edge and ± 1.0 mm (bottom)). Specimens for mechanical testing were obtained by injection moulding with a JSW 85 EL II electric injection machine (Tokyo, Japan) by following ISO 178 and ISO 527 standards. These were tested and broken samples were used to study the structural properties.

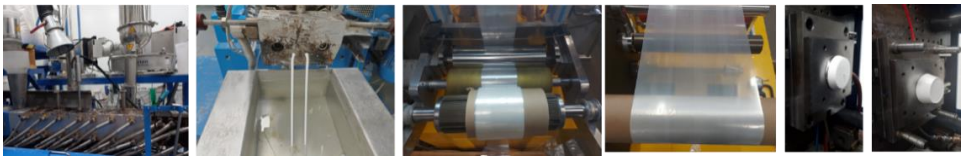


Figure 1. From left to right, extrusion-compounding, film blowing for and injection moulding processes.

2. 3 Characterization Analyses

2. 3. 1 Tensile and Flexural Testing

Mechanical tests were conducted under ambient conditions using a Zwick Roell Z 2.5 (Zwick GmbH & Co. KG, Ulm, Germany). At least five specimens per material were tested, according to ISO 178 (flexural properties) and ISO 527 1-2 (tensile test) methodology. The distance between the grips was set to 60 mm. The presented values of elasticity modulus (Et), bend strength (σM), and elongation at break (εb) are an average from at least six replicates from each final material.

2. 3. 2 Home compostability ("OK compost HOME" scheme, developed by TÜV Austria)

The Home compostability is carried on according to the "OK compost HOME" scheme, developed by TÜV Austria, as international recognised Certification Body, taking into account that there is no existing international recognised standard method specifically addressed to the evaluation of the compostability under domestic condition. This scheme defines that the EN 13432 standard is applied at lower temperatures (between 20°C and 30°C) and increased test duration (1 year for biodegradation according to ISO 14855-1 and 6 months for disintegration according to ISO 16929) compared to the industrial compostability.

2. 3. 3 Biodegradability test (ISO 14855-1:2012)

Biodegradation is tested at ambient temperature (between 20°C and 30°C) and maintained below 30°C for all test duration.

The required percentage of biodegradation is the same as specified in EN 13432, namely absolute or relative 90 % (compared with cellulose microcrystalline, as reference material), assessed based on the organic carbon that is transformed into carbon dioxide during the composting process. The period of application for the Home biodegradation test is 12 months as maximum duration.

All constituents and their maximum concentrations as specified on the positive list are regarded as fulfilling the biodegradation requirements as defined by the Certification Body.

2. 3. 4 Disintegration test (ISO 16929:2021)

To determine the degree of disintegration of plastic materials in a pilot-scale aerobic composting test under defined conditions the test method ISO 16929:2021 has been followed. The pilot-scale aerobic composting test simulates as closely as possible a real and complete composting process in composting bins of 200 l. The test item is mixed with the organic fraction of fresh, pretreated municipal solid waste (biowaste) and introduced in an insulated composting bin after which composting spontaneously starts. Like in full-scale composting, inoculation and temperature increase happen spontaneously. The test is considered valid if the maximum temperature during composting is below 30°C. The composting process is directed through air flow and moisture content. The temperature and exhaust gas composition are regularly monitored. The composting process is continued till fully stabilized compost is obtained (6 months). During composting, the contents of the vessels are turned manually, at which time test item is visually evaluated. Disintegration is defined as a size reduction to pieces < 2 mm at the end of the test.

3 RESULTS AND DISCUSSION

3. 1 Mechanical properties

The flexion modulus (Ef), flexion strength (σM) and elongation at break (εb) are presented in table 2. The values are compared to control samples, with the same composition except for the addition of the enzymated masterbatch. In general, the values of the flexural modulus obtained for the resulting materials with addition of enzymated masterbatch significatively decrease in all the samples, flexible and rigid packaging. The values obtained for the bending strength also decreased significantly with the addition of the enzymatic masterbatch and the

elongation at breack slightly increases. This means that the materials need less strenthg to bend and that the elongation is higher until they break, so are more elastic materials compared to the control ones.

Table 2. Flexural results.

Sample	***E_f (MPa)***	***σ_m (MPa)***	***ε_b (%)***
$Control_{(SSTF5)}$	*1176 ± 24*	*33.2 ± 0.3*	*4,88 ± 0,1*
SSTF5	*627 ± 17*	*24.8 ± 0.3*	*5.51 ± 0.15*
$Control_{(SFSF6)}$	*2633.80 ± 42.45*	*75.36 ± 0.57*	*3.79 ± 0.03*
SFSF6	*1922 ± 160*	*60.5 ± 1.3*	*3.85 ± 0.1*
$Control_{(SRP2)}$	*2708 ± 23*	*55.9 ± 0.7*	*3.26 ± 0.11*
SRP2	*2220 ± 33*	*49.5 ± 0.5*	*3.46 ± 0.02*

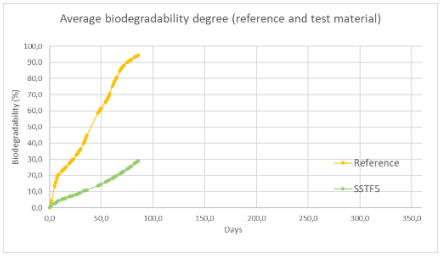
Results for tensile modulus (Et), tensile strength (σM) and elongation at break (εb) are presented in table 3. The values are compared to control samples, with the same composition except for the addition of the enzymated masterbatch. In general, the values of the tensile modulus obtained for the resulting materials with addition of enzymated masterbatch significatively decrease in all the samples, flexible and rigid packaging. The values obtained for the tensile strength also decreased significantly with the addition of the enzymatic masterbatch and the elongation at breack slightly increases. This means that the materials are less hard than plain PLA or Biodolomer controls.

Table 3. Tensile test.

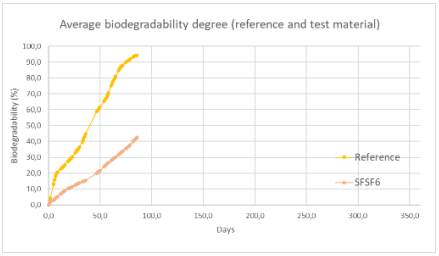
Sample	***E_t (MPa)***	***σ_m (MPa)***	***ε_b (%)***
$Control_{(SSTF5)}$	*1378 ± 105*	*21.4 ± 0.7*	*3.06 ± 0.17*
SSTF5	*670 ± 57*	*11.9 ± 0.5*	*4.04 ± 0.34*
$Control_{(SFSF6)}$	*2637.80 ± 93*	*49.84 ± 0.3*	*3.38 ± 0.23*
SFSF6	*2041 ± 124*	*36.4 ± 0.4*	*3.4 ± 0.09*
$Control_{(SRP2)}$	*2549 ± 74*	*31.6 ± 0.6*	*2.27 ± 0.07*
SRP2	*2057 ± 89*	*26.9 ± 0.7*	*2.37 ± 0.05*

3. 2 Biodegradation results

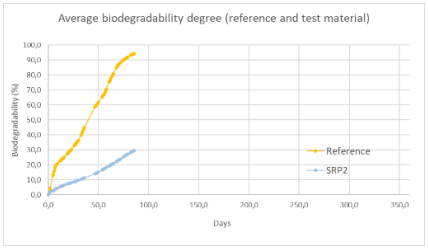
After 85 days of biodegradation, PLA based samples for film packaging with a 5% of enzymatic masterbatch and a thickness of 50 microns, reached between a 40% and a 30% of biodegradation. Although the injected sample has higher thickness (Lid: ± 4.3 mm (edge) and ± 5.9 mm (top) – Outer cup: ± 6.3 mm (sidewall), ± 4.9 mm (bottom) – Inner cup: ± 1.0 mm (sidewall), ± 0.9 mm edge and ± 1.0 mm (bottom)) the Biodolomer based sample and with 10% of enzymatic masterbatch also reached a 30% of biodegradation. In conclusion, the samples are performing well and will reach the biodegradation necessary to comply with the standards.



SAMPLE SSTF5 vs Reference



SFSF6 vs Reference



Sample SRP2 vs Reference

Figure 2. Biodegradation results.

3. 3 Disintegration results.

The disintegration of the cosmetic jar SRP2 proceeded well in spite of the quite high thickness of the product. The different parts (lid, outer cup and inner cup) of the cosmetic jar were evaluated separately for disintegration, but also the complete jar with closed lid was examined to simulate worst-case conditions. Figure 3 shows a visual presentation of the contents of a test bin with SRP2 (last picture), after 85 days of composting. According to previous experiences the cosmetic jar SRP2 has the potential to be compostable at home composting conditions. As for the films, they were produced with PLA matrix and a 5% of enzymatic masterbatch with lower thickness than the injected jars, also have the potential to disintegrate under home composting conditions. In a next stept the other requirements of EN 13432 will be examined and the overall home compostability performances will be verified.

SSTF5 *SFSF6* *SRP2*

Figure 3. Home disintegration tests on selected formulations & samples 2023.

4 CONCLUSIONS

The present study has shown that enzymated masterbatch can be an interesting alternative to enhance biobased and compostable sustainable packaging, contributing to create a new value chain and to the circularity of the European Economy.

The tensile and flexural properties are influenced by this additive and the results shows that the samples are less rigid and more flexible than those made of PLA and Biodolomer without the enzymated masterbatch.

The small variation on the tensile strength confirmed good mixture. The addition does not limit the chain movements in the polymer system and resulted in lower stiffness and higher elongation at break.

Finally, the cosmetic jar and the developed films have the potential to be compostable under HOME composting conditions. After 85 days, the biodegradation reaches a 30%-40% and the disintegration is ongoing as expected even in high thickness samples, thanks to the enzymated masterbatch.

Acknowledgement: *The research leading to these results has received funding from the European Union's Horizon 2020 Research and Innovation programme under Grant Agreement No 101037796.*

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VALUE CHAIN GENERATOR

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Professional paper
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Abstract: *The circular bioeconomy can significantly reduce waste and lower the need for mining of primary new materials, but many companies are unable to find and connect with businesses that can utilize their bioresources. In this context, VCG.ai plays a vital role. The Value Chain Generator (VCG) is a digital solution that matches companies based on their resources, including waste, within the scope of the circular bioeconomy. Leveraging artificial intelligence, big data, and machine learning, VCG empowers clusters, business support organizations, and companies to explore and develop new value chain designs, fostering knowledge transfer and enhancing overall knowledge in this economic field. It also connects stakeholders in the regions and beyond.*

VCG finds unexploited business opportunities for bio-based value chains based on available data to overcome the existing information gaps. It matches companies according to their resources, including waste, and on established good practices in value chain design. New value chain designs are done by matching production inputs and outputs across industrial sectors. VCG also provides a knowledge transfer network by facilitating the sharing of good (bio)links with other clusters and organisations to increase the overall knowledge. The good practices shared within the system can be applied to individual companies, enabling them to find the right partners to implement selected circular value chain models.

For example, in a new circular business model, waste, particularly bio-waste, can be transformed into bio-plastics through a process of bioconversion or chemical recycling, offering a sustainable alternative to traditional, petroleum-based plastics. This approach not only gives a second life to waste materials, reducing landfill and environmental pollution, but also aids in the creation of a circular economy, where waste is viewed as a valuable resource not as an endpoint.

Keywords: circular economy, bioeconomy, value chains, bioresources

1 INTRODUCTION

Every year, agri-food value chains waste staggering amounts of resources - equivalent to one-third of all food produced for human consumption – culminating in a severe environmental problem (Searchinger et al., 2018). The repercussions are far-reaching, with annual food loss & waste emerging as the world's third largest emitter, trailing only behind the entire economies of the US and China. The financial burden is equally significant, with the industry incurring tens of billions of euros annually in Europe alone (Poore & Nemecek, 2018)).

At this pivotal moment, governments and industries are investing billions into climate solutions, and companies are committing to science-based targets and climate goals. We stand on the threshold of a transformative wave where sustainable practices will shape the future of business. The global market for new circular products from agri-food value chains is projected to reach over 2.6 trillion € by 2030 (WBCSD, 2020). Alongside the growing pressures for sustainability, this presents a compelling financial incentive for companies to explore circular solutions and diversify their business. Many companies are working hard to change their business in the hope of getting additional value streams and becoming less vulnerable to the changes we are facing. Various studies imply that reorganising value chains is imperative to make them more resilient (CIRAIG, 2015). And while the world is turning to the circular economy, and bioeconomy to become more sustainable, companies are having trouble making the necessary changes. Circular business models enable a step towards these objectives (Hansen & Revellio, 2020). Nevertheless, it is a challenge for them to find compatible actors in the newly created value chains. Many companies have abundant bioresources that could be further utilised for new products or services but have trouble finding and connecting with a business that could take advantage of their resources. On the other hand, a company might be searching for bioresources and wouldn’t know where to turn.

1. 1 Value creation

The value chains needed to create business between companies in the scope of circular bioeconomy are in many cases completely missing. Companies are still trapped in the linear way of thinking, where the value creation is straight forward and end-of-life for the product is waste disposal or, at best, recycling of its parts.

Business models in a circular economy offer a wider selection of value creation approaches than in linear value chains. The reason is that instead of simply

relying on consumption, value is created based on the use (CIRAIG, 2016). Circular business models support the prolonged lifetime of a product by following the 4R principle of repairing, reusing, remanufacturing, and recycling (Tapaninaho & Heikkinen, 2022). Focus is shifted from a single use cycle to resource recovery and multiple use cycles to preserve the value of the products, materials, and parts as long as possible. Additional life cycles are created to enable even more possibilities for valorisation. Consequently, waste is reduced or used as a secondary raw material, which in turn reduces the need for mining of primary new materials.

To achieve multiple value creation, a number of stakeholders from various circular economy system levels must work together in a collective and interorganisational way (Tapaninaho & Heikkinen, 2022). New and diverse value networks for cycling resources and parts must be created. Value chain actors must collaborate to secure viable links between them, for example, to deliver a constant quality and quantity of secondary raw materials (SRMs). SRMs are technically the materials that can be recycled and then injected back into the economy as new raw materials (European Commission, 2015). They are typically obtained either from production waste or from End-of-Life products, sent to recycling plants at the end of their lifespan (RMIS).

1. 2 Digital tools

Circular economy has already gained a very important place in EU politics. Consequently, many countries have adopted accompanying regulations and tax measures, for example, to support repair and reuse of products instead of disposing and recycling their parts. The policy is also trying to extend the warranty period for products to discourage their low quality and short-term usage. Boosting the circular economy plan in EU, supported by the Commission's EU Circular Economy Action Plan (March 2020), includes measures along the entire life cycle of products promoting circular economy processes, fostering sustainable consumption, and guaranteeing less waste. The focus is currently on the food chain, textiles, packaging and plastics, construction and buildings, batteries and vehicles, electronics, and ICT.

To enable the necessary changes for the transition to a circular economy, technological development is one of the crucial drivers. New technologies will enable the circulation of energy and materials, improve resource efficiency and utilisation of secondary raw materials, including what has been until recently considered as waste. Digitalisation plays a very important role in this scenario as the digital environment supports a broad range of platforms that connect suppliers to producers.

Underdeveloped or non-existing technology is currently an important barrier that can hinder company's ability to adopt the circular approach. It may not be technically possible to reuse, refurbish, or remanufacture existing products to meet current performance demands. Concerns also exist about the technical performance properties of recovered and recycled materials.

While circular business models' goal is to replace primary production and enable environmental sustainability, there can be situations when circular offerings do not deliver environmental benefits. For example, recycling and remanufacturing of products can be very energetically demanding. Circularity thus doesn't inherently imply sustainability and must be actively driven in this direction. Companies therefor need a system that not only establishes circular value streams but enables them to evaluate the outcomes of various circular solutions.

2 METHODS

In the face of increasing sustainability demands, VCG.AI offers a transformative solution. Our pioneering AI & big data platform is designed to convert waste in bio-based value chains into lucrative circular opportunities. By analyzing companies' production processes and local industries' material flow data, the platform aligns with various mandatory and voluntary circular economy reporting standards, addressing the challenges many companies face due to decentralized data on their material and waste streams.

Central to VCG.AI's methodology is the BioLink models, a smart matching system that seamlessly connects businesses with the right technology, service, and supply chain partners. Our platform's strength is derived from its proprietary database and unique matching engine, which pinpoints high-potential circular solutions for companies and suggests prospective partners for implementation. Integrated with the widely-used ERP system, Oracle, VCG.AI ensures that businesses are expertly paired with the most efficient circular solutions and partners, setting the stage for a sustainable and profitable future.

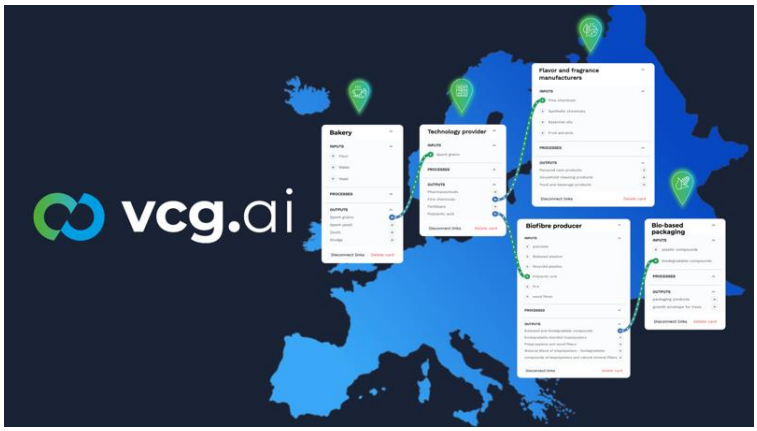

Figure 1. An example of building new value chain with VCG.ai.

3 CASE STUDIES

3. 1 Bioplastics from Organic Waste

Bioplastics, as alternatives to conventional petroleum-derived plastics, have garnered significant attention due to their potential to mitigate global pollution concerns. Derived primarily from renewable sources, these bio-based and/or biodegradable materials can be produced using various feedstocks, including agricultural residues and food waste. Organic waste, especially food waste, represents a significant fraction of the municipal solid waste stream (Gustavsson et al., 2011). These organic waste streams are a rich source of carbon and can be converted into high-value products such as bioplastics through biological or chemical processes (Kourmentza et al., 2017).

Acquavia et al. (2021) highlighted the utilization of fruit and vegetable wastes as raw materials for bioplastics production, emphasizing the potential of these waste sources to be converted into biomaterials through both simple and complex processes. Gröndahl et al. (2021) further explored the promise of lignocellulosic biomass from agricultural and industrial waste sources, particularly focusing on nanocellulose production from non-wood waste sources and its diverse applications.

The conversion process typically involves hydrolysis of organic waste to fermentable sugars, which are then converted into lactic acid or polyhydroxyalkanoates (PHA) using specific bacteria in a fermentation process (Chen, 2009). These bioplastics can be used in a variety of applications, including packaging, agriculture, and medicine (Avérous & Pollet, 2014).

3. 2 Breweries residues as a resource

The food and beverage industry is increasingly focusing on sustainable practices and circular economy principles to mitigate environmental impacts. Breweries produce a large amount of waste or residues that still contain significant amounts of nutrients and minerals, including carbohydrates, proteins, fibers, and fat. To produce 100 L of beer, around 20 kg of waste is generated (Adams et al., 2022). Traditionally, these by-products have been used as animal feed or disposed of in landfills (Biala et al., 2017). However, their use is much wider, encompassing the production of high-value products like PHA or extracting enzymes, polyphenols, antioxidants, and various chemical compounds (Ganeva et al., 2020; Cimini & Moresi, 2021; Cuomo et al., 2022).

To become truly circular, several challenges have to be overcome. For example, the high moisture content of Barley Spent Grain makes it prone to microbial spoilage, thus it is challenging to transport it to other processing sites (Cuomo et al., 2022). Costs for drying BSG greatly increase the price of the dried product compared to analogous conventional lignocellulose residues (Cimini & Moresi, 2021).

Recently, the bioconversion of brewery waste into high-value products using insects has emerged as a sustainable alternative. Black soldier fly (Hermetia illucens) and the common housefly (Musca domestica) are among the insects found to be effective in converting organic waste into protein-rich biomass (Cickova et al., 2015). The insect-derived protein can be used as a sustainable alternative to fishmeal or soy in animal feed, which has the potential to alleviate pressures on marine ecosystems and reduce the carbon footprint associated with soy cultivation (Makkar et al., 2014). Frass, as an organic fertilizer, also contributes to sustainable agriculture practices by reducing the dependence on synthetic fertilizers and enhancing soil health (Lalander et al., 2015).

3. 3 Algae as a bridge between companies in circular economy

Algae can be utilized to create a sustainable closed-loop system by treating wastewater, reducing pollution, and producing biomass (Mohsenpour et al., 2021; Berden Zrimec et al., 2020). Algae cultivation in wastewater offers oxygenation benefits, and the harvested biomass can be used for various applications, reducing the need for energy-intensive treatment processes. In biogas plants, algae can stabilize the liquid phase of anaerobic digestate (Figure 2), which is rich in nutrients, reducing storage, transportation costs, and greenhouse gas emissions (Berden Zrimec et al., 2023; Rossi et al. 2023; Bauer et al., 2021).

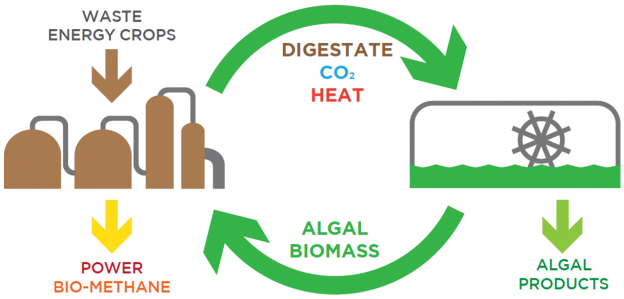

Figure 2. Circularity in biogas plants with algal systems (source: Algen, algal technology center, llc (www.algaebiogas.eu)).

Macroalgal biomass can be stabilized through composting or pyrolysis for agricultural use (Cole et al., 2016). Composting uses algae as a nitrogen source, while pyrolysis converts it into biochar, which enhances soil quality, nutrient retention, and promotes soil microbiota. The algal biomass is also rich in amino acids, fatty acids, and vitamins, making it an ideal raw material for a biorefinery approach to produce biofuels, bioplastics, cosmetics, and aquafeed, among other products (Tawfik et al., 2022).

Algae can also be integrated into existing technological systems without requiring major structural changes, making them attractive for industries. They can be added to wastewater treatment systems or industrial technologies as side-streams (Mohsenpour et al., 2021; Oviedo et al., 2022). For instance, algae raceway ponds can reduce the production of sludge in wastewater treatment.

For the successful implementation of algae cultivation in wastewater or digestate, innovative business models are essential (Bauer et al., 2021; Lawton et al., 2017). These include producing algae for specific industries, developing integrated systems for wastewater treatment and resource recovery, forming circular economy partnerships, generating carbon credits, and creating direct-to-consumer products. These models can help in creating sustainable and profitable businesses while contributing to a circular bioeconomy.

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EVALUATION AND ENHANCEMENT OF RECYCLABILITY FOR COATED PACKAGING PAPERS

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Original scientific paper
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Abstract: *In order to meet the European target for recyclability of packaging materials in general, and paper packaging in particular, harmonized guidelines have recently been published to test and assess the recyclability of coated papers, based on repulping and screening of recycled fibers in combination with visual evaluation of the quality of papersheets. Based on a design-for-recycling strategy, a first estimate can be made for the recyclability of current paper coatings, but the constant new developments in the sector and the commercialization of new coating materials require a standardized framework for experimental evaluation of recyclability. In this study, the testing protocol was validated in relation to variations in the repulping conditions such as repulping temperature, and number of revolutions for a selection of industrial packaging papers, including acrylic dispersion coatings or LDPE laminated paper. The testing procedure seems robust as influences of repulping temperature are inferior in the range of 30 to 50°C, while the influence of the number of revolutions is more critical and levels off within a given operation window. The statistical differences between repulpability of non-recyclable and recyclable packaging papers are detected in a benchmarking study against newspaper or tissue paper. For difficult-to-recycling papers, opportunities for improvement of coating removal or valorization of mixed fiber/coating brokes collected in the reject fraction should be further explored. As such, the functionality and circularity of coated papers can simultaneously be enhanced.*

Keywords: packaging paper, coating, recyclability, testing

1 INTRODUCTION

The paper and paperboard materials have become a widespread origin for alternative packaging materials and are more often considered as potential replacement for traditional single-use plastic packaging. They benefit from the renewable origin of cellulose fibres, their high specific strength, flexibility, and light weight. Depending on the needs for food packaging purposes, the paper properties can be adapted towards required barrier properties against water, oxygen, moisture, oils, and aroma by application of a coating (Tyagi et al., 2021). In view of their use in a more sustainable and circular economy, the recycling of coated packaging papers and recovery of the fiber fraction is preferred above biodegradation or composting (Sridach et al., 2006). Indeed, ambitious targets are set both at European and Belgian level. European legislation dictates that 65% of all packaging waste needs to be recycled by 2025 and even up to 70% by 2030 (European Commission, 2020). On Belgian level, the Belgian Food Industry states that all food packaging should be recyclable, reusable, or biodegradable by 2025 (FEVIA, 2021). A renewed focus on paper-based packaging materials has therefore been put in parallel with the development of novel and barrier coatings for better preservation and shelflife of the packed food, while being compatible with the paper recycling process.

The conventional barrier coatings of extruded polyethylene are difficult to recycle as a significant fraction of the paper fibers remains embedded in the PE film and is not easily recovered by repulping (Bilek et al., 2021). Alternatively, the separation of a PLA melt coating may also be problematic due to its strongly hydrophilic properties (Kunam et al., 2022). As a result, both the coating fraction and the recovered fibers are highly contaminated and have low value for recycling, while additional layers eventually need to be developed as an intermediate release coating (Al-Gharrawi et al., 2021). However, the design of multilayer coating systems should be avoided to reduce the complexibility of recycling (Koppolu et al., 2019). A series of waterborne dispersion coatings are promising for recycling, where the emulsion particles will either stick to the fibers or fillers and/or can be more easily separated during the stock preparation via screening (Kathuria et al., 2022). The repulping yield of acrylic emulsion coated papers was reported to be potentially above 99% with little contamination of the wet-end process (Lee et al., 2020). Depending on the composition of the polyacrylate-based polymer, however, the problems with disintegration of the coating on a pilot pulper were reported as a fraction of soft flakes could not be removed by slot screening due to the large deformability of the coating fragments (Lee et al., 2017): consequently, additional mechanical treatment of the accept fraction was needed for fragmentation and removal of the

contaminants up to 95%. Alternatively, the bio-based dispersion coatings of hydroxypropylated starch and hydroxypropyl cellulose may also cause high number of rejects (> 50%) being worse compared to synthetic polymer coatings (Ovaska et al., 2017).

Repulping and recyclability testing has a long history and, highly depending on a number of parameters and conditions, it only has recently been harmonized in a European guideline that is currently valid for mills with standard recycling technology (CEPI, 2022). In this study, we have validated the recyclability testing procedures for a series of commercially available coated packaging papers, in order to determine significance, repeatability and sensitivity of the method to operational conditions. Present evaluations provide us with a reference framework for further testing and assessment of paper recyclability.

2 MATERIAL AND METHODS

2. 1 Samples

Four types of industrial packaging paper samples have been introduced as examplatory cases, including a reference uncoated paper (A), 2 recyclable coated paper samples (B, C) and 1 non-recyclable coated paper sample (D). The Kraft paper 60 g/m^2 (A) was used as a reference substrate with a standard 5 g/m^2 proprietary precoating. The two recyclable coated papers contain on a proprietary acrylic dispersion coating with two different compositions and were applied by curtain coating: the sample B has a coating grammage of 10 g/m^2, the sample C has coating grammage of 7 g/m^2. Both the coating thickness and composition for the recyclable samples is different, but further details are not known and not relevant for present validation study. The non-recyclable sample D contains an extrusion coated LDPE film with coat weight of 15 g/m^2 (common folding carton weight).

Furthermore, a benchmarking study was performed for the recycling of a tissue paper grade (sample E, Tork Dry Multi-Purpose Wipes) and uncoated newsprint paper (sample F).

2. 2 Recyclability testing

Assessment of recyclability is done according to the document (version October 2022): “Harmonised European laboratory test method to produce parameters enabling the assessment of the recyclability of paper and board products in standard paper and board recycling mills” (CEPI, 2022). A practical implementation of the testing protocol is schematized in Figure 1.

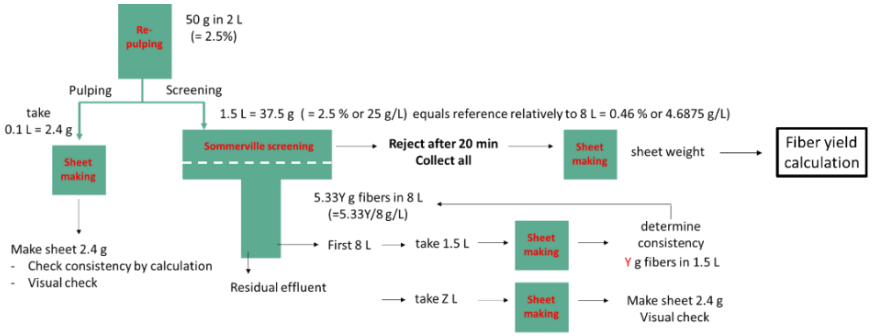

Figure 1. Schematic interpretation of the testing protocol for paper recyclability.

- The repulping is done in a disintegrator compliant with ISO 5263-1 (Figure 2a) on an oven-dry sample of 50 ± 1 g. The 25 x 25 mm^2 cut pieces are diluted with tap water at mildly alkaline pH = 7 to 8. The total volume of sample and water is approximately 2000 g, resulting in a stock consistency of 2.5 %. No pre-wetting or soaking was done. The disintegration time was varied, while a fixed time of 10 min (30,000 revolutions) is requested in the guidelines. The desintegration was done at different temperatures of 52, 40 and 30°C to evaluate the influence on testing results, while an intermediate temperature of 40 ± 1°C is required by the guidelines.
- The screening is done on a Sommerville screen with plates of 5 mm diameter holes (coarse screening) and 150 µm wide slots (fine screening) (Figure 2b), using a pulp sample size of 1.5 liter. The rejects are collected on top of the screen after 20 min to determine their oven-dry weight. The fiber yield is calculated from the oven-dry weight of collected rejects relatvely to the 1.5 liter sample corresponding to 37.5 g virgin pulp.
- The accept and reject fractions from the screening tests are further used for sheetmaking (Figure 2c). Optical evaluation is done under a microscope with lens magnification 5x and stitching of 4x4 fields of view.

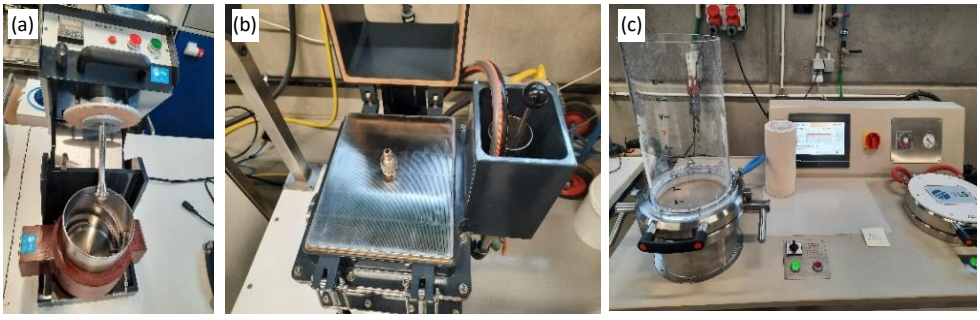

Figure 2. Set-up of pilot line at Sirris (Leuven, Belgium) for paper recyclability testing, with (a) pulp disintegration, (b) screening, (c) sheetmaking in watercolumn and dryer.

3 RESULTS AND DISCUSSION

3. 1 Desintegration – repulping

The influence of disintegration variables on fiber yield for coated paper samples A to D is presented in Figure 3, indicating the effect of disintegration time (Figure 3a) and temperature (Figure 3b). The reference uncoated paper (sample A) has clearly best repulpability with fiber yield of > 99.5 % and little influences of the repulping parameters, only the very low times of 10000 rmp are not sufficient to disintegrate the entire sample. Both dispersion coated papers (samples B, C) present very similar results once a sufficient repulping time of 30000 rpm is applied. As expected, the repulpability for LDPE laminated paper (sample D) is worse with fiber yield of 70 to 85 %. The fiber yield for unrecyclable papers more strongly depends on the repulping conditions as an in-homogeneous recycled pulp is obtained. The effect of temperature change did not affect repulpability in a significant way for recyclable samples B, C. Therefore, it can be concluded that differences in fiber yield are insignificant small and both types of dispersion coated paper can be repulped according to this method with representative fiber yield.

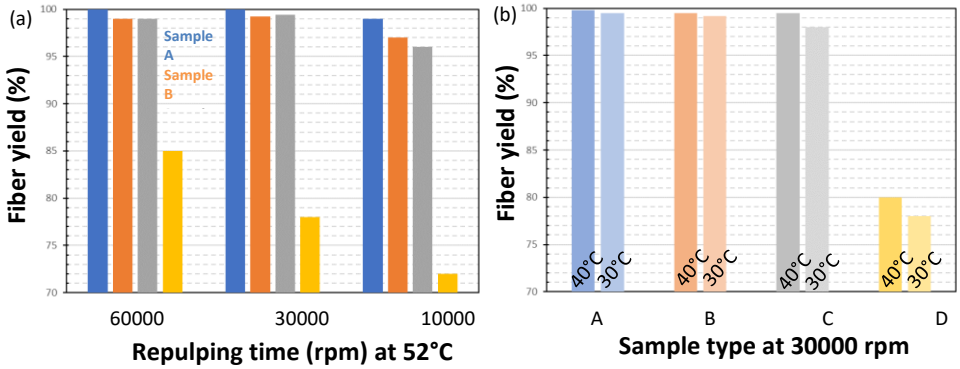

Figure 3. Influence of repulping conditions on fiber yield after fine screening, (a) different repulping times at 52°C, (b) different temperatures at 30000 rpm.

3. 2 Screening

The variations in fiber yield after coarse and fine screening for a non-recyclable coated packaging paper (Figure 4a) and recyclable coated packaging paper (Figure 4b) were determined on five independent sample runs for sample D and B, indicating better reproducibility for recyclable papers (fiber yield min 95.3 %,

max 97.6 %, standard deviation 2.3 %) compared to non-recyclable papers (fiber yield min 25.5 %, max 41.0 %, standard deviation 15.5 %), owing to the large influence on screening efficiency by the accumulation of non-recyclable fractions as visualized by a photograph of the rejects on the fine screen. The coarse rejects for non-recyclable papers include broken plastic remainants of the LDPE coating not passing through the grid. In addition, the fine rejects include agglomerated paper fibers with coating substances. The almost full fiber recovery of uncoated paper substrates suggest that wet-end additives and eventual presence of fillers/pigments (proprietary information) did not strongly hinder recyclability in present case.

The results of the benchmarking study for tissue and newsprint paper grades, show that the papers clearly can be categorized with significant statistical differences in the recovered fiber yield (Figure 5). However, the recyclability of tissue paper is inferior dueg to the use of strong wet-end chemicals in the fabrication of tissue paper to provide higher mechanical strength properties. The latter hamper the recyclability process mainly during fine screening, which is different compared to the non-recyclable packaging paper grades that mainly fail in recyclability during the coarse screening process. The fiber agglomerates formed in presence of the strong wet-end chemicals indeed seems to be mainly separated during a fine screening test (sample E).

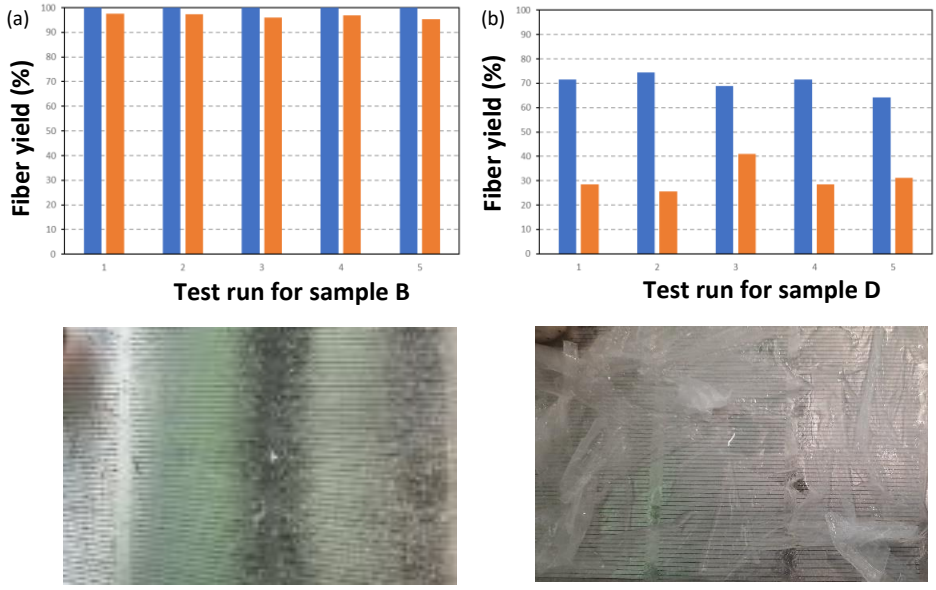

Figure 4. Influence of screening conditions (coarse screening = blue bars, fine screen-ing = orange bars) on fiber yield during repetitive testing and photographs of fine screening rejects for (a) sample B, (b) sample D.

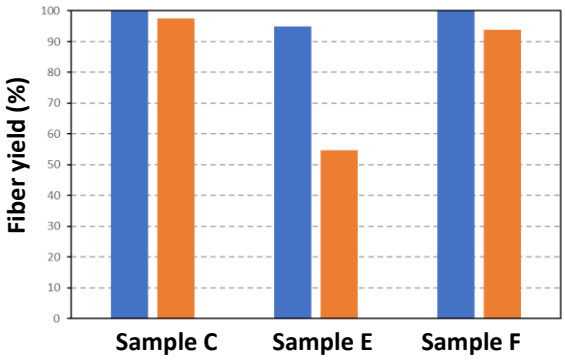

Figure 5. Benchmarking study for fiber yield after coarse screening (blue bars), fine screening (orange bars) of tissue paper (sample E) and newsprint paper (sample F).

3. 3 Sheet evaluation

The handsheets from accept and reject fractions after fine screening of coated packaging papers are evaluated by optical microscopy, providing an overview micrograph (stitching area 4x4) (Figure 6) and detailed views (Figure 7).

For recyclable paper grades (sample B), the sheets from accepts are very homogneous with still a broad distribution of fiber sizes present comparable to the virgin pulp. Still some particles of impurities originating from broken fragments of the acrylic coating remain present in the accepts, with sizes below 0.5 mm that do not hinder the homogeneous sheetmaking. The large fiber agglomerates observed in the original sample after disintegration are removed and transferred into the reject fraction that forms a weak sheet.

For non-recyclable paper grades (sample D), fibers after disintegration are strongly compacted and transferred into the reject fraction to a large amount, where they are strongly clogged together within a polymer fraction originating from the coating. Also the accepts from fine screening still contain significant amount of residual polymer fractions that were not yet fully removed by the screening process.

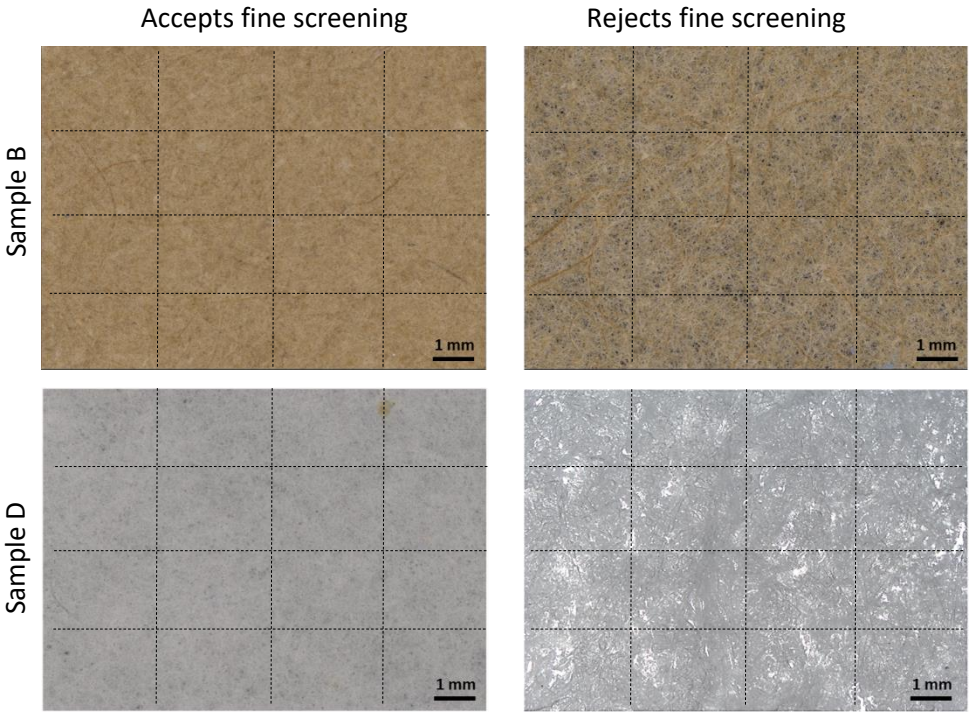

Figure 6. Large-area optical microscopy visualizing homogeneity of handsheets made from accept and reject fractions after fine screening for recyclable paper (sample B) and non-recyclable paper (sample D).

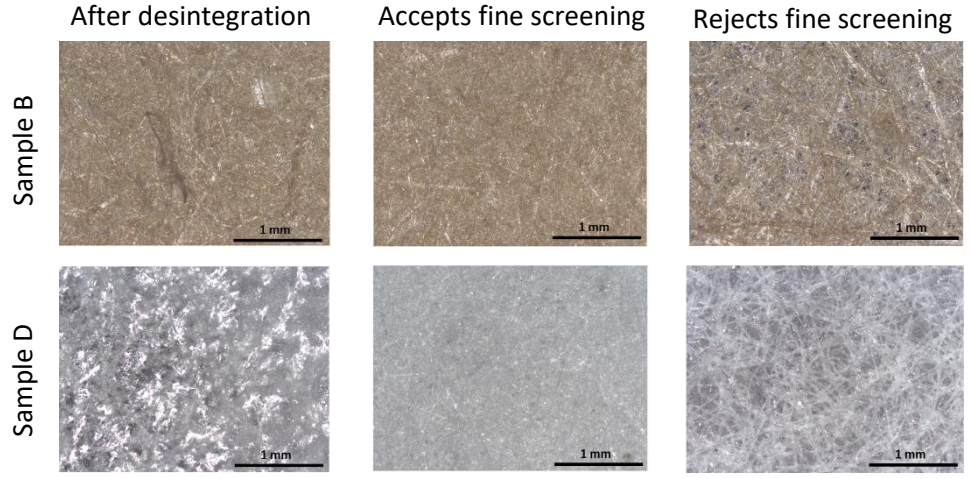

Figure 7. Detailed optical microscopy visualizing homogeneity of handsheets made from accept and reject fractions after fine screening for recyclable paper (sample B) and non-recyclable paper (sample D).

4 CONCLUSION

The laboratory-scale pilot line for recyclability testing of coated paper has successfully been validated for some industrial cases of coated packaging papers, resulting representative fiber yields recyclable versus non-recyclage papers. The repulping conditions are most sensitive to a threshold value for repulping time rather than repulping temperature. The coarse screening does not yield fiber rejects for recyclable coated papers, while it contains significant amount of polymer residues for non-recyclable papers. Alternatively, based on reference testing with soft tissue and newsprint paper, the coarse screening also separates a significant fraction of fiber agglomerates containing strong wet-end chemicals.

Acknowledgments: *This research was conducted as part of the CORNET project "REPAC²: Functional & recyclable coated paper packaging for food products". The funding for this research was provided by the Flemish Government through the grant number HBC.2021.0288, administered by the Agency for Innovation and Entrepreneurship (VLAIO-TETRA). We thank Patrick Doumen and Arne Derluyn for technical assistance.*

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INFLUENCE OF RAW MATERIAL CHARACTERISTICS ON THE PULP MOLDING PROCESS

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Original scientific paper
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Abstract: *Due to the negative impact of fossil-based, plastic packaging on the environment and the demand for sustainability, the molded pulp industry has been growing tremendously in recent years. The sustainable qualities of these packaging materials, as well as certain government regulations and the growing customer demands for a more 'green packaging', is making companies eager to find suitable alternatives to those currently used oil-based forms of packaging. Molded pulp packaging is produced from biodegradable lignocellulosic fibers like wood-based fibers, hemp fibers or other fibrous materials, therefore, it became focus of research and gained importance in industrial applications. Although molded pulp packaging is a rather old technology, as it has been around for over a hundred years now, scientific understanding of the whole process and the needed material properties is incomplete. Here, an overview of the different production procedures will be given. Furthermore, first results of measurements obtained for the so-called thermoforming process will be presented. The goal of this work was to emphasize the importance of understanding the characteristics of the used raw materials in order to optimize the molding process. For this reason, different types of fibrous materials, which are already being used in pulp molding processes and their characteristics, like the lignin content, fiber length distribution, ash content and drainage level, have been compared.*

Keywords: molded pulp, lignocellulosic material, material properties, sustainable packaging

1 INTRODUCTION

Plastic and their related products are common due to their light weight, high performance, low cost and ease of processing. People have become addicted to disposable plastic and the proliferation od plastic products in the last decades has been extraordinary (Zhang et al., 2022).

Since the usage of fossil-based, plastic packaging is increasingly considered unsustainable, the demand for environmentally friendly, biodegradable packaging is growing. Furthermore, the increasing awareness of the population regarding the negative impact of plastic packaging is one of the main driving forces for research and development in the field of "green packaging" materials and technologies (Jacobsen, Pedersen and Thøgersen, 2022). One of green and sustainable packaging materials, molded fiber and its products have attracted increasing amount of attention due to its recyclability, renewability, biodegradability and sustainability (Didone and Tosello, 2019; Zhang et al., 2022).

According to the International Molded Fiber Association (IMFA), the whole pulp molding process can be split into four sub-group technologies. These are thermoforming, transfer molding, thick-wall molding and processed molding:

- Thermoforming: This is the most established production process in industry. The molded parts are formed in four steps: first, the molded form is captured in a heated mold, then it is getting pressed, densified, and, finally, dried. The greatest advantage of this technology is that additional oven curing is not needed. The obtained forms are of high-quality, with rather smooth surfaces and walls with thicknesses ranging from 2 mm to 4 mm.

- Transfer molding: For this technology, a forming mold and a transfer or take-off mold, as well as a drying oven, are required. The molded forms have wall thickness between 3 mm to 5 mm with smooth surfaces on both sides.

- Thick-wall molding: During this molding process an open mold is used, and the molded forms are dried in an oven. The forms, which are typically made from a mixture of Kraft and recycled paper, have two different surfaces – the inside surface is rather smooth, while the outer side is very rough. The thicknesses of those forms can range from 5 mm to 10 mm.

- Processed molding: Already produced molded pulp forms that need special treatments, like additional coatings, printing or additives are belonging to this category. (Didone et al., 2017)

Historically, the molding technology already dates back to 1890 and the early 1900s, where the first patents by Keyes (Keyes, 1903, 1904) appeared. Even though, molded pulp packaging was already used in daily life, since egg cartons were produced with the molding process, the first technologies were not described until 1966 by Emery (Emery et al., 1966). Now, over 40 years later, molded pulp packaging is still a very popular packaging material for electronic devices, eggs, beverages and is used as support material for transport protection of various devices as well (Didone et al., 2017). Despite its application for such a long time, there is little knowledge available on how the raw materials must be prepared to guarantee a smooth production process. Therefore, it is necessary to understand the raw material characteristics and, to be even more accurate, the fiber properties, since they can have a big impact on the production process and the final product properties. That is why in this work, different raw materials, which are currently used for the production of molded pulp packaging, were analyzed. It is important to have knowledge of the characteristics of the raw material, like the lignin content, refining degree and the ash content in order to adapt the whole molding process including the parameters accordingly. Furthermore, depending on this, decisions for the need of additional devices, like a refiner or deflaker, or supplementary agents, like retention aids, can be made.

2 MATERIAL AND METHODS

2. 1 Raw material

The raw materials used for the measurements in this study are already utilized for the production of molded pulp packaging with the thermoforming process. In this work, samples of corrugated cardboard, grey board, chemical pulp and different kinds of coated cardboard of type GC1 and GC2 (labelled as A GC1, B GC1 and A GC2) from different suppliers were used. GC1 means that it is a pigment coated virgin mechanical pulp board with a white reverse side and GC2 is the same board type but with a cream reverse side.

2. 2 Kappa number

The Kappa number serves as a measure of the relative hardness, the bleachability or the degree of the pulping process. With this method, the determination of residual lignin present in the pulp is enabled. The basis of the Kappa number measurement, according to Tappi Method T 236 om-13, is the reaction of

potassium permanganate ($KMnO_4$). It is a strong oxidizing chemical which reacts with lignin and a small amount of other organic impurities remaining in the pulp (Czibula, 2021).

2. 3 Refining degree (Schopper Riegler)

The refining degree (SR°) was determined after the procedure of Schopper Riegler according to DIN EN ISO 5267-1. The obtained value from the measurement indicates the drainage rate of a defined volume, namely 1000 mL of an aqueous pulp suspension, through a fiber cake which forms on the sieve during the test (Blechschmidt, 2013; Mandlez, 2017).

2. 4 Ash content

The ash content, which is basically the ash residue of the sample, was determined according to DIN 54370 and ISO 1762. It is the residue, given in weight percentage, remaining after burning either a paper or pulp sample at a specified temperature until the weight is constant. Depending on the sample nature, different annealing temperatures of 525°C, 575°C, or 900°C are used. In our case the method was applied at 525°C (paper and cardboard samples) and 575°C (chemical pulp sample). The obtained values serve as a guide, but are not a quantitative measure of the real amount of inorganic components in a sample (Blechschmidt, 2013).

2. 5 Fiber analysis

In order to characterize the different kinds of raw materials, morphological Fiber Tester measurements were conducted to know the fiber shape (curl), the fines content and the average fiber length. For this, the L&W Fiber Tester Plus device from ABB (Zürich, Switzerland) was used to analyze fiber dimensions, as well as the fiber form, from which the mean kink-index and kink-angle were acquired.

3 RESULTS AND DISCUSSION

The measured raw material characteristics, like the Kappa number, Schopper Riegler, ash content and pH-value are summarized in Figure 1. The Kappa number as well as the pH-value were only measured for the coated A GC1 and A GC2 pulp board. Here, the comparison between those two materials was important since they were behaving quite different during the molding process. One type of the coated pulp boards was leading to a high frequency of machine blockages and foam formation and it was believed that the root for this cause might be in a

difference of the fiber properties. However, the measurements proofed that these two materials are very much alike in view of the parameters tested.

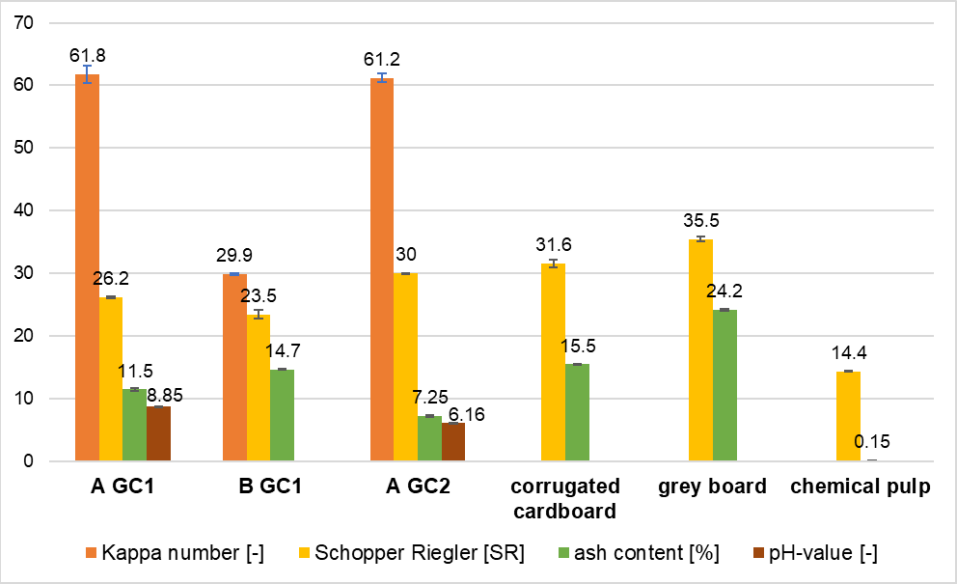

Figure 4. Summary of the raw material characteristics: Kappa number [-], Schopper Riegler [SR°], ash content [%] and pH-value [-] as used in the pulp molding process. A GC1, B GC1 and A GC2 are the samples of different types of pigment coated virgin mechanical pulp board.

The results of the raw material characteristics (see Figure 1) are also showing that the grey board contains the highest amount of inorganic components, like fillers, with 24.2% while the used chemical pulp has little to no ash content with 0.15%. The corrugated cardboard and the coated pulp boards are comparable, but it is obvious that the sample A GC2 has a much lower ash content. The reason for this could be the non-coated reverse side of this product.

Besides the raw material characteristics, it was important to gain knowledge about the morphological fiber properties, which are presented in Figure 2. The results of the measurements are indicating that the used raw materials are varying not that much from each other, except for the fibril area. Since the chemical pulp was not refined, it is containing the longest fibers but is having the lowest percentage of fibrillated area with only about 0.8 %, while the fibrillated area of the other materials is ranging between 3.4 to 6.7%. For some packaging geometries the unrefined fibers are advantageous, since they contribute the most to the geometric stability of the packaging. The other fiber morphology values, like the curl , the mean kink-angle and kink-index are very similar for all the samples.

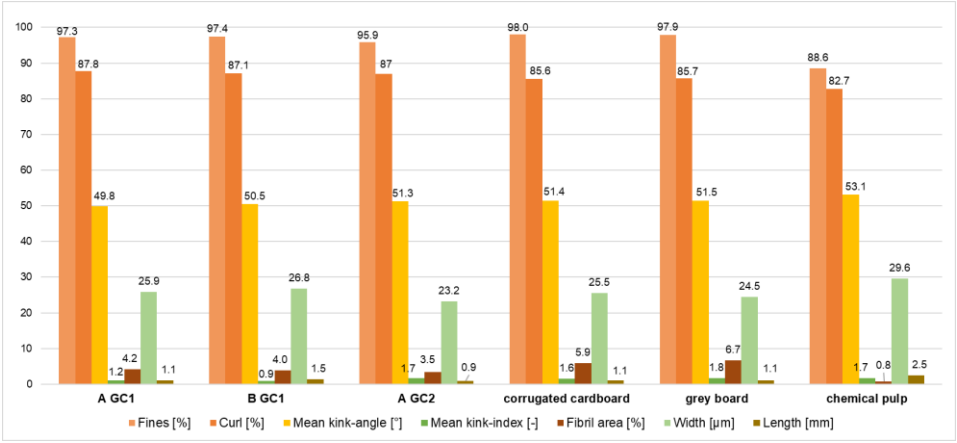

Figure 5. Summary of the measured fiber properties obtained with the L&W Fiber Tester Plus: fines content [%], curl [%], mean kink-angle [°] and kink-index, as well as the fibrillated area [%] and the length and width of the different raw materials used for the pulp molding process. A GC1, B GC1 and A GC2 are the samples of different types of pigment coated virgin mechanical pulp board.

4 CONCLUSIONS

Here, the basic properties of raw materials used for the pulp molding process were presented. They should set the base for further understanding the whole molding process, especially the thermo-forming process, to optimize the whole production technology. With the knowledge of the different characteristics of the raw materials and how they perform in the process, ideal mixtures to produce costumer-specific molded packaging forms can be determined.

The results of the fiber properties have shown that a certain fiber length distribution of the fiber suspension is necessary to have the molding process running smoothly without having blockages or quality losses in the products. However, fiber properties like curl, mean kink-angle and kink-index were very similar for all the raw materials, therefore, they are not considered to affect the process. Another important parameter is the ash content of the used raw material, because if the content of inorganic residuals is high, retention aid is needed to retain these small particles to diminish the material losses during the process, and to improve the process water quality.

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MECHANICAL RECYCLING OF SHRINK PE FILMS

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Original scientific paper
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Abstract: *Packaging recycling is often more economically feasible than other sectors of the plastic market due to high turnover rates of the collected post-consumer waste in Europe. The stability of plastics, a key performance feature that has promoted their use, also reduces their ability to degrade. Packaging films are primarily made of linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE). The global plastics economy is largely linear. Plastics are produced, used and more than half of them are disposed with no recovery. There are four main types of recycling processes: primary recycling, secondary recycling, tertiary recycling and quaternary recycling. Primary recycling involves extruding preconsumer polymer or pure polymer streams. Secondary recycling requires sorting of polymer waste streams, reduction of polymer waste size, followed by extrusion. With proper control over processing conditions, many polymers can undergo several cycles of primary and secondary mechanical recycling without concern for loss of performance. Tertiary or chemical recycling is often complementary to traditional recycling methods, and can retain significant value. Quaternary recycling is applied to plastics that are unsuitable for any other type of recycling and are used for energy recovery via pyrolysis. The need for improved plastic circularity is clear. Mechanical recycling will remain the most effective method to recycle plastics – in terms of time, economic cost, carbon footprint and environmental impact. This paper explores mechanical up-cycling challenges and solutions for shrink PE films. Our work demonstrates that mechanical recycling is key in improving waste shrink PE films by highlighting the influence of the used compatibilizer and processing aids connected with processing parameters on the mechanical properties to enable recycling via up-cycling.*

Keywords: PE, shrink films, compatibilizer, up-cycling, mechanical recycling

1 INTRODUCTION

As the plastics industry continues to grow, so does the amount of generated waste generated, not only as post-consumer waste, but also as waste generated during the production process. Instead of disposing of it as waste, it is granulated and reprocessed. This makes economic sense as it reduces both production waste and the use of raw materials. An example of this is extrusion blow moulding, where the amount of waste during production can be as high as 40%. When recycling PE multiple times, the properties of the material change drastically, affecting processability and mechanical properties (Oblak *et al.*, 2015). During degradation through multiple processing of PE, chain scission of linear PE occurs, focusing on the addition of processing additives used during processing. LLDPE is predominantly crosslinked during degradation (Felgel-Farnholz *et al.*, 2023). In PEHD for the production of packaging, pipes and closures, tensile stiffness and strength as well as impact strength were increased and elongation at break decreased when recycled 10 times (Raghuram *et al.*, 2023). The addition of PE -g- MA improved mechanical properties by promoting adhesion between incompatible polymer phases in multilayer packaging films(Jönkkäri *et al.*, 2020). Processing recycled PP composites reinforced with jute fabric at high temperatures improved tensile stiffness, higher pressure improved tensile strength (Rokbi *et al.*, 2020). Municipal solid waste PE contained 7.6% ash after mechanical recycling, most likely CaCO3 with a mean size of 0.3 mm. Processing tests showed the best optical results without unmelted particles at an extrusion temperature of 215°C and a head temperature during blow moulding of 190°C (Soto *et al.*, 2018). The low content of PE in PP allows recycling of these blends without significant impact on the thermomechanical properties (Saikrishnan *et al.*, 2020). Contamination of PE films with PLA increased tensile stiffness and brittleness. Tensile strength increased when 50 % PLA was added and decreased when 25 % was added. When 2 % PLA was added to PE, the material could be processed and used without significant changes in properties (Gere and Czigany, 2018). The best method for sorting films based on PE is near-infrared-assisted flake analysis, which allows sorting by different types of PE. Mixing different types of PE reduces impact strength. Adding PP to PE waste films had no effect on tensile stiffness, increased tensile strength and elongation at break, but drastically lowered impact strength (Thoden van Velzen *et al.*, 2021).

2 MATERIAL AND METHODS

2. 1 Materials and processing

Polyethylene as collected industrial waste was supplied by Adria polymers, Croatia. The material was in ground form with a particle size of approximately 10 mm x 10 mm. The commercial compatibilizer PEHD-g- MA (maleic anhydride grafted high density polypropylene) was obtained from Exxon Mobil, Germany, under the trade name Exxelor PE 1040. A commercial antioxidant with the trade name AT 10 was purchased from AMIK ITALIA S.p.A, Italy.

Pre-treatment of the materials was not necessary. The addition of PEHD-g- MA was 0.1 wt% and 10.0 wt%, and the addition of antioxidant was 0.1 wt% and 0.4 wt% (Table 1). The screw speed was 100 RPM and 800 RPM, the compounding temperature was 180°C and 220°C and the pressing temperature was 180°C and 220°C. With these parameter settings, the design of experiments (DoE) was carried out in 8 runs. In addition to the eight DoE compositions, the reference test was conducted with recycled PE without additives at a pressing temperature of 220°C (Table 1). For all runs, the materials were mixed together separately and extruded on the Labtech LTE 20-44 twin screw extruder. The screws had a diameter of 20 mm and an L/D ratio of 44:1. The material was extruded through the dye with two circular holes with a diameter of 3 mm. After extrusion, the two filaments were cooled in a water bath at a temperature of 25°C and granulated on a Scheer granulator to the approximate dimensions of 3 mm diameter and 5 mm length.

Table 1. Composition of the samples and varying processing parameters.

Sample	***rPE (wt.%)***	***PE-g-MA (wt.%)***	***AO (wt.%)***	***RPM (min^{-1})***	***T_c (°C)***	***T_p (°C)***
rPE	*100*	*0.0*	*0*	*0*	*0*	*220*
rPE-DoE1	*99.8*	*0.1*	*0.1*	*100*	*180*	*180*
rPE-DoE2	*99.5*	*0.1*	*0.4*	*100*	*180*	*220*
rPE-DoE3	*89.9*	*10.0*	*0.1*	*800*	*180*	*180*
rPE-DoE4	*89.6*	*10.0*	*0.4*	*800*	*180*	*220*
rPE-DoE5	*89.9*	*10.0*	*0.1*	*100*	*220*	*220*
rPE-DoE6	*89.6*	*10.0*	*0.4*	*100*	*220*	*180*
rPE-DoE7	*99.8*	*0.1*	*0.1*	*800*	*220*	*220*
rPE-DoE8	*99.5*	*0.1*	*0.4*	*800*	*220*	*180*

Due to the water bath cooling of the material after extrusion, the pellets were dried to a moisture content of max. 0.1 % at 80°C for 4 hours. The pressing of the samples was carried out on the hydraulic press Baopin BP -8176-ZB with a pressing pressure of 90 bar. The pressing time was 90 s (60 s preheating and 30

s pressing). Thin films with a thickness of about 0.15 mm and a round shape (approximate dimensions of 20 cm diameter) were produced.

2. 2 Methods for characterization

Tensile tests were carried out in accordance with ISO 527-1 on the Shimadzu AG -X plus, equipped with a load cell of maximum 10 kN, at a crosshead speed of 1 mm/min until elongation of 0.25 %, then at 50 mm/min until failure, with elongation measured at mid-span of each specimen using a Shimadzu TRViewX optical extensometer. TrapeziumX software, version 1.3.1, was used to analyse the results. Five replicates of two parallels, rectangular in shape, 10 mm wide and 80 mm long, were tested for each sample. All tests were performed at 23°C. Tensile stiffness (E_t), tensile strength (σ_m) and elongation at break (ε_{tb}) were determined in the tensile tests. Melt index measurements were carried out according to ISO 1133 standard using LIYI MFI LY – RP apparatus at 190°C and with 2.16 kg weight. 5 replicates were measured for each sample. Thermal measurements were performed using a differential scanning calorimeter (DSC 2, Mettler Toledo) under a nitrogen atmosphere (20 mL/min). The temperature of the samples was raised from -50 to 190°C at a heating rate of 10°C/min and held in the molten state for 5 minutes to quench the thermal history. After cooling at 10°C/min, the samples were heated to 300°C at 10°C/min. The melting temperature (T_m) and enthalpy of fusion (ΔH_m) were determined from the cooling scan and the second heating scan.

3 RESULTS AND DISCUSSION

3. 1 Mechanical properties

The tensile strength results are shown in Table 2 and Figure 1. The tensile modulus ranges from 254 MPa to 355 MPa. The biggest influence on the tensile modulus was the addition of compatibilizer (a higher amount of compatibilizer increased the tensile modulus). Also RPM of the extruder had an influence on the tensile modulus (higher RPM lowered the tensile modulus). The addition of antioxidants had a lesser influence (a higher amount of AO increased the tensile modulus). The compounding temperature (higher T_c increases the tensile modulus) and the pressing temperature (higher T_e lowers the tensile modulus) had a minimal influence.

The tensile strength ranges from 9.2 MPa to 12.1 MPa. The greatest influence on the tensile strength was the addition of compatibilizer (a higher amount of compatibilizer increased the tensile strength). Also RPM of the extruder had an influence on the tensile strength (higher RPM lowered the tensile strength).

Pressing temperature (higher T_e lowered the tensile strength) and compounding temperature (higher T_c lowered the tensile strength) had a smaller influence. The addition of antioxidants had a minimal influence (a higher amount of AO increased the tensile strength).

The elongation at break is in the range of 162 % to 768 %. The greatest influence on the elongation at break was RPM of the extruder (higher RPM increased the elongation at break). The extrusion temperature and the addition of compatibilizer also had an influence on the elongation at break (higher T_e and the amount of compatibilizer reduced the elongation at break). The addition of antioxidants had less influence (a higher amount of AO increased the elongation at break). The press temperature (higher T_c lowered the elongation at break) and the compounding temperature (higher T_c lowered the elongation at break) had a minimal influence.

Table 2. Summarized results from the tensile tests.

Sample	***E_t (GPa)***	***σ_m (MPa)***	***ε_{tb} (%)***
rPE	*283 ± 22*	*10.3 ± 0.6*	*221 ± 120*
rPE-DoE1	*283 ± 10*	*9.9 ± 0.3*	*514 ± 155*
rPE-DoE2	*291 ± 37*	*10.1 ± 0.4*	*527 ± 170*
rPE-DoE3	*301 ± 43*	*11.2 ± 0.6*	*635 ± 86*
rPE-DoE4	*314 ± 24*	*10.5 ± 0.8*	*533 ± 110*
rPE-DoE5	*316 ± 28*	*10.8 ± 0.7*	*298 ± 108*
rPE-DoE6	*351 ± 20*	*11.4 ± 0.4*	*514 ± 121*
rPE-DoE7	*269 ± 29*	*9.5 ± 0.8*	*576 ± 116*
rPE-DoE8	*261 ± 13*	*9.5 ± 0.5*	*725 ± 80*

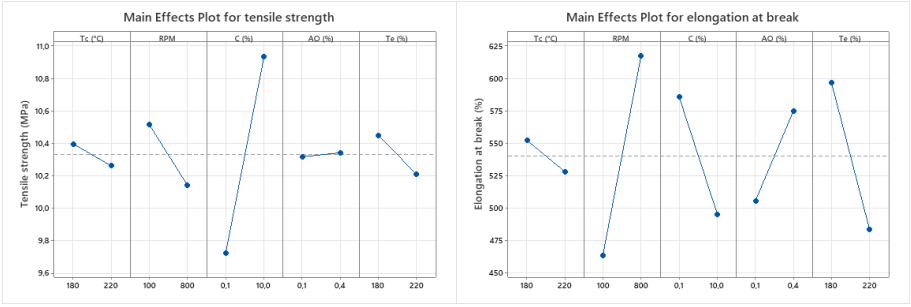

Figure 1. Summarized results of DoE for tensile strength (left) and elongation at break (right).

From the results we could conclude that the compatibilizer allows a good surface interaction between the impurities and at the same time PP and the PE main matrix, therefore the stiffness and strength increase with the amount of compatibilizer added and the elongation at break is reduced. At low RPM, PP acts

as a reinforcement for the main matrix PE, due to the two-phase system, diluting PP in the main matrix PE. At a higher RPM, the two-phase system becomes a single-phase system due to the higher shear, in which PE and PP are mixed into a single- phase system. At a lower RPM diluted PP acts as reinforcement and increases stiffness and strength and reduces elongation at break. Due to the partially degraded matrix, the addition of antioxidants prevents PE and PP from further degrading during processing. Higher processing temperatures reduced the strength, stiffness and elongation at break due to the degradation of the cousin during processing, except for the higher compounding temperature, which increases the Young's modulus.

3. 2 Melt flow index results

The MFI (Figure 2 and 3) ranged from 1.19 g/10 min to 2.36 g/10 min. The greatest influence on the MFI was the addition of compatibilizer (a higher amount of compatibilizer lowered the MFI). Also RPM of the extruder had an influence on the MFI (higher RPM lowered the MFI). The addition of antioxidants had a lesser influence (a higher amount of AO increased the MFI). The compounding temperature (higher T_c lowered the MFI) and the pressing temperature (higher T_e lowered the MFI) had a minimal influence.

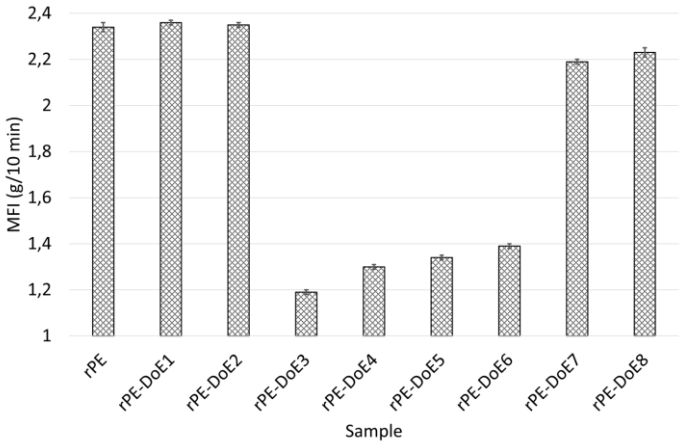

Figure 2. Summarized results of MFI test results.

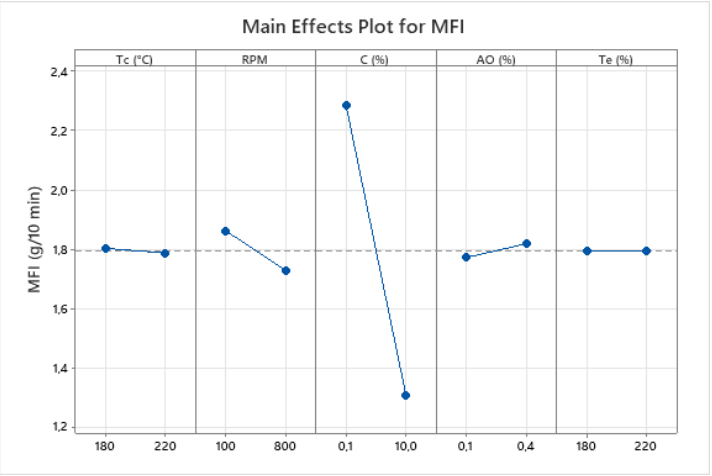

Figure 3. Summarized results of DoE for MFI.

From the results, it can be concluded that the compatibilizer allows good surface interactions between the main matrix PE, PP and impurities. This leads to a more homogeneous system where both PP and the impurities are mixed in the PE main matrix and therefore the viscosity is higher under the processing conditions, which lowers the MFI values. Due to the cross-linking of the PE matrix caused by degradation during processing, higher processing temperatures and the addition of antioxidants also prevent a drop in MFI values.

3. 3 Thermal properties

The results of the DSC evaluation are shown in Table 3. The thermal properties show that in addition to PE, a small amount of PP is also present in all samples. The melting temperatures of the PE matrices are between 109°C and 124°C. The melting temperature of PP is between 155°C and 160°C. High processing temperatures lead to cross-linking of PE, which can be seen from the decrease in the enthalpy of fusion of PE.

Table 3. Summarized results from the 2nd heating from DSC tests.

Sample	***T_{mPE} (°C)***	***ΔH_{mPE} (J/g)***	***T_{mPP} (°C)***	***ΔH_{mPP} (J/g)***
rPE	*123.3 ± 0.1*	*117 ± 10*	*159.3 ± 0.1*	*0.5 ± 0.1*
rPE-DoE1	*121.5 ± 0.4*	*119 ± 2*	*159.2 ± 0.1*	*0.4 ± 0.0*
rPE-DoE2	*121.9 ± 0.1*	*119 ± 4*	*159.0 ± 0.1*	*0.7 ± 0.5*
rPE-DoE3	*124.2 ± 0.2*	*123 ± 2*	*159.3 ± 0.0*	*0.4 ± 0.0*
rPE-DoE4	*123.9 ± 0.1*	*116 ± 6*	*158.7 ± 0.8*	*0.3 ± 0.1*
rPE-DoE5	*124.1 ± 0.1*	*115 ± 9*	*157.3 ± 3.3*	*0.6 ± 0.4*
rPE-DoE6	*124.2 ± 0.3*	*122 ± 6*	*159.9 ± 0.1*	*0.3 ± 0.0*
rPE-DoE7	*121.9 ± 0.4*	*115 ± 13*	*159.1 ± 0.6*	*0.4 ± 0.0*
rPE-DoE8	*122.3 ± 0.1*	*119 ± 3*	*159.4 ± 0.1*	*0.4 ± 0.0*

In the DoE tests, the tensile strength was increased, but at the same time the elongation at break was also increased. The P-values (Table 4) showed a strong dependence of the amount of added compatibilizer on MFI, while stiffness and strength were less pronounced. The dependence of screw rotation on elongation at break and MFI was also shown. The pressing temperature has the greatest influence on the toughness, the compounding temperature and the addition of antioxidant alone do not drastically affect the mechanical properties or the MFI.

Table 4. Summarized results from DoE for P values (Minitab evaluation with Taguchi design).

	P_{Tc}	P_{RPM}	P_C	P_{AO}	P_{Te}
Tensile E modulus	*0,871*	*0,149*	***0,052***	*0,375*	*0,887*
Tensile strength	*0,696*	*0,337*	***0,056***	*0,941*	*0,507*
Elongation at break	*0,546*	***0,044***	*0,113*	*0,174*	***0,076***
MFI	*0,673*	***0,048***	***0,001***	*0,264*	*0,954*

4 CONCLUSIONS

For the highest modulus of elasticity we recommend: a high percentage of compatibilizer, a low RPM, a high percentage of antioxidants, a high compounding temperature and a low pressing temperature. For higher tensile strength we recommend: a high percentage of compatibilizer, a low RPM, a low pressing temperature, a low compounding temperature and a high percentage of antioxidant. For the highest elongation at break, the following is recommended: low percentage of compatibilizers, high RPM, high percentage of antioxidants, low compounding temperature and low pressing temperature. For the highest MFI, the following is recommended: low percentage of compatibilizer, low RPM, high percentage of antioxidant, low compounding temperature and low pressing temperature.

The main objective of improving the toughness of the recycled PE films was successfully achieved. In addition to the main objective, the stiffness and strength could also be improved at the same time. For the further studies, different compatibilizers with high tensile strength should be investigated, focusing on different MFI values.

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CHALLENGES IN DESIGNING SUSTAINABLE PAPER PACKAGING FROM INVASIVE PLANTS

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Original scientific paper
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Abstract: *Consumer goods are usually enclosed in protective packaging to protect them from vibration and impact shocks during handling and transportation. Bio-degradable materials such as moulded pulp and honeycomb paper panels have emerged as formidable and sustainable alternatives to EPS. These materials exhibit distinct nonlinear and orthotropic behaviour and can be characterized by a relatively high stiffness. These makes them far from being regarded as an ideal cushioning material. Due to the inferior paper-based packaging performance, the improvement of protective and cushioning properties relay on the structural optimization of the packaging design. With proper design in terms of minimizing the vibration transfer path to the product itself and by avoiding extensive plastic deformation it is possible to significantly enhance cushioning performance of paper-based packaging even at multiple impacts. This requires advanced numerical models using finite element models using a highly nonlinear material models. This article presents the process of creating a numerical model for samples made from paper pulp, which also incorporate fibres from invasive plants, and introduces the method to identify its material properties. Leveraging this strategy enables to predict the static and cushioning characteristics of the pulp using numerical simulations.*

Keywords: paper pulp, numerical simulation, lignocellulosic material, packaging, finite element model

1 INTRODUCTION

Commercial goods are commonly encased in protective-packaging buffers to protect them from damage due to vibration and impact shock during handling and transportation (Kun et al., 2017). The materials used to fabricate protective packaging are usually plastic foam, such as EPS, with good cushioning performance and cost effectiveness, but they are not friendly to the environment (Andena et al., 2018). To prevent impact-induced damage to a product, a reliability test has traditionally been carried out using the "design-prototype-test-redesign" approach, which can be expensive, tedious and time consuming (Lye et al., 2004). More advanced approaches rely on a numerical, statical structural analysis of the packaging in connection with an experimentally obtained material cushioning curve to determine the optimum contact area and thus achieve the best cushioning performance (Sanchez et al., 2019; Ozturk et al., 2011).

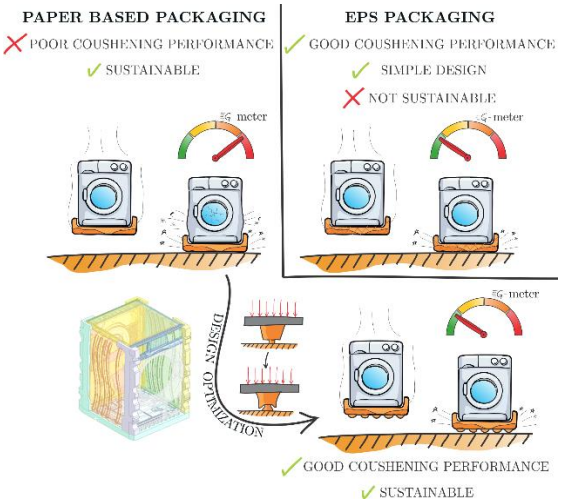


Figure 1. Replacement of EPS with paper based packaging solutions.

However, for sustainability reasons, expressed as renewability and recyclability, biodegradable alternatives such as paper-based packaging are being introduced (Lye, 2004) (Figure 1). In the home-appliance packaging industry, corrugated and honeycomb paperboard materials have been widely used for the packaging of lightweight household appliances (Kun et al., 2017; Fadiji et al., 2018). A lot of research has been carried out to quantify the cushioning properties of packaging materials such as moulded pulp using an aqueous slurry of cellulosic fibres (Hua et al., 2020). The packaging industry, being a significant contributor to

environmental degradation, has indentified the need for transition towards more sustainable production (Čepon et al., 2021). Leveraging invasive plants in the production of paper packaging presents a novel approach to address both environmental concerns and the issue of invasive species. However, this approach is not without its challenges. Due to the inferior performance of paper-based packaging that incorporates invasive species, enhancing its protective and cushioning features necessitates a numerical structural optimization of the packaging design. From this prospective and taking into account the intricate behaviour of paper material, it becomes challenging to rely on traditional packaging design methodologies through trial and error. Instead, structural optimization should leverage advanced modeling strategies, such as finite element methods.

This structural optimization is usually based on coupled dynamics simulations of the packaging, together with the product. Recent advances of the finite-element method (FEM) have further promoted the development of a detailed modeling packaging dynamics response. The major challenges to be coped with are the multi-physic, multi-scale and nonlinear nature of the paper and the complex geometry of the packaging design that results in huge models and long computational times.

In this paper, we introduce a modeling strategy based on the experimental characterization of deformation curve and Finite Element Method (FEM) for determining the material properties and performance, as well as delineating the cushioning curves for moulded pulp that incorporates invasive plants. These standard methods provide us general guidance for the evaluation of cushioning performance of pulp with inclusion of invasive plants fibres.

2 PAPER PULP MATERIAL MODEL

Utilizing a bi-kinematic hardening material model in paper modeling is crutial to accurately predict the paper's behavior under various mechanical loadings. This approach integrates both isotropic and kinematic hardening, hence offering a detailed insight into the evolution of the material's yield surface during the deformation process. This model combines two distinct hardening mechanisms: isotropic hardening and kinematic hardening, to provide a more comprehensive description of a material’s behavior under cyclic loading conditions (Figure 2). In the context of this model:

Isotropic Hardening: This aspect considers the uniform expansion of the yield surface in the stress space. Essentially, it portrays how a material hardens

uniformly when exposed to plastic deformation, leading to an increase in yield stress.

Kinematic Hardening: This aspect focuses on the translation of the yield surface in the stress space, depicting the alignment of the material's internal structure as it undergoes deformation. It helps in describing phenomena such as the Bauschinger effect, where a material exhibits different yield stresses under reversed loading due to the translation of the yield surface.

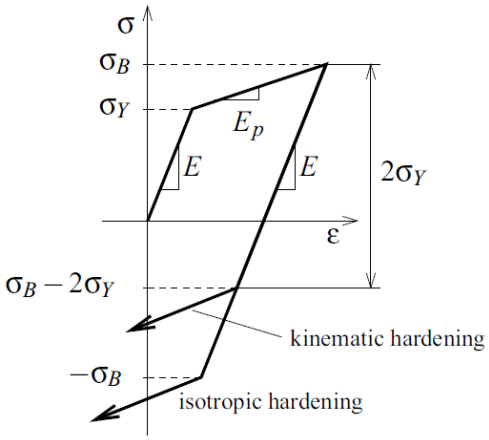


Figure 2. Isotropic and kinematic hardening.

This type of material model was sucessfully applied in this paper to determine the mechanical behaviours of paper pulp under different forces and deformations. Paper pulp, which primarily comprises of cellulose fibers, is a complex material whose characteristics are markedly non-linear, anisotropic, and viscoelastic. At the macroscopic scale, the paper pulp is considered as a continuum, where the focus is primarily on its bulk properties. The modeling here takes into account the overall response of the paper pulp to external forces, including its elastic, plastic, and viscous behaviours. Using bi-kinematic hardeing material model, it is possible to model and anticipate how the pulp material will behave during mechanical loads, taking into consideration factors like density, fibre orientation, and moisture content, which significantly affect the pulp's mechanical characteristics.

3 EXPERIMENTAL IDENTIFICATION OF FORCE-DEFORMATION CURVE

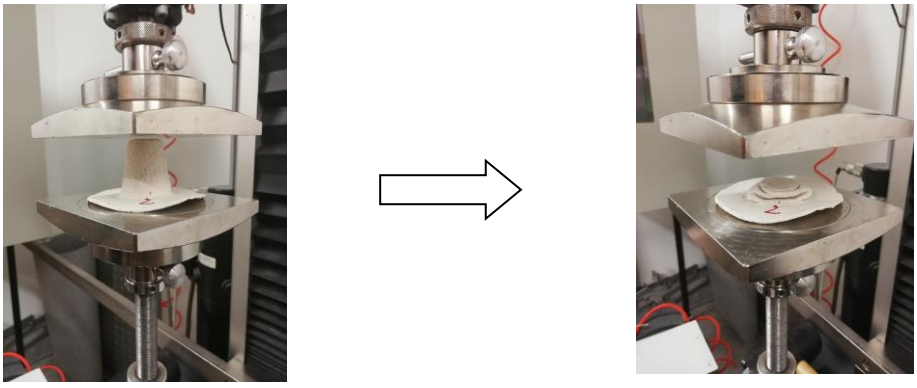
Experimental characterization of deformation curve was conducted on sample pulp cubs with two configuration:

- Configuration 1 – Raw pulp
- Configuration 2 – Raw pulp with 20% of Japanese knotweed

In the Figure 3 the samples of pulp pots are presented that were produced using the 3D printed moulds.

Figure 3. Pulp pots produced using printed mould.

The purpose of the first experimental part was to conduct a compression test of the sample pots for both analysed configurations with to determine pot material properties. The pot was placed between the jaws of a tensile-compression device and then measured the reaction force on the upper jaw versus displacement of the jaws. For a more detailed demonstration, Figure 4 below showcases one of the samples in both undeformed and deformed states.



a) b)

Figure 4. Pulp pot static compression test: a) undeformed configuration, b) deformed configuration.

During a compression test, the applied force and the resulting deformation are analysed to indirectly determine the material's mechanical properties. Initially, in the elastic region, the material undergoes reversible deformation, where it can return to its original form once the force is removed. As the force increases, the material enters the plastic region, where the deformation becomes permanent. Understanding this force-deformation relationship is vital as it helps in predicting

how the pulp material would behave under various stress conditions. It is essential to note that the specific force-deformation characteristics can vary based on the intrinsic properties of the pulp material, including its density, fibre orientation, and moisture content.

As is can be seen from Figure 5, incorporating shorter fibres of Japanese knotweed into the pulp material results in only slightly worser material properties. This suggests a justification for using Japanese knotweed in the pulp.

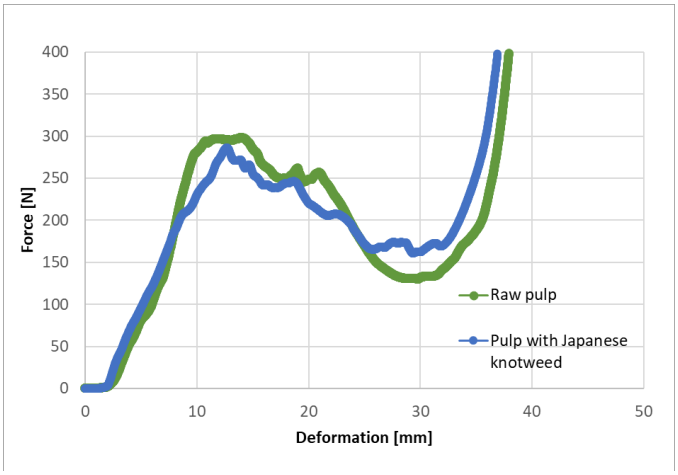
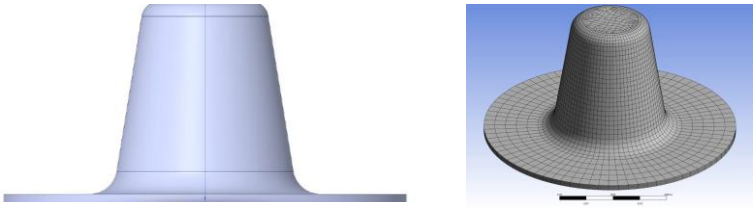


Figure 5. Force-deformation curve for pulp pots.

4 NUMERICAL MODEL AND IDENTIFICATION OF PULP MATERIAL PROPERTIES

The development of numerical model began with the CAD model of analysed pots. The CAD model of the pot is presented in Figure 6a and the corresponding FEM model is presented in Figure 6b. The elements used in numerical simulation where shell elements in order to improve the computational efficiency and convergence of numerical model.



a) *b)*

Figure 6. Numerical model of pulp cup; a) CAD model, b) FEM model.

Material properties of pulp was determined by updating the numerical model with real-time data obtained from actual pulp force-deformation measurement (Figure 5). This iterative process, which integrates experimental data into the computational framework, allows for a more precise and reliable prediction of the pulp's performance in various applications. Based on this optimization process finally the material parameters of pulp material where deduced as indicated in the table 1.

Table 1. Identified material parameters of bi-kinemeatic hardening material model for raw pulp.

Parameter	***Value***	***Unit***
density	*650.1*	*MPa*
Young modulus	*50.5*	*MPa*
Poisson ratio	*0.01*	
resistance to compression	$1.72*10^7$	*Pa*
Shear modulus	$2.5*10^7$	*Pa*
Yield strength	*0.075*	*MPa*
Tangent modulus	*100*	*MPa*

The correlation between the deformation data from the numerical model and the results obtained from experimental observations at various load stages are presented in Figure 7. By adopting the identified material parameters defined in Table 1 a high degree of correlation between the simulated and experimentaly obtained behaviour can observed. In addition, the numerically predicted and experimentally obtained deformation-force curve are presented in Figure 8.

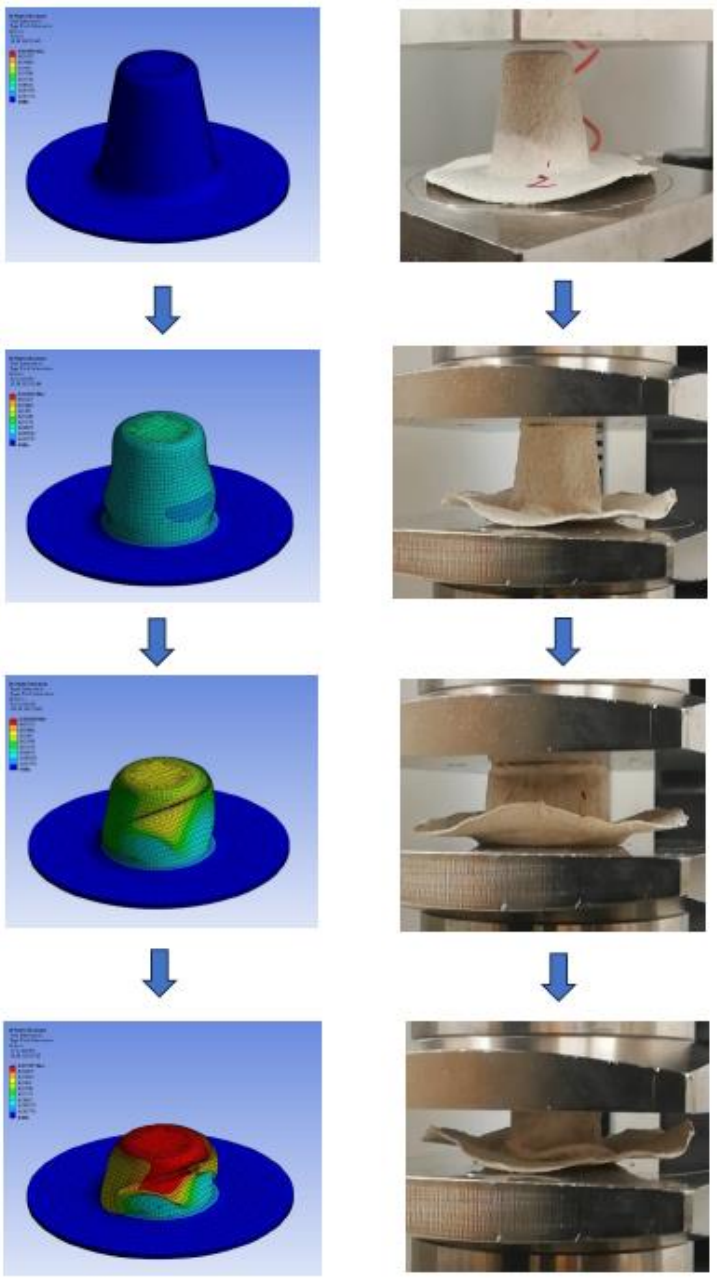


Figure 7. Comparison of deformation shape between the numerical model and actual experiment of paper pulp samples.

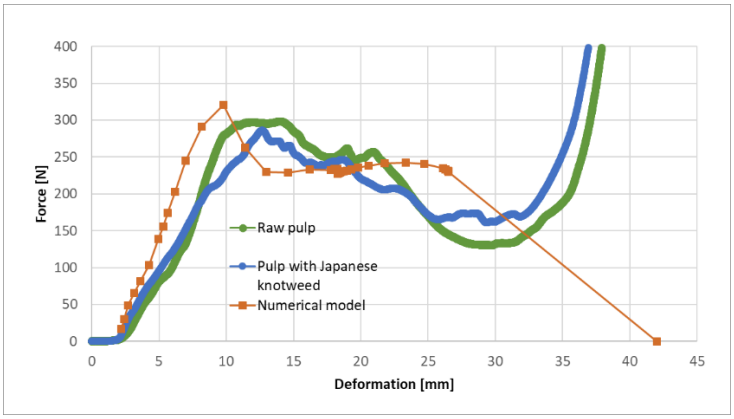


Figure 8. Comparison of numerically and experimentally obtained force-deformation curve for pulp pots.

5 CONCLUSION

In this study, we introduced a strategy for simulating paper pulp structures utilizing a bi-kinematic hardening material model. Our findings indicate a comparable mechanical performance between pure pulp and pulp composed of a 20% incorporation of Japanese knotweed, thereby justifying the use of invasive plant materials in pulp production. Leveraging numerical models together with an iterative process enabled accurate identification of pulp material properties. This methodology offers a significant potential to numerically predict packaging deformations under static and dynamic loads that encoures during transportation.

Acknowledgments: *The authors acknowledge financial support from the Ministry of Cohesion and Regional Development of the Republic of Slovenia, provided under the Norway grants, according to grant agreement No. C1541-22B710043 (LEAP project).*

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CHALLENGES IN THE REPLACEMENT OF EPS PACKAGING WITH THE BIOBASED ONE IN A LARGE SCALE PRODUCTION ENVIRONMENT

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Professional paper
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Abstract: *The environment and sustainable behavior is in modern society increasingly important topic. The white goods producers have made in the last decade significant effort to reduce the energy consumption of the home appliances, a little less attention was made to the recyclability of products and packaging. Today plastics components of the home appliances and EPS packaging and foil is predominately made from fossil oil. In Gorenje location in Velenje in 2022 astounding 2.200 tons of EPS was used only for packaging. Out of this 57% was used for packaging of kitchen appliances, 25% for laundry appliances and 18% for dishwashers. The EU green deal and connected sustainable product initiative and the legislation adopted puts a lot of pressure on the Gorenje predevelopment and category packaging teams to come with more sustainable packaging option. The challenges in the implementation were threefold: technical due to large impact forces that can with the heaviest appliances easy overcome 100 g; organisational, where solution has to be easy to implement and must allow gradual transitioning; technical capabilities of the paper packaging suppliers. All these aspects will be presented in the article, demonstrating difficulties in the company sustainable packaging transitioning.*

Keywords: sustainablity, packaging, white goods, cushioning

1 INTRODUCTION

The environment and sustainable behaviour is in modern society increasingly important topic. The white goods producers have made in the last decade significant effort to reduce the energy consumption of the home appliances, a little less attention was made to the recyclability of products and packaging. Today plastics components of the home appliances and EPS (expanded polystyrene) and foil is predominately made from fossil oil.

The EU Green deal and the proposal for a new Ecodesign for Sustainable Products Regulation (ESPR), published in March 2022, is the cornerstone of the EU Commission's approach to more environmentally sustainable and circular products. The proposal establishes a framework to set ecodesign requirements for specific product groups to significantly improve their circularity, energy performance and other environmental sustainability aspects. It sets the performance and information requirements for almost all categories of physical goods placed on the EU market.

The framework will allow for the setting of a wide range of requirements, including on:

- product durability, reusability, upgradability, and reparability
- presence of substances that inhibit circularity
- energy and resource efficiency
- recycled content
- remanufacturing and recycling
- carbon and environmental footprints
- information requirements, including a Digital Product Passport

The incoming regulations and the legislative proposals of Australia, France and United Kingdom, where tis countries plan to ban, restrict or heavily tax the usage of oil-based EPS for packaging after 2025 puts a lot of pressure on the producers of different goods to shift towards more sustainable packaging solutions.

The white goods producers have made in the last decade significant effort to reduce the energy consumption of the home appliances, a little less attention was made to the recyclability of products and packaging. Today plastics components of the home appliances and EPS packaging and foil is predominately made from fossil oil. In Hisense Europe company Gorenje only in Velenje location in 2022 astounding 2.200 tons of EPS was used only for packaging. Out of this 57% was used for packaging of kitchen appliances, 25% for laundry appliances and 18% for dishwashers.

In the present paper the challenges in the replacement of EPS packaging with the biobased one are explained more in detail (Kun et al., 2017; Andena et al., 2018).

2 EPS PACKAGING REPLACEMENT CHALLENGES

2. 1 Available options study

At the begining of the project the overview of possible options was performed. It is obvious that the biobased alternatives offer more sustainable and eco-friendly options than EPS, which commonly known as Styrofoam, and is widely used packaging material, but it is not environmentally friendly as it is non-biodegradable and can persist in the environment for hundreds of years. Here are some potential biobased replacement options:

1. **Biodegradable Polymers:** Materials like polylactic acid (PLA), polyhydroxyalkanoates (PHA), and polybutylene adipate terephthalate (PBAT) can be used as substitutes for EPS. These biodegradable polymers are derived from renewable sources such as corn starch or sugarcane, and they can break down naturally in the environment.
2. **Mushroom Packaging:** Mycelium, the root structure of mushrooms, can be used to create biodegradable packaging materials. It's grown on agricultural waste, making it both biobased and biodegradable. Mushroom packaging is strong and can replace EPS in various applications.
3. **Paper-Based Packaging:** Traditional paper packaging is biodegradable and can be used as a replacement for EPS in many applications. Additionally, advanced paper-based materials, like corrugated cardboard, can offer sufficient protection for fragile items.
4. **Bioplastics:** Bioplastics are plastics derived from renewable sources, such as starch, cellulose, or algae. Some bioplastics, like polyhydroxyalkanoates (PHA), can serve as alternatives to EPS in various packaging applications.
5. **Agricultural Residues:** Agricultural waste products like wheat straw, rice husks, or cornstarch can be used to create biobased packaging materials. These materials are not only renewable but can also be composted or biodegraded.
6. **Seaweed-Based Packaging:** Seaweed-derived materials, like agar or alginate, have been explored as biobased packaging options. They are abundant in the ocean and can be used for single-use packaging solutions.

7. **Recycled Paperboard:** Using recycled paper and cardboard for packaging is an environmentally friendly alternative. These materials can often be recycled again after use.
8. **Edible Packaging:** Edible packaging materials made from ingredients like rice, potatoes, or tapioca can replace EPS for certain food packaging applications. Consumers can either consume the packaging or compost it.
9. **Plant-Based Foams:** Some companies have developed foam-like materials from plants like cornstarch or soybeans. These materials can be used for cushioning and insulating purposes in packaging.
10. **Biodegradable Air Pillows:** Instead of traditional EPS-filled air pillows for cushioning, biodegradable alternatives made from materials like PLA or PBAT are available.

When considering biobased alternatives to EPS, it's essential to assess the specific application, considering factors such as durability, cost, and end-of-life options (e.g., composting or recycling). Sustainable packaging solutions often involve a combination of these materials and a thoughtful approach to reduce waste and environmental impact.

Based on all above-mentioned arguments and availability of the ready industrialized solutions we have decided to continue our research with the paper based biodegradable solutions.

2. 2 First tests with corrugated cardboard

The first idea was to replace the EPS packaging with the corrugated cardboard. After first few transport tests on the testing facility, it was clear that the corrugated cardboard is not a viable solution for heavier home appliances like washing machines and tumble driers. The multiple impact accelerations that the relatively thin carboard packaging must withstand exceed 100 g. The results of the test were completely damaged home appliances.

2. 3 Entering in the uncharted waters

It was clear from the first tests that Trial and error method will take to much time and will be to expensive due to large number of experiments needed and resulting in the large number of damaged and destroyed appliances. The obvious solution was to do the test on digital twins (Lye et al., 2004; Kun et al., 2017). But for this you need a number of material caracteristics which were not available. Therefore, the main challenge was to get paper packaging properties that would

allow us the numerical simulation of the cushioning properties. By this we have made paper construction material where we can simulate dynamic behavior.

Fortunately, the Gorenje Predevelopment department was already working on the research of the biobased packaging solution for the washing machines in cooperation with the Faculty of mechanical engineering in Ljubljana (Mihelič et al., 2023).

The first obstacle was to build the test site and determine the standard measurement procedure. It showed that the ASTM D1596 standard, could help the team to get needed material and cushioning properties of different cushioning materials and especially the cardboard and paper honeycomb.

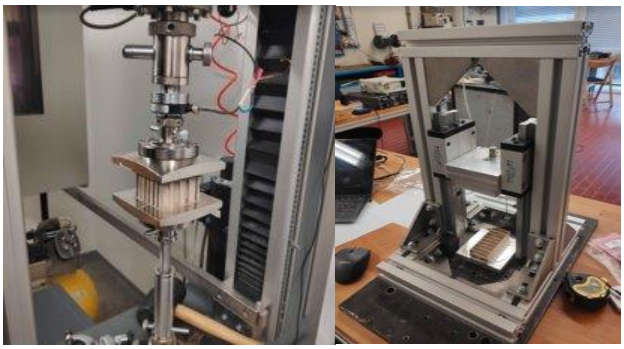

Figure 1. Testing equipment to determine the cushioning properties of the cardboard and paper honeycomb.

The following tests performed at the Faculty of mechanical engineering in Ljubljana:

- Measurement of damping curves
    - Vertical damping
    - Horizontal damping
- Dependance from contact surface/ static pressure

took us more than one month. Anyway, the performed tests provide the necessary data which enable us to use the mechanical and dynamical properties in the digital twins of the packaging.

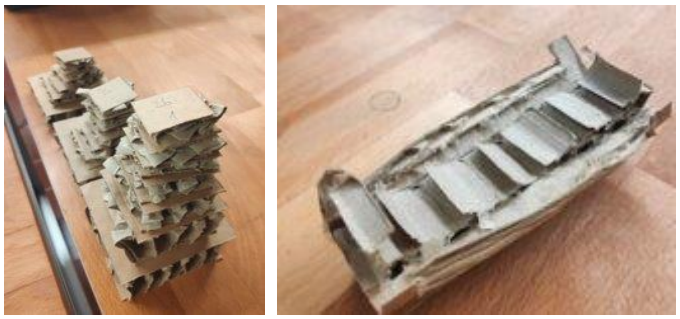

Figure 2. Testing equipment to determine the cushioning properties of the cardboard and paper honeycomb.

The main conclusion of the test was the curve which demonstrate the ability of different cushioning materials to withstand multiple impact force (Fadiji et al., 2018).

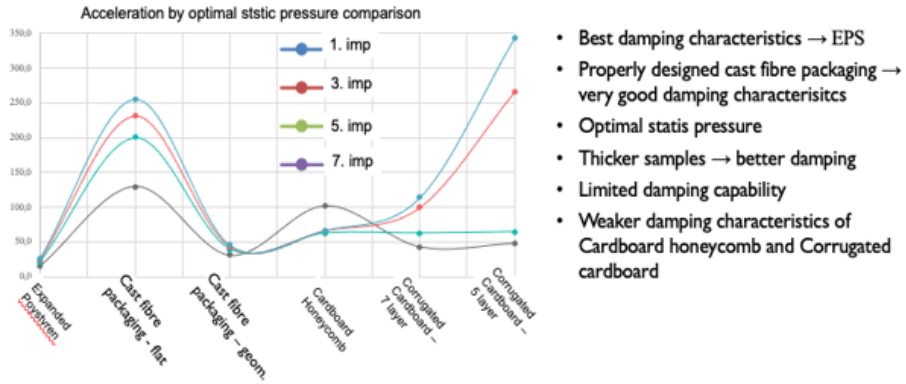

Figure 3. Cushioning characteristics of different materials after multiple impacts.

2. 4 Packaging design

Based on the knowledge gained by material testing then the tedious work of designing the packaging for different home appliances begins. In the continuation there are some pictures that represent some of the digital twin design testing. The digital twins performed quite well, since we manage to reduce dramatically the number of need physical transportation tests. In majority of cases the first physical test was nearly OK, then some smaller modifications of the packaging design on the critical parts was perform. In one case there was a large scatter of the test results, which puzzeled the team. At the end it showed that it was not problem in packaging but that the design of tested appliance needed some modifications to be more resilient to extreme transportation forces and accelerations (Čepon et al., 2021).

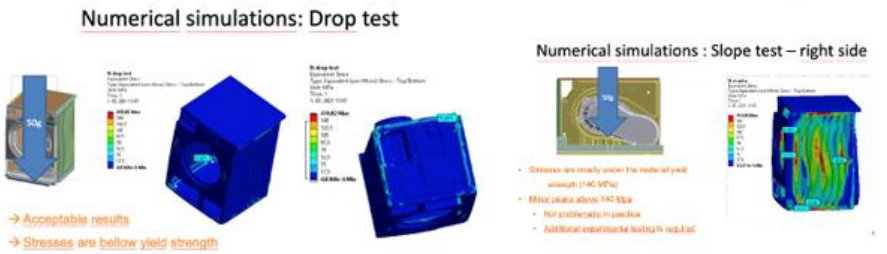

Figure4: Numerical simulation examples

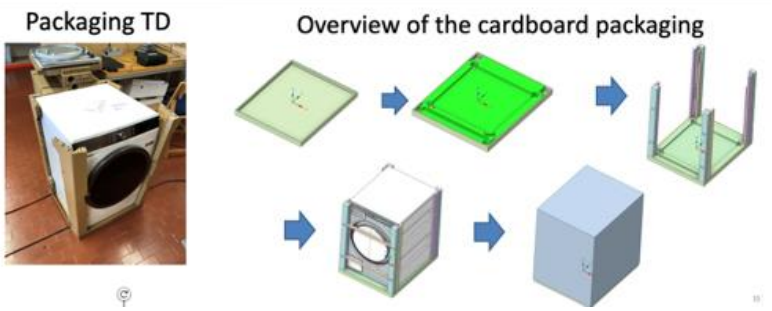

Figure 5. Design of tumble dryer cardboard and honeycomb packaging.

3 TESTING OF THE BIOBASED PACKAGING SOLUTION

Gorenje is selling their home appliances all over the world. In recent years the trend is more and more changing away from large retailers, but we observe that the transport goes through several warehouses where different transporting and manipulation facilities are used.

Therefore, the test procedures that appliances and packaging has to withstand are relatively strict and are composed of following procedure and tests:

1. Test on min. 2 packaged test samples
2. Transportation tests: lateral compression test, stacking test, vibration test, free fall test – 5 drops, impact test (slope) on all 4 sides, reload test.
3. Unpackaging and inspecting samples after completed tests
4. Additional test in moisture chamber for overseas transport

The development work of a large team of colleagues working on the design and improve of packaging resulted in biobased design of packaging for all Gorenje home appliance products that withstand strict transport regulations.

The only issue that is partially solved is the moisture resistance. The designed packaging can easily withstand the oversee transport in containers and relatively humid environment. The difficulty is in the warehouses and transport means

where they left appliances standing in the water, so the cardboard has the time to absorb the water, and by this loosing a lot of its cushioning properties. For mentioned cases the team manage to find a solution for bottom cover, which is unfortunately not biodegradable, but it is 100% recyclable and reusable and has a good water resistance.

4 INDUSTRIALISATION

With the proof of concept that the paper based biodegradable packaging is a suitable replacement for the existing EPS packaging the industrialization phase begins. In this phase the Gorenje experts need to do the following steps:

- The qualified suppliers have to be found for honeycomb and corrugated cardboard
- Adapt with the producer's manufacturability requests
- Test the assembly on the production line
- Repeat the tests to prove the quality
- Approve the samples
- Negotiating the prices and other conditions
- Adopt Gorenje standard for honeycomb cardboard packaging to ensure the quality of subsequent deliveries.

In the process of industrialization Gorenje has discussion with different suppliers of corrugated cardboard and paper honeycomb. It was interesting to see that the large majority of suppliers are only available to provide results on Trial and error method. They are more focus on the esthethic design and relay mainly on their experiences. We have seen that the usage of digital twins to actually calculate the material properties need for the adequate protection is really novel in the paper making industry.

This process of industrialization is still taking place in Gorenje and we are progressing product by product. The adoption of the biodegradable packaging in the regular production is also dependent on the category, negotiated prices and market demand. Some appliances like hood in hob, gas hobs, RedBull refrigerators, induction plates, under counter wine chiller are already having paper packaging. The rest are to be introduced during the year 2023 and 2024.

5 FURTHER RESEARCH TO IMPROVE EVEN MORE THE ENVIRONMENTAL IMPACT

During the two-year development and industrialization phase we have seen that there is only relatively little number of suppliers of paper honeycomb in Europe. This mean that the logistic has very strong environmental impact, since the honeycomb has a large volume filled with air. One of the suppliers has also offered solution that we can assemble honeycomb on site, which involves relatively high investment and production space requirement.

Anyway, in R&D we have also started research of alternative paper-based solutions that will have even lower environmental impact. We were lucky to get co-financing of LEAP project through the Norwegian fund mechanism to explore the cast pulp solutions from invasive plants.

6 CONCLUSION

The work of the group was successful as we have demonstrated that cardboard packaging with paper honeycomb inserts if properly designed is suitable eco-friendly solution for all categories: washing machines, tumble dryers, dishwashers, ovens, induction and gas hobs, hoods, hood in hob, refrigerators, and wine chillers.

From the Gorenje journey it was clear that large companies with enough R&D capabilities can make this transition. The situation is much more complex for the small sized companies, where more support will be needed from the paper industry or specialized centers that will help the transitioning from EPS to bio-based packaging.

Acknowledgments: *The authors acknowledge financial support from the Ministry of Cohesion and Regional Development of the Republic of Slovenia, provided under the Norway grants, according to grant agreement No. C1541-22B710043 (LEAP project).*

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A PRELIMINARY ENVIRONMENTAL ANALYSIS OF THE USE OF ALTERNATIVE LIGNOCELLULOSIC FIBRES IN INDUSTRIAL PACKAGING

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Preliminary report
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Abstract: *this is a preliminary environmental analysis of a new packaging material that incorporates biomass of non-native invasive plants and enables the production of new high-performance packaging solutions. We compare several environmental impact categories of the bio-mass collection process used in the benchmark packaging production, with that of the proposed one. Several analysis methods indicate improvement in impact categories that relate to freshwater ecotoxicity, human carcinogenic toxicity, marine ecotoxicity, and terrestrial ecotoxicity to name a few.*

Keywords: eLCA, industrial packaging

1 INTRODUCTION

This work is part of a project that develops new packaging material for industrial purposes. The contribution to the project is the environmental life cycle analysis that accompanies different process designs developed by the partners, in order to produce the new packaging material. The environmental assessment can help favour some design decisions over others, and will be considered together with corresponding economic and social assessments.

The project is titled: learning and demonstration network for the design and production of sustainable industrial packaging made of alternative lignocellulosic fibres, hereafter referred to as LEAP. It incorporates biomass of non-native invasive plants to produce high-performance packaging solutions for heavier industrial applications. The ambition is to replace Expanded Polystyrene (EPS) packaging. More details can be found on https://www.project-leap.com/

At this stage we are assessing the environmental impact of a sub-process that involves the collection of biomass to produce both the benchmark and new packaging solutions. In the existing benchmark processes the Invasive Alien Plants (IAP) are harvested in a central collecting facility together with mixed biomass coming from various sources. The biomass is then either grinded and sent to composting, or dried and burned for energy production. There is no separate treatment of biomass from IAP. The proposed new collection sub-process separates the biomass coming from IAP from other biomass types already at the individual collection points. Separated biomass is transported to a central collecting facility, where each IAP species is treated individually; stalks (80% of biomass) are separated from the residues like roots and leaves, dried, and grinded into woodchips. Then, they are sent to cellulose pulp production process while the residues (20 % of biomass) for composting. By this change in collection process the IAP biomass can be used as a raw material for cellulose pulp production, a product with higher added value compared to compost and energy produced. See Figure.

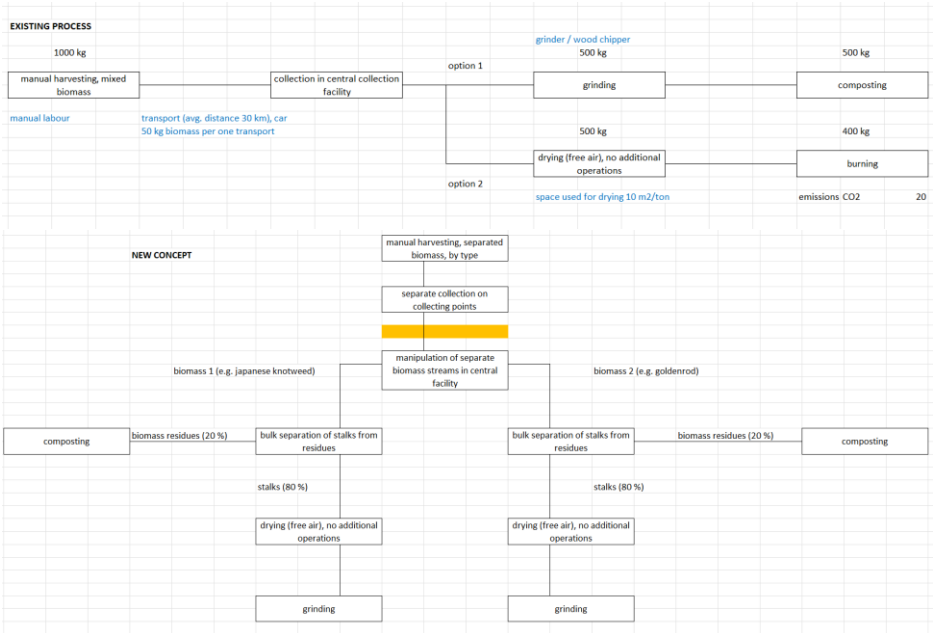

Figure 1. A schematic of the biomass collection process for the benchmark and new concepts.

2 METHODS AND RESULTS

The contribution of this work to the LEAP project is the environmental assessment of the two biomass collection processes. SINTEF used the software SimaPro to simulate models for both processes, while the project partner, ICP, did the process modelling and data collection as far as environmental impacts are concerned. Several analysis methods were tested to see if there is a general conclusion about which impact categories are improved or degraded. We selected the following methods: ReCipe, IMPACT endPt, and IMPACT midPt. Selection was based on the number of processes each method can account for when simulating the biomass collections. Other methods can be used as well.

The results at this point should be interpreted in relative terms, rather than absolute ones because of the high-level abstraction in the models and crude data available at this time. That said, the following relative changes were observed. Negative numbers indicate an improvement.

Table 1. Relative changes using the ReCipe method.

Impact category - ReCipe	***Unit***	***Relative change***
Fine particulate matter formation	*DALY*	*-10.07*
Fossil resource scarcity	*USD2013*	*-3.13*
Freshwater ecotoxicity	*species.yr*	*-12.47*
Freshwater eutrophication	*species.yr*	*-8.43*
Global warming, Freshwater ecosystems	*species.yr*	*-1.72*
Global warming, Human health	*DALY*	*-1.72*
Global warming, Terrestrial ecosystems	*species.yr*	*-1.72*
Human carcinogenic toxicity	*DALY*	*-14.14*
Human non-carcinogenic toxicity	*DALY*	*-3.36*
Ionizing radiation	*DALY*	*-0.49*
Land use	*species.yr*	*-50.92*
Marine ecotoxicity	*species.yr*	*-12.22*
Marine eutrophication	*species.yr*	*-1.41*
Mineral resource scarcity	*USD2013*	*-45.69*
Ozone formation, Human health	*DALY*	*-7.59*
Ozone formation, Terrestrial ecosystems	*species.yr*	*-7.59*
Stratospheric ozone depletion	*DALY*	*-5.33*
Terrestrial acidification	*species.yr*	*-5.01*
Terrestrial ecotoxicity	*species.yr*	*-83.46*
Water consumption, Aquatic ecosystems	*species.yr*	*-3.53*
Water consumption, Human health	*DALY*	*-1.03*
Water consumption, Terrestrial ecosystem	*species.yr*	*-1.36*

Table 2. Relative changes using the IMPACT endPt. method.

Impact category – IMPACT endPt.	***Unit***	***Relative change***
Climate change, ecosystem quality, long	*PDF.m2.yr*	*-1.07*
Climate change, ecosystem quality, short	*PDF.m2.yr*	*-0.88*
Climate change, human health, long term	*DALY*	*-1.07*
Climate change, human health, short term	*DALY*	*-0.88*
Freshwater acidification	*PDF.m2.yr*	*-5.97*
Freshwater ecotoxicity, long term	*PDF.m2.yr*	*-15.57*
Freshwater ecotoxicity, short term	*PDF.m2.yr*	*-14.41*
Freshwater eutrophication	*PDF.m2.yr*	*-25.21*
Human toxicity cancer, long term	*DALY*	*-9.32*
Human toxicity cancer, short term	*DALY*	*-16.00*
Human toxicity non-cancer, long term	*DALY*	*-1.43*
Human toxicity non-cancer, short term	*DALY*	*0.46*
Ionizing radiation, ecosystem quality	*PDF.m2.yr*	*-7.35*
Ionizing radiation, human health	*DALY*	*-3.12*
Land occupation, biodiversity	*PDF.m2.yr*	*-9.93*
Land transformation, biodiversity	*PDF.m2.yr*	*204.81*
Marine acidification, long term	*PDF.m2.yr*	*-1.10*
Marine acidification, short term	*PDF.m2.yr*	*-1.10*
Marine eutrophication	*PDF.m2.yr*	*-9.76*
Ozone layer depletion	*DALY*	*-48.91*
Particulate matter formation	*DALY*	*-7.64*
Photochemical oxidant formation	*DALY*	*-6.74*
Terrestrial acidification	*PDF.m2.yr*	*-5.94*
Thermally polluted water	*PDF.m2.yr*	*-1.28*
Water availability, freshwater ecosys.	*PDF.m2.yr*	*-0.51*
Water availability, human health	*DALY*	*0.20*
Water availability, terrestrial ecosys.	*PDF.m2.yr*	*-2.09*

Table 3. Relative changes using the IMPACT midPt. method.

Impact category – IMPACT midPt.	***Unit***	***Relative change***
Climate change, long term	*kg CO2 eq*	*-1.81*
Climate change, short term	*kg CO2 eq*	*-1.71*
Fossil and nuclear energy use	*MJ deprived*	*-2.83*
Freshwater acidification	*kg SO2 eq*	*-7.39*
Freshwater ecotoxicity	*CTUe*	*-18.60*
Freshwater eutrophication	*kg PO4 eq*	*-28.85*
Human toxicity cancer	*CTUh*	*-14.34*
Human toxicity non-cancer	*CTUh*	*-0.36*
Ionizing radiation	*Bq C-14 eq*	*-4.00*
Land occupation, biodiversity	*m2yr arable*	*-12.54*
Land transformation, biodiversity	*m2yr arable*	*469.18*
Marine eutrophication	*kg N eq*	*-11.21*
Mineral resources use	*kg deprived*	*-44.08*
Ozone layer depletion	*kg CFC-11 eq*	*-163.73*
Particulate matter formation	*kg PM2.5 eq*	*-9.44*

Photochemical oxidant formation	*kg NMVOC eq*	*-7.75*
Terrestrial acidification	*kg SO2 eq*	*-7.22*
Water scarcity	*m3 world eq*	*-1.56*

These results only indicate that the new collection process is promising from an environmental perspective, nothing else. Absolute improvement, or degradation, numbers have little meaning at this stage. The reader should not interpret the results as: the new process causes an improvement, or degradation, in category x or y, as there is no causal relationship established at this stage. Yet, the reader can benefit from the modelling process in SimaPro, or the like, in terms of processes selected, and the logic connecting them if he is to replicate a similar biomass collection process.

3 CONCLUSION

This work presented a SimaPro "model" of two biomass collection processes with the LEAP project. Comparing the two models showed a number of environmental improvements across several impact categories. This further encouraged the project team to continue developing the new packaging material. Continuous environmental assessments are necessary as we extend on the biomass collection process and integrate it with the overall production.

Acknowledgments: *The authors acknowledge financial support from the Ministry of Cohesion and Regional Development of the Republic of Slovenia, provided under the Norway grants, according to grant agreement No. C1541-22B710043 (LEAP project).*

STRATEGIES FOR THE MANAGEMENT OF INVASIVE PLANT SPECIES

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Professional paper
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1 INTRODUCTION

The LEAP project directly addresses the challenges of the EU strategy for plastic packaging waste, in terms of replacing it with more sustainable materials; addresses the challenge of the transitioning to more sustainable resource management with a low ecological footprint. The idea of the LEAP project is to develop the next generation of advanced functional packaging that incorporates the biomass of non-native invasive plants and enables the production of new high- performance packaging solutions.

The project indirectly faces another challenge regarding the widespread and the lack of control methods for invasive alien plants. For thousands of years, humans have been transmitting plant and animal species, as well as other organisms, between different environments, either intentionally (importing cultivated, ornamental plants) or unintentionally (stitched passengers - ballast water, together with seeds, plants, fruits, various cargo). The species that were not originally presented in the environment are called a non-native species. The transfer of species between different environments have been on an even greater scale in the last few decades due to increased international trade (Strgulc Krajšek, 2016).

Only a small amount of the non-native organisms are able to survive in the new environment. Some species are unable to adapt to the new environment and their survival and reproduction depends on the help of humans. But there is still a small share of species that have a significant impact on nature and people. Usually, such species have strong adaptability, fast reproduction, spreading capabilities, undemanding in terms of environment and conditions, mechanisms for surviving unfavorable conditions, that contribute to their success in their new area. They are called invasive alien species (in the following IAS). IAS usually cause serious negative consequences in places outside their natural environment

(economic damage, health problems), especially have big negative impact on native biodiversity, ecosystem services (habitat degradation). In the new environment, they compete with native species for habitat, food, water, light and other important resources. IAS are also often carriers of different diseases and parasites against which native species are not resistant (Strgulc Krajšek, 2016).

IAS spread very quickly and form dense stands that can completely change ecosystems in the environment. Eradication of invasive plants is often very expensive and difficult. With effective strategies and measures we can restrict and limit their spread (Eler, 2018):

a) primarily by preventing entry into the country (restriction of trade in potentially invasive organisms, customs inspections, quarantine),

b) with early detection and timely removal (before flowering, suppression of smaller, initial populations),

c) preventing and limiting the spread (washing of work machines, appropriate handling of excavated soil, greening the open areas),

d) to regular control of already widespread species (mechanical, chemical, biological; removal of entire plants with root system, regular mowing).

The framework regulation that primarily covers non-native species in Slovenia is the Nature Conservation Act.

2 STRATEGY FOR ESTABLISHING A METHOD TO COLLECT AND CONTROL INVASIVE ALIEN PLANT SPECIES

Company Surovina, together with other project partners, is trying to develop and demonstrate a solution for the design of protective packaging made of lignocellulosic plant fibers, which will be an alternative to EPS packaging, also for heavier industrial products. Invasive plants will be use as a source of recyclable materials to produce paper pulp, and later protective packaging for household appliances. The key role of the company Surovina is to determine clear rules and develop the correct procedure for the removal, collection and pre-treatment of plant waste of invasive species for the establishment and demonstration of a circular-sustainable business model for the collection of lignocellulosic biomass, design and production of industrial packaging. The main purpose is the establishment of the new collection system of non-native plants and suitable preliminary preparation for the use of the packaging production. As a result, Surovina established a waste collection center at business unit in Maribor, where

they accept from individuals and companies invasive plants wastes of two different species: Canadian/Giant goldenrod and Japanese/Czech knotweed.

Figure 1. Invasive plants waste collection point at PE Pobrežje, Zrkovska 105, 2000 Maribor.

In the production of paper pulp, which is the first step in the manufacture of the more sustainable protective packaging, only lignocellulose can be use, which is mostly found in the stems. For the needs of using plants as an input material in new advanced processes, we need to remove the leaves, flowers and roots from the stems. For a compact and suitable paper pulp that can be used in the production of protective packaging, the stems must be properly dried and previously ground into smaller pieces. Since these are non-standard processes, most of the work is done manually, using various tools adapted to our needs.

Figure 2. Pre-treatment scheme of the invasive plants used in the manufacturing processes of protective packaging.

Removing and preventing the spread of IAS is essential, first and foremost to reduce the damage they cause to the environment and at the same time it is

necessary to consider the European Regulation No. 1143/2014 on the prevention and management of the introduction and spread of invasive alien species.

The suppression over IAS is the responsibility of the landowner. On private lands, the owners are known, while the maintenance of the public areas are carried out by the economic public services. In Slovenia, landowners are obliged to suppression of invasive plants from the genus Ambrosia, which is regulated by the Decree on measures for the control of harmful plants from the genus Ambrosia. For all other non-native species, prevention and control is recommended. To optimize the collection of non-native plant species, company Surovina prepared a questionnaire, based on which a strategy for the development of new collection system and the method of the pre-treatment of the invasive plant species were prepared. The invitation to complete the survey was send to all registered public service providers and municipalities.

Provider of public services carry out cleaning and maintenance of public areas, which also includes mowing and pruning of trees. Maintaining of green areas, also reduces and prevents the spread of non-native plants.

72 % of the public service providers have established the system for collecting and removing of non-native plant species. When removing invasive plants, it is crucial to take proper precautions and understand their life cycle. Improper disposal can allow invasive plants to regrow or be transported to previously uncontaminated areas. 44 % of the maintainers of public areas collect and remove IAS regularly, more than three times a year. About third remove IAS once a year, and 22 % only remove IAS on request. Cautiously handling of invasive plant parts is extremely important. Not every disposal method is appropriate for every species. Around third of the maintainers of public areas provide for the collected non-native plants the incineration, either handover them to the incineration facility or burn the debris on the site. 26 % handover the collected plants to composting facilities. Only a third of non-native species are handover to landfill sites, which is not a suitable disposal method for certain species, as they can regrow and spread (Data from survey: Removal, collection and management of invasive native plant species (and other green waste) by public service providers, 2023). Also, additional caution is required in aerobic and anaerobic decomposition processes, as the seeds of some plants are extremely resistant to the conditions and if the requirement parameters of hygienization are not met, incomplete destruction of the seeds may occur.

Slightly more than half of the public service providers remove and collect non-native plant species separately from native species, even in areas where plants

coexist (Data from survey: Removal, collection and management of invasive native plant species (and other green waste) by public service providers, 2023).

Proper disposal of removed invasive plant material is critical to the control process. Invasive alien plant species usually spread quickly and successfully in nature, their debris can re-root in an area or spread to another environment. To reduce their populations in the environment, it's important to remove the whole plant, even as much of the root system as possible; even a small portion can restart the infestation. Of course, this is possible in the case of individual specimens or smaller populations. In the case of larger populations, the regular mowing is necessary to reduce the populations. To be effective, you will need to mow or cut infested areas three or four times a year for up to five or more years. Almost half of the maintainers of public areas are aware of the proper control over the IAS, as they remove the entire plants (Data from survey: Removal, collection and management of invasive native plant species (and other green waste) by public service providers, 2023).

Pre-treatment actions of the plants used for manufacture of the paper pulp and later for production of packaging is very important, as we mention before. In the production only stems are used because they are rich in lignocellulose. The use of waste from invasive plant species to control invasive populations were perform by several studies on a laboratory scale, but most of them exclude a cost-benefit analysis. Most of the studies cannot be transfer in real lifetime management. The use of invasive waste should be adopted within a clear regulatory framework to avoid bias in the utilization of this waste (Lorenzo and Morais, 2023). Because of the lack of real scale examples using plants for recycling purposes, the majority of public area maintainers (70 %) are not willing to separate plants parts and thereby contribute to increasing the share of recycling. To such high percentage also contributes the fact, that pre-treatment preparation of the plants is time-consuming mainly manual work and the lack of staff (Data from survey: Removal, collection and management of invasive native plant species (and other green waste) by public service providers, 2023).

There is a variety of non-native species that distinguish from each other. Some plants, such as Japanese knotweed and spotted knapweed, have resilient rhizomes, extensive root structures, and hardy seeds that can survive and regrow (Department of Environmental Conservation, 2019). The proper handling of the plant parts of IAS varies among the species themselves. Certain species are very well adapted to difficult environmental conditions and have different survival mechanisms (e.g. the seeds of some plants can survive for several years before germinating). A quarter of public area maintainers already separately collect

invasive plants by species. So far, separate collection of invasive species has been shown to be the key in the recycling processes.

The Institute of Nature Protection of the Republic of Slovenia prepared the document TREATMENT OF RESIDUES OF INVASIVE NON-NATIVE PLANTS: Expert opinion based on a study of the literature, which is helpful with the questions/ambiguities of handling with different parts of invasive plants.

	GREEN PARTS (LEAVES AND STEMS)				FLOWERS, SEEDS, FRUITS AND ROOTS		
English name	*Scientific name*	Home composting	Aerobic and anaerobic decomposition	Incineration facilities	Home composting	Aerobic and anaerobic decomposition	Incineration facilities
IAS of Union concern							
Common Milkweed	*Asclepias syriaca*	√	√	√	x	√	√
Himalayan balsam	*Impatiens glandulifera*	√	√	√	x	√	√
Kudzu	*Pueraria lobata*	x	x	√	x	x	√
Giant Hogweed	*Heracleum mantegazzianum*	√	√	√	x	√	√
Tree of Heaven	*Ailanthus altissima*	√	√	√	x	x	√
Water hycinath	*Eichhornia crassipes*	√	√	√	x	√	√
Skunk Cabbage	*Lysichiton americanus*	√	√	√	x	√	√
Nuttall's Waterweed	*Elodea nuttallii*	√	√	√	√	√	√
Other selected IAS							
Canadian Waterweed	*Elodea canadensis*	√	√	√	√	√	√
Canada Goldenrod	*Solidago canadensis*	√	√	√	x	√	√
Giant Goldenrod	*Solidago gigantea*	√	√	√	x	√	√
Japanese Knotweed	*Fallopia japonica*	x	√	√	x	√	√
Common Ragweed	*Ambrosia* spp.	√	√	√	x	x	√
American Pokeweed	*Phytolacca americana*	√	√	√	x	x	√
Indian pokeweed	*Phytolacca acinosa*	√	√	√	x	x	√
daisy fleabane	*Erigeron annuus*	x	√	√	x	√	√
Hacienda Creeper	*Parthenocissus* spp.	√	√	√	x	√	√
Wild Cucumber	*Echinocystis lobata*	√	√	√	x	√	√
Staghorn sumac	*Rhus typhina*	√	√	√	x	x	√
Indigo Bush	*Amorpha fruticosa*	√	√	√	x	√	√
Black Locust	*Robinia pseudoacacia*	√	√	√	x	√	√
Foxglove Tree	*Paulownia tomentosa*	√	√	√	x	√	√

Figure 3. Guidelines for handling with different parts of invasive plant species. Source: Strgulc Krajšek, 2016.

Generally, the safest way to dispose invasive plant material is by putting plant material in bags and dispose it at a landfill or incineration station, followed by composting in composting plants and anaerobic decomposition in biogas plants. Due to large invasive plant populations and resulting high quantity of green waste in some regions, burying it at a landfill may not be the most environmentally-friendly option. Composting facilities may not reach high enough temperatures to inactivate certain invasive plant material, such as seeds. Knotweeds and hawkweeds are two groups of invasive plants that are able to survive high compost temperatures (Invasive Species Council of BC, 2021). For

this reason, it is extremely important these species are disposed of properly through incineration or disposal in landfill, and don't end up in home composter.

It is even more difficult to obtain data or draw a conclusion about the method of collection and handling of non-native plants in case of the removal on private land. In most cases, private landowners throw IAS into the domestic compost bin or leave the biomass at the removal site. Such handling, especially in the case of invasive plants, is very questionable, as invasive plants are highly adaptable and easily move into to new areas by seed or vegetative fragment dispersal, especially during the flowering period. If private landowners bring green garden waste to the collection center, with the questionnaire we obtained some insight of further removal actions.

30 % of collection centers already collect non-native plants separately if citizens bring them separately from other green waste. A little less than half of the collection centers handover the collected non-native plants to aerobic decomposition to the composting facilities (44 %). Only a smaller share is sent to incineration (8 %). Around a quarter of the collection centers handover the green garden waste to landfill sites, which is not the best option of further handling with IAS, as in the mix of the green garden waste there could be some problematic invasive species (Data from survey: Removal, collection and management of invasive native plant species (and other green waste) by public service providers, 2023).

According to the diverse results of the survey questionnaire, currently in Slovenia is a lack of guidelines and regulations regarding the invasive species control. Based on this, our strategy within the LEAP project is to provide residents, businesses and the local community with collection point to handover problematic plant species, where efficient and correct handling of invasive plants are taken and preparation for secondary purposes, production of paper pulp and later protective packaging for household appliances. At the same time, different educational and awareness materials about invasive species, production and importance of packaging based on alternative cellulose fibers are design, which will be reflected in the development of the teaching-demonstration network. As part of this, consortium is setting up an online info point and a demonstration center with various learning content for different target populations.

In the scope of the LEAP project, Surovina organized a removal invasive plants day in the month of May, in order to educate and raise awareness regarding the invasive plants, problems and proper disposal processes. During that day, correct method of removing invasive plants and pre-treatment procedure, that need to be taken for the use of stems in the manufacturing processes, was demonstrated

to local community. Example of the correct preparation of invasive plant waste for handover to collection center in Maribor was presented. For awareness purposes, Surovina prepared educational material regarding two invasive plant species.

Figure 4. Educational material for awareness purposes.

3 PROPER MANAGEMENT OF INVASIVE NATIVE PLANT SPECIES

Handling with invasive species always open the question, how to disposal plant parts, to avoid spread in the environment. Improper disposal is a major pathway of introduction, as invasive plants are often disposed of in ways that allow their seeds or plant parts to be dispersed. In Slovenia is the lack of information and places, such as collection points, to properly dispose of invasive species. The results of the survey questionnaire show us, that handling with invasive plants is very different among of the economic public service providers. Everything between burning debris on-site, which is not legally and formally sufficiently regulated, to handing it over to incinerator plants, composting facilities, or landfill plants, and leaving waste material at the place of origin. Removal and control of invasive alien species is essential from the point of view of prevention and reducing damage.

There are three main disposal options available for invasive plants: land filling, incineration (in incineration plants, on-site) or biological decomposition (aerobic and anaerobic). Removal of invasive alien plant species is most effective before flowering, as the most common way of spread is by seeds. How we treat a plant depends very much on the part of the plant (Invasive Species Council of BC, 2021).

Table 4. Disposal options for invasive plants. Source: Invasive Species Council of BC, 2021.

Disposal Method	***Slovenian Regulation***	***Pros***	***Cons***
Landfilling	*Regulation on waste disposal sites*	• *By putting plant material in bags minimizes the spread in the environment* • *Special precautions must be taken to ensure separate burial from other waste and that plastic bags are not torn at landfills that dispose invasive plants*	• *Takes up space in landfill* • *Contributes to greenhouse gas emissions* • *Increases plastic in landfills* • *Good option for disposing of small volumes of invasive plant material (time consuming process)*
Burning on-site	*Regulation on fire protection in the natural environment*	• *Minimizes movement of plant material* • *Limits potential spread of invasive materials during transport* • *Cost-effective* • *Easy*	• *Special precautions must be taken to ensure that wind don't spread seed through the air (e.g. goldenrod, large linden)* • *Home burning don't destroy most resilient parts of plants* • *Drying*
Industrial incineration	*Regulation on waste incinerators and waste co-incineration plants*	• *Most efficient and reliable disposal option for invasive plants (for all parts of plant, including seeds, fruits, roots) - effectively destroy all parts of the plants* • *Does not take up space in a landfill*	• *Not always available* • *Uses resources (fuel, electricity) to burn* • *Source of greenhouse gas emissions*
Composting – is a controlled, aerobic (oxygen-required) process that converts organic materials into smaller constituent parts, with the help of chemical reactions	*Home composting: Regulation on handling biodegradable kitchen waste and green garden waste*	• *Environmentally-friendly* • *Closed composting: all requirement parameters such as humidity, the highest temperature reached, the duration of the highest temperature reached, the minimum number of days with the highest*	• *Open composting: Not guaranteed for all invasive plant species that reproductive parts will be rendered non-viable – good option for certain species.* • *Home composting: special precautions must be taken (regular monitoring*

of micro- and macro-organisms. Home composting Open composting Closed composting	*Industrial composting: Regulation on the processing of biodegradable waste and the use of compost or digestate*	*temperature reached and the number of turns of the compost mass are reached – hygienization (destroy all parts of the plants, including seeds)* • *Compost*	*of composter) to ensure/prevent invasive alien plants to resprout.*
Anaerobic decomposition – is a controlled, anaerobic (absence of oxygen) process that converts organic materials into smaller constituent parts, with the help of chemical reactions of micro- and macro-organisms.	*Regulation on the processing of biodegradable waste and the use of compost or digestate*	• *Suitable for waste with a high moisture content (food waste, sludge from sewage treatment plants, IAS)* • *No large amounts of additional structural material needed* • *Biogas - energy source (for heating, electricity, biofuel)* • *Digestate (fertilizer)*	• *Smells* • *Not guaranteed for all invasive plant species that reproductive parts will be rendered non-viable – good option for certain species.*

Disposal of invasive plants mostly dependent on the local waste facilities and their contracts with the recycling or incineration companies. The most efficient method to dispose invasive plant material is incineration. With the high temperature in incineration plants all parts of the plants burned. But on the other hand, incineration plants are very energy consuming (fuel, electricity) and source of greenhouse gas emissions.

By using the stems of invasive plants for secondary purposes, we reduce the consumption of primary raw materials for the production of paper pulp products. At the same time, the project contributes to the implementation of Directive (EU) 2019/904 on reducing the impact of certain plastic products on the environment with a sustainable transition to a circular economy based on biodegradability, increasing reuse and recycling, reducing the disposal and incineration of waste packaging and the use of raw materials. Also, by switching from EPS to bio-cellulose packaging, we directly influence the reduction of CO_2 emissions, which is in line with the action plan of the European circular economy, which is an important pillar of the European Green Agreement.

4 CONCLUSION

The strategy of the LEAP project is to establish a suitable system for collecting, preparing and producing protective packaging or other paper pulp-based products, out of invasive alien plants. The first very important step is to develop efficient collecting method for invasive plants. Company Surovina inaugurate a collection point in Maribor, to accept invasive plant wastes and properly prepare stems for production of paper pulp and the product. In this manner, any help from local communities is more than welcome, therefor Surovina organized demonstration-collection day, where new strategy for collecting invasive plants was presented. New strategy was devised with the help of the results of a survey conducted among public service providers. Because it is a new way of collecting ang preparing plants for secondary purposes, which demand additional work and is time consuming, the maintainers of public areas are not in favor of such a method of collection.

Based on the current situation in the field of removal and handling of invasive alien plant species, we devised new recommendations and established a teaching-demonstration network with the aim of raising awareness and educating the public.

The removal of invasive species from the environment must always be undertaken thoughtfully and in compliance with the regional/national regulation. Handling with invasive plants requires planned strategy to prevent spreading in the environment. Invasive plant species always removed before or after flowering to avoid involuntary seed dispersal. Removal is most effective in the case of individual plants or small stands, consider how the invasive plant grows (tubers, fragments, and seeds) and removed all reproductive parts. To decrease the bigger populations, regular mowing is necessary. The most important measure, however, is to inform and raise awareness among the public about the impacts of invasive species and the correct removal and handling of plant parts, which the LEAP project is committed to.

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Regulation on handling biodegradable kitchen waste and green garden waste (Official Gazette of the RS, No. 39/10 and 44/22 – ZVO-2).

Regulation on the processing of biodegradable waste and the use of compost or digestate (Official Gazette of the RS, No. 99/13, 56/15, 56/18 and 44/22 – ZVO-2).

Regulation on waste disposal sites (Official Gazette of the RS, No. 10/14, 54/15, 36/16, 37/18, 13/21 and 44/22 – ZVO-2)

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Commission Implementing Regulation (EU) 2017/1263 updating the list of invasive alien species of Union concern established by Implementing Regulation (EU) 2016/1141 pursuant to Regulation (EU) No 1143/2014 of the European Parliament and of the Council

Commission Implementing Regulation (EU) 2019/1262 amending Implementing Regulation (EU) 2016/1141 to update the list of invasive alien species of Union concern

Commission Implementing Regulation (EU) 2022/1203 amending Implementing Regulation (EU) 2016/1141 to update the list of invasive alien species of Union concern

DEVELOPMENT OF MOULDED PULP PROTECTIVE PACKAGING FROM ALTERNATIVE FIBERS

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Original scientific paper
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Abstract: *Expanded polystyrene foam is a standard protection element for many packaging solutions which needs cushioning properties against mechanical stresses. While its protective functions are very good (lightweight good cushioning properties, easy to 3D-form with tooling) the environmental aspect of this material is questionable due to bulkiness (high space volume) and low rates of real and viable recycling infrastructure. Due to that producers have switched to fiber solutions (corrugated board inserts, fiber foams and biopolymer fiber composites) as an alternative solution. Even though this fiber-based alternative solutions are environmentally friendlier the overuse of cellulose fibers from wood sources can also be a burden on the environment. On the other hand, invasive alien plants due to their negative impact on biodiversity and other economic damage (riverbank degradation) are one of the possible solutions for producing fiber elements.*

In this paper the development of moulded fiber cushioning elements, made from locally sourced invasive fiber alien plants (Japanese knotweed and Canadian goldenrod) and processed in Slovenia is presented as a part of the protective packaging system for household appliances. The fiber morphology and processing as well the prototyping of the moulding tools have influenced the mechanical properties needed for protection simulation due to different fiber bonding and entanglement. The obtained results serve as a basis for further development and structural analysis (finite elements modelling) of stress points for building simulation software for the use of alternative fiber solutions.

Keywords: pulp moulding, invasive alien plants, protective packaging, mechanical properties, CNC

1 INTRODUCTION

Protective packaging presents materials that are created to safeguard and cushion products during shipping, storage and handling to protect them from potential physical damage. For that purpose, different types of materials (e.g., paper, plastic, metal etc.) can provide protection and present protective packaging. While the global market of protective packaging is expected to grow at 5.1% CAGR till 2030 (Bloomberg), the development of new, environmentally friendly and recyclable, protective packaging is essential. In use are already different solutions (paper fill, shredded paper, shredded corrugated board) for protecting goods that are recyclable. However, when packing heavy industrial products there is currently no alternative at scale to EPS (Styrofoam). While there is an ongoing debate about recycling rates at scale of EPS packaging between stakeholders (Ellen McArthur foundations, NGOs and EPS producers), a recent common agreement declared EPS as recyclable (Ewasa, 2023) these figures are between 30 and 40% of post-consumer waste ratio. These figures are lower than the industry average for the pulp and paper industry (recycling rate of 82.3% (4Evergreen, 2022), and due to the tight requirements on the time schedule of the draft version of the New Packaging Waste Directive EPS recycling infrastructure and collection business models cannot currently match the fiber-based industry.

One of the challenges regarding the use of cellulose based protective packaging is the high volume and density of fibers which can further burden the EU biomass availability. In a report by Materials Economics (2021) it is estimated that with the projected rise of the use of cellulose based sources for different applications (beside the use for energy generation) EU will have a shortage of 40–70% of available biomass (around 5–6 EJ per year). The attention regarding the importance of carbon sequestration in woody species due to their long-term replenishment also shifted the focus to alternative fiber solutions.

Fiber-based cushioning and protective packaging come in different forms. Fiber foams have already been introduced to the markets (Stora Enso Papira from 2021) which are produced from sustainable managed forests (wood-based cellulose). On the other hand, moulded pulp packaging is increasing its presence on the market. Moulded pulp can be produced with injection moulding processes where most usually a natural fiber - starch or other biopolymers are used. In a review by Rabbi, Islam and Islam (2021) point out that in this production

processed the final material properties are dependent on the chemical treatment of the fiber, matrix combination, and the fabrication process itself. The so-called Pulp Injection Moulding (PIM) method, already present on the market, is based on injection moulding (similar to plastic production) and can achieve complicated 3-dimensional structural parts which are difficult to create by conventional paper packaging or other pulp mould technology.

Beside the injection moulding systems there are the more conventional production processes related to classic wet moulding where the forming and drying process is integrated in one mould (Zhang et al, 2022). During the moulding process, two main steps are involved: vacuum forming process and drying process. Specifically, a wide variety of custom-designed moulds/tools allow the pulp to form different geometries/shapes. After that, dewatering occurs, usually by vacuum sucking to remove a sufficient volume of water (35%–50%) to form a desired shape. This process is known as the forming process (Didone et al., 2017). Other variations also include a dry mould process promoted by PulpPac where wood-based fibers are air treated on a vacuum belt to form an air-laid fiber structure (200–1500 g/m^2) which is coated and laminated on a tissue material before forming by heat pressing.

The moulded protection packaging was previously analysed by Hoffman (2000), who has determined the static and dynamic properties of moulded protection packaging elements, and found that the used equation shows good correlation to the results achieved for small static loads. Similar results were obtained from the earlier research of Eagleton and Marcondes (1994), whose results showed that the moulded-pulp test samples had good cushioning characteristics for low static loadings, low drop heights, and single impacts. However, the cushioning characteristics of the material were inferior to those of EPS foam at static loadings above about 5 kPa, and where higher drop heights or multiple impacts occurred. These properties were improved by using two samples with interlocking dimples (engineered elements) - where the number of the “dimple” proved to be beneficial if in larger numbers for moulded cushioning solutions. In a more recent study conducted by Alptekin A, Çallioğlu H (2023) different mixtures (eucalyptus or pine fibers (48 wt %) compound with cationic starch (48 wt %) and carboxymethyl cellulose (CMC) (4 wt %)) and processing methods (moulded pulp, extrusion and compression moulding techniques) were tested. Composite samples indicated significantly better tensile, flexural, and compressive values, at least four times, compared with the moulded pulp samples. On the other hand, the moulded pulp samples had more than 2 times better impact characteristics against composites.

For moulded packaging applications there are several research papers which tested 80/20 straw pulp/kraft pulp mixes (Curling et al. 2017), while Be Green Packaging has introduced material made of six different resources, including bulrush, wheat straw, sugar cane, and bamboo (OAS Cataloging-in-Publication Data, 2016). These materials however do not have widely available cushioning data. One of the solutions to overcome this depletion of the available biomass in the EU is to use under-utilised cellulose sources, also for packaging papers are the so-called invasive alien plants (Kavčič, Lavrič and Karlovits, 2023). Invasive alien plants are non-native in the ecosystem where their spreading can cause economic and environmental harm to the local environment. Direct economic impacts were reported in the Eschen et al. (2023) as they may profoundly change ecosystem functioning by altering species composition, physical habitat components, nutrient cycling, primary production and damages in the flood defence structures. Their quick replenishment and spreading can be made useful if appropriate utilisation can be organised, and recently alternative papers made based from invasive alien plants have been found to be appropriate materials for packaging (Vrabič and Možina, 2022; Karlovits et al., 2021).

The aim of this paper is to describe the production process of moulded protective fiber packaging of the two invasive alien plants; Japanese knotweed and Canadian goldenrod utilisation in production. As the process of producing the protective elements is wet moulding the process of the mould with the appropriate parameters is also described. As fibers from these plants are usually shorter the strengthening of the fiber structures against mechanical stresses can be done with the addition of nanocellulose solutions. In this research the samples were mixed with wood-based cellulose nanocrystals (CNC) solution in different ratios and mechanical properties of the samples were tested. These samples will be the starting point of building up appropriate finite element models for the development of open-source software for designing protective packaging elements.

2 MATERIAL AND METHODS

The experimental part consisted of several steps: designing and 3D-printing of the polymer mould, preparation of aluminium mould and counter-mould, fiber preparation, its mixing with CNC and mechanical evaluation of compression/cushioning properties.

2. 1 The mould preparation – designing and 3D printing

The desired shape of the protective packaging was firstly engineered to present a truncated cone geometry, conceptualized, and designed using CAD software.

The mould has overall dimensions of approximately 50 mm in height, a base diameter of 95 mm, and a bottom diameter of 50 mm. The wall thickness was 3 mm to ensure appropriate structural rigidity and mechanical integrity. Thickness was empirically determined to be sufficient for maintaining the screen's structural integrity throughout the filtration and drying operations, without sacrificing porosity or flow-through efficiency.

According to the length of the fibers used in the study, the mould geometry features a pattern of square-shaped apertures designed to execute the filtration function. Apertures on the curved surface measure 1.2 mm in width and 0.8 mm in height. The dimensions of the apertures were selected to ensure effective dewatering while preserving the shape of the filtered cellulose fibers.

The 3D-printing process was executed using a Bambu Lab 3D-printer, which has been validated for its precision, reliability and speed in similar applications. Utilizing a 0.4 mm nozzle, process was parameterized with a layer height of 0.2 mm to ensure optimal resolution and mechanical integrity of the screen.

2. 2 Aluminium mould and counter mould for thermoforming

To provide dimensionally more stable samples, the wet pulp was blown into a heated aluminium mould and pressed with a heated counter-mould. Both, aluminium mould as well as counter-mould were prepared to fit with the 2 mm thick sample. The aluminium mould and counter mould for thermoforming were prepared by CNC mechanical processing.

2. 3 Fiber suspension preparation

Before the final recipe for paper made of invasive alien plants were made, basic morphological properties of fibers obtained from them needed to be measured in terms of length and width were measured (Table 1) and were taken into account for final paper recipe since they can affect final paper properties.

So called JK - “Japanese knotweed paper” was made of 60% of bleached commercial softwood and hardwood pulp in the ratio 50:50, refined to 25°SR prior to use. 40% of fibers obtained from Japanese knotweed were added to this mixture. In order to improve the efficiency of the papermaking process and the quality of the final paper, 10% of fillers, 1% of cationic starch and 3% of sizing agent were added.

For CG - “Canadian goldenrod paper” 55% of bleached commercial softwood and hardwood pulp in the ratio 50:50, refined to 25°SR and 45% of fibers obtained

from Canadian goldenrod were used. The amounts of filler and cationic starch stayed the same, while the amount of sizing agent was increased to 3.5%.

Both papers were disintegrated and diluted to 1% concentration, being known as blank samples, and marked as JK (Japanese knotweed paper) and CG (Canadian goldenrod paper). Sample where 10% dry mass CNC was added were marked as JK + CNC and CG + CNC.

Table 1. Basic morphological properties of the fibers obtained from invasive alien plants.

	Parameter	***Japanese knotweed (JK)***	***Canadian goldenrod (CG)***
Fiber properties	*Fiber length (mm)*	*0.775*	*0.452*
	Fiber width (µm)	*18.66*	*13.85*

For the presented research commercial CNC produced by NAVITAS d.o.o., Slovenia was used. The preparation was performed as described by Kunaver et al. (2016). The CNC particles were suspended in water solution with the concentration of 2.68%.

2. 4 Sample preparation

For the sample preparation, the 3D-printed mould which was fitted on a vacuum head was immersed into the fiber suspension and 500 ml suspension with 1% fiber concentration was sucked through the mould to form the fiber sample on the surface of the mould. After the formation, the sample was counter blown into the heated aluminium mould and manually pressed with a heated (340°C) counter-mould for 30 seconds. After this step the final drying was done by a 30-minute oven drying at 110°C with additional thermoforming every 10 minutes.

2. 5 Mechanical testing

After the 3D thermoformed moulds were dried the samples were conditioned for 24 hours at 50% relative humidity and 23°C according to the ISO 187 standard. To check the influence of the fiber and CNC mixtures mechanical compression testing was performed on the multi testing machine (ZwickRoell, Ulm, Germany) using compression plates and a 10 kN measuring head.

3 RESULTS AND DISCUSSION

3. 1 Mould preparation

As mould and tools were also prototyped to achieve good formation results there were adjustments to the design and processing of the 3D printed mould. During

the mould designing it was important that the vertical dimension of apertures is synchronized with the layer height setting to maximize the aperture size accuracy. In other words, a precise alignment strategy was employed wherein each aperture begins or ends precisely where a new layer of the print starts or concludes. This alignment was meticulously calibrated to synchronize with the predefined layer height of 0.2 mm, optimizing the structural coherence and mechanical properties of the device. This ensured a uniform flow distribution and minimization of clogging risks, contributing to both the mechanical robustness and functional effectiveness of the mould. This setting was critical in preventing any deformities or inconsistencies that might compromise the filtration effectiveness. A specific attention was directed towards the mould's apertures on both the top and bottom flat surfaces. The design eliminated the conventional top and bottom layers in the 3D-print, utilizing a grid infill pattern with infill density set at 68%. It provides an optimal combination of mechanical strength and open spaces, ensuring that the cellulose fibers were efficiently formed on the surface of the mould.

To address the challenges posed by overhang structures during the 3D-printing process, particular attention was paid to the printing angle. Angles greater than 45° were avoided in overhang features to prevent print failure or the need for excessive support structures. The geometric attributes of the screen similar to a small cup or a truncated cone enable it to act as a mould, guiding the cellulose fibers into a specific form as it undergoes the separation and partially the drying phase.

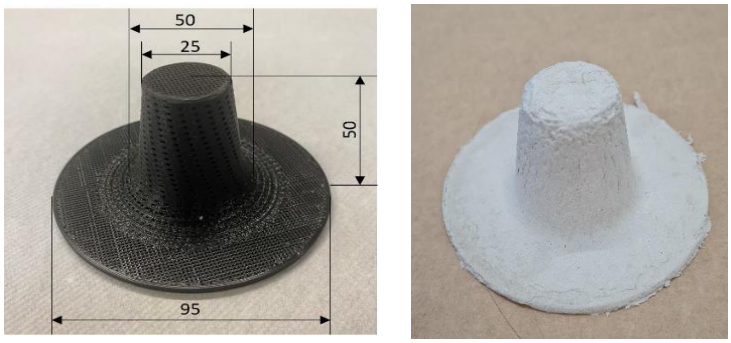

Figure 1. 3D-printed mould (left) and final moulded pulp product (right).

3. 1 Mechanical testing

The dried thermoformed samples were checked to continual compression load with compression test to test the influence of CNC addition in different invasive alien plant mixtures. In Figure 2 one can see the sample before and after the performed test.

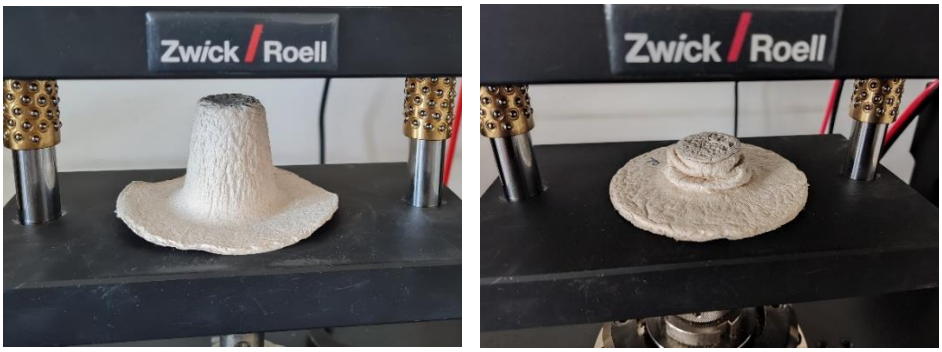

Figure 2. Sample before (left) and after (right) the compression test.

We have assessed the compression force for the first 35 mm of compression test. As can be seen in Figure 3, the force needed for compression increase in first 15 mm, the maximum force is achieved when the sample is compressed between 15 mm and 20 mm. After that distance, the force is slowly decreasing. However, after 35 mm or 40 mm the force unpredictably increase again, due to the compressed material. This effect is due to the thickening of the base of the moulded 3D elements due to settling at the base of the shape which can be seen at Figure 2 (right). The addition of CNC for both invasive plants increase the overall values for the analysed distance.

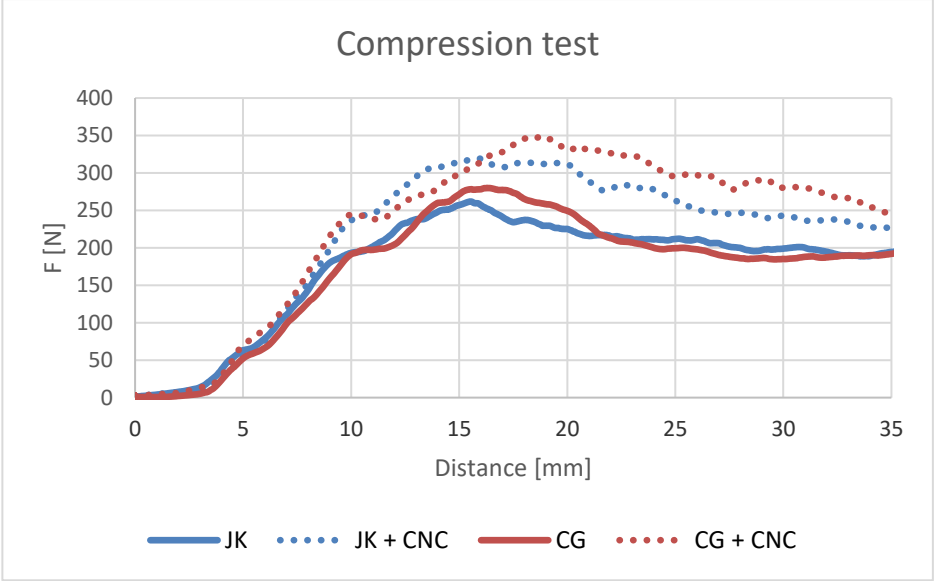

Figure 3. Compression test of protective packaging samples.

Comparing maximum forces among samples with different fibers and added CNC, the maximum forces for each sample were also determined. From Figure 4 we can observe that the highest forces during compression test were obtained with both samples that contain CNC. Maximum force for CG + CNC sample was 375 N, while JK + CNC has slightly lower values (347 N). Actually, the same maximum forces were achieved with JK and CG samples (287 N and 288 N respectively). Even though the standard deviation among samples is quite high, the average values show, that CNC has great influence on compression strength and increase the maximum force of samples regardless of used alternative fibers (JK or CG). The high surface area of CNC enables highly reactive surfaces that increase connection between fibers as well as stiffness of the sample.

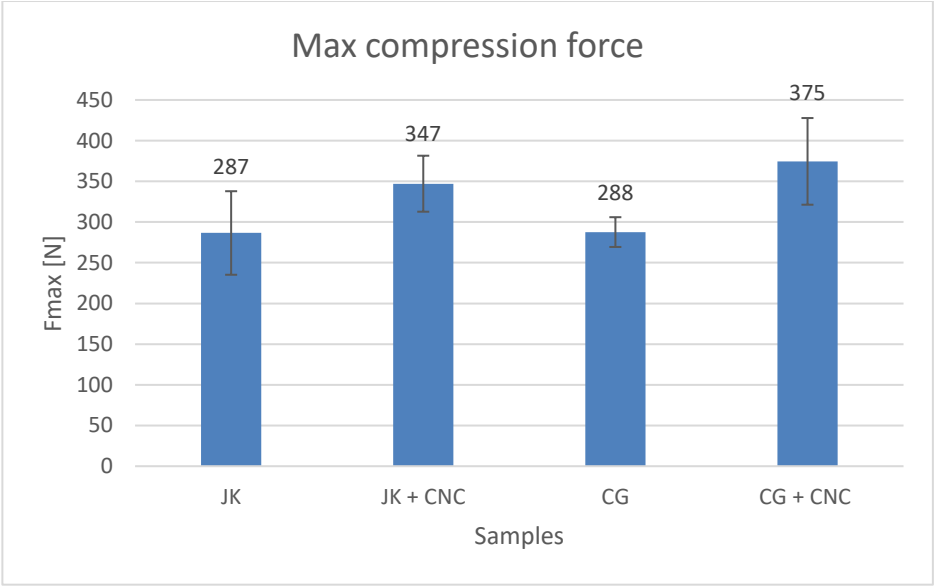

Figure 4. Max compression force.

4 CONCLUSIONS

In the presented research, the possibility of using 3D-printed mould for moulded pulp protective packaging production was analysed. Based on results it can be concluded that 3D-printed mould could be a useful tool for laboratory testing and development of new biodegradable and recyclable (protective) packaging. During the development and 3D-printing of mould, different factors should be taken into consideration. To ensure adequate dewatering, especially the shape and size of apertures (which are dependent on used fibers) should be consider. Regarding forming the fibers in the developed moulds not just commercially available fibers but also alternative fibers sourced from invasive alien plant

species have a great potential for that kind of applications, which helps biodiversity to be preserved. Comparing the overall compression strength of samples and the achieved maximum force, it can be concluded, that the addition of CNC into the pulp before formation has positive impact on higher maximum compression strength and overall strength of the moulded samples. Future research will include further optimization of the fiber preparation and mixtures with the appropriate additives (CNC, starches) with the designed mould and tools to achieve maximum cushioning properties even for higher static loads (>5KPa).

Acknowledgments: *The authors acknowledge financial support from the Ministry of Cohesion and Regional Development of the Republic of Slovenia, provided under the Norway grants, according to grant agreement No. C1541-22B710043 (LEAP project). We would also like to express our gratitude to the company NAVITAS for donating CNC used in this research.*

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SUSTAINABLE PACKAGING INNOVATIONS IN THE FASHION SECTOR: PROGRESS, CHALLENGES, AND FUTURE DIRECTIONS

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Abstract: *The European Commission has proposed EU-wide regulations for recyclable packaging by 2030. Sustainable packaging innovations in the fashion sector have attracted public attention in recent years. However, it is uncertain how effective these companies are in reducing their use of virgin plastics, as the focus remains on improving the sustainability of garment production rather than packaging. Apparel and footwear brands are taking seven approaches to improving packaging: rethinking solutions, downsizing, eliminating plastic, reusing, recycling and composting. A study using a data-mining approach examined 400 international brands that promote sustainable packaging. The brands were categorized as progress, implementation, commitment and rethinking based on their sustainability mission statements. The results show that nearly 60% of fashion brands have made progress on sustainable packaging, with over 30% moving to improved packaging. Others have committed to future improvements. Footwear and apparel brands are adopting various sustainable packaging strategies, including The Plastic Global Commitment, Noissue Eco Packaging Alliance, One Tree Planted, The Responsible Packaging Movement and Re:Pack. This study presents the advances in sustainable packaging for apparel, footwear, accessories, etc. To manage environmental impact, sustainable packaging solutions should be evaluated on a case-by-case basis, taking into account government initiatives and regulations. Although brand manufacturers*

are striving to find better packaging solutions, innovation in this area remains restrained.

Keywords: Sustainable packaging, fashion sector, plastic reduction, packaging innovations, apparel and footwear brands.

1 INTRODUCTION

The fashion industry has long been synonymous with creativity, style and self-expression. However, its rapid growth and global expansion have also led to significant environmental challenges, particularly in terms of packaging waste. As the fashion sector has taken center stage in addressing sustainability issues, there has been an increased focus on adopting environmentally friendly practices, with particular attention paid to sustainable packaging solutions. This study looks at the evolving landscape of sustainable packaging initiatives in the fashion industry. With the goal of reducing the harmful effects of packaging on the environment, numerous fashion brands have committed to redesigning their packaging to be reusable, recyclable or compostable. The urgency to curb plastic pollution has been reinforced by the European Commission's proposed EU-wide regulations that require all packaging to be recyclable by 2030 (European packaging waste, 2023). Despite the increased attention given to sustainable packaging innovations in recent years, the transition has not been without challenges. Fashion brands have historically prioritized improving the sustainability of their apparel production, often relegating the importance of sustainable packaging to the background (Boz et al., 2020, Ahmed et. al., 2021). This represents a knowledge gap when it comes to how effectively companies in the fashion sector are addressing the critical issue of reducing the consumption of virgin plastics (García-Arca et al., 2017; Escursell et al., 2021). This study takes a comprehensive approach by examining the multiple strategies used by apparel and footwear brands to improve the sustainability of their packaging. In addition, this research provides a detailed analysis of the different approaches used by fashion brands to improve their packaging. The "7R" framework, which includes rethinking solutions, reducing, reusing, repurpose, refuse, recycling and rot packaging, serves as the guiding principle for our research (Jestratijevic et. al, 2022).

The 7 R's of Sustainability: Eco-Friendly packaging solutions are (Jestratijevic et al., 2022):

1. Rethink: Businesses should reconsider traditional plastic and paper wrapping methods, exploring eco-friendly alternatives like bioplastics derived from

renewable sources, reducing the environmental impact of packaging materials.
2. Refuse: Advocate avoiding single-use plastics such as bags, cutlery, and straws, while rejecting overpackaging practices to reduce plastic waste and its adverse effects.
3. Reduce: Emphasize minimizing the need for certain products or packaging by opting for reusable containers and environmentally friendly materials that cannot be easily recycled.
4. Repurpose: Encourage businesses to transform discarded items into useful products, prolonging the life cycle of materials and reducing overall waste.
5. Reuse: Emphasize the benefits of reusing materials like cardboard, PET, HDPE, or investing in durable containers like glass or stainless steel to promote sustainable packaging practices.
6. Recycle: Prioritize recycling to keep materials at their highest value for as long as possible, considering factors like shape, size, and composition to optimize the recycling process.
7. Rot: Composting organic matter offers a solution for packaging contaminated with food scraps, contributing to nutrient-rich soil production and reducing landfill waste.

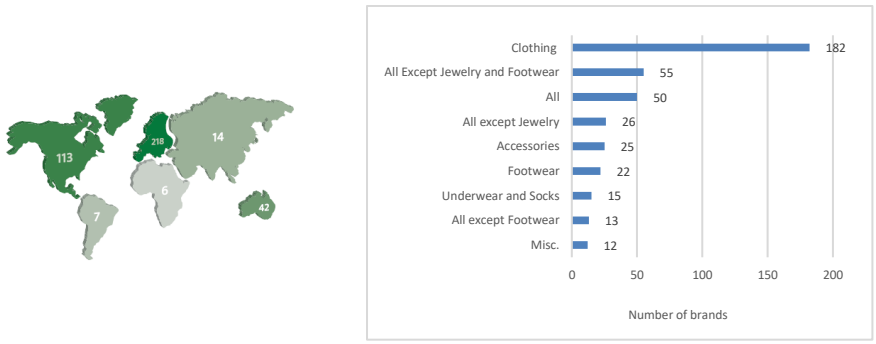
By providing up-to-date insights into the practical progress of sustainable packaging in the fashion industry, this study aims to stimulate further discussion and action. We emphasize the need for case-by-case consideration of sustainable packaging solutions, considering the complex interplay between environmental impacts and government regulations. Ultimately, this research aims to contribute to ongoing efforts to make the fashion industry more sustainable by addressing the critical role of packaging practices in sustaining our planet for future generations.

2 MATERIAL AND METHODS

A systematic review methodology was employed, using data-mining to collect sustainable packaging information from eligible brands (Zawacki-Richter et al., 2020). Only primary sources from brands' official websites and sustainability reports were reviewed, excluding secondary sources like social media and press articles without a link from the brand's website from November 2020 to January 2021. The final sample comprised 400 brands from various sectors and continents. Thematic content clustering facilitated iterative data analysis through five research stages.

3 RESULTS

European brands were found to lead innovation in sustainable packaging innovation with 55% of the sample (n=218). North America followed with 28% (n=113) of fashion brands offering sustainable packaging solutions, while South American, Australian, Asian and African regions accounted for 2-11% of the total sample (Figure 1a). In addition, the research showed that fashion brands in certain regions tend to comply with national and local regulations that influence their packaging choices. European brands were observed to avoid using single-use plastic bags, while brands in Australia often offer packaging that is 100% recyclable, compostable or biodegradable. In addition, sustainably oriented retailers in Africa and Asia often sourced packaging materials locally from artisanal communities.



a) b)

Figure 1. a) Distribution of analyzed brands across five continents; b) Subcategories per product category and number of brands.

Further analysis focused on the relationship between packaging improvements and specific product categories. Results revealed that clothing brands (45.5%) were the most committed to improving their primary packaging, which directly protects the product. Footwear (5%), accessories (6.25%), underwear, and socks (3.75%) brands followed with improvements in their primary packaging. Secondary packaging improvements were seen in footwear, accessories, and jewelry categories, while many brands did not specify the types of packaging they improved. Sustainability-related packaging certifications were explored, indicating that only a limited number of brands used such certifications. Among 400 analyzed brands, 55 had Forest management certification (FSC certificate), 24 promoted the Global Organic Textile Standard (GOTS), and 17 advertised having the Global Recycle Standard (GRS) for their packaging products. Most

brands (284) had no packaging certificates, raising questions about the sincerity of their sustainable packaging commitments.

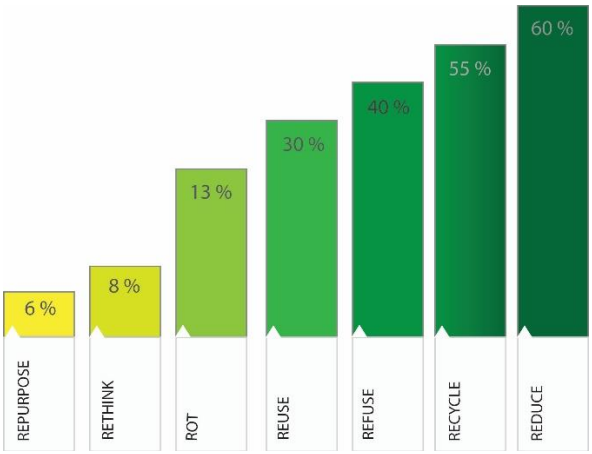


Figure 2. The shift from traditional to improved packaging solution.

Our findings illuminate the progress nearly 60% of fashion brands have made in adopting sustainable packaging practices, with over 30% having already initiated the shift from traditional to improved packaging solutions (Figure 2). The remaining brands have committed to rethinking or improving their packaging strategies in the near future.

We also examined the specific sustainable packaging strategies of leading apparel and footwear brands, highlighting prominent initiatives such as The Plastic Global Commitment, Noissue Eco Packaging Alliance, One Tree Planted, The Responsible Packaging Movement and Re:Pack.

The research demonstrated varied trends in sustainable packaging practices among fashion brands across different geographic regions. European brands led in sustainable packaging innovations, while the adoption of sustainable packaging certificates and partnerships remained relatively low.

3. 1 Opportunities

European fashion brands have demonstrated leadership in sustainable packaging innovation, presenting an opportunity for other regions and brands to follow suit (Islam et al., 2021). By adopting eco-friendly practices, fashion brands can position themselves as industry leaders in sustainability and attract environmentally conscious consumers. The study identified stronger preferences for sustainable product attributes among specific categories of consumers.

Understanding and catering to these preferences can open up new market segments and increase brand loyalty among environmentally conscious customers. Fashion brands in Africa and Asia have successfully sourced packaging materials from local artisanal communities. This presents an opportunity for other brands to support local economies and showcase their commitment to sustainable sourcing practices.

3. 2 Progress and challenges

The prevalence of sustainable packaging certifications is still relatively low among the fashion brands studied. Overcoming the challenges associated with obtaining and promoting such certifications could be a hurdle for many brands seeking to establish themselves in the sustainability credentials. On the other hand, some fashion brands didn't specify the types of packaging they improved. This lack of transparency may create doubts among consumers regarding the authenticity of a brand's sustainability claims, highlighting the importance of clear and open communication (Chirilli et. al., 2022). While there are partnerships focusing on sustainable packaging, a significant number of brands still lack such collaborations. Establishing strategic partnerships can be challenging due to resource allocation and alignment of long-term goals.

3. 3 Future perspective

As consumers become more environmentally conscious and demand eco-friendly practices, fashion brands are likely to increasingly adopt sustainable packaging solutions. This shift could drive industry-wide improvements and encourage the development of new eco-friendly packaging materials and technologies. The study revealed that clothing brands were most committed to improving their primary packaging. In the future, there may be a greater emphasis on developing innovative packaging solutions for other product categories, such as footwear, accessories, and jewelry, to further reduce environmental impact. The growing awareness and demand for sustainable practices may lead to an increased focus on obtaining and promoting credible packaging certifications. Brands that prioritize obtaining recognized certifications could gain a competitive advantage in the market. The fashion industry may witness more widespread collaboration and partnerships among brands and packaging providers to develop comprehensive, sustainable packaging solutions. These efforts could accelerate the transition to environmentally friendly packaging practices.

4 CONCLUSION

The findings from the study present both opportunities and challenges for the fashion industry's adoption of sustainable packaging. Embracing innovative practices, promoting transparency, and collaborating with stakeholders will be crucial for shaping a more sustainable future for fashion packaging. As consumer awareness continues to grow, sustainable packaging will likely become an essential aspect of a brand's overall sustainability strategy.

The main considerations and challenges that addressing sustainable packaging in this field are:

- Certification: Ensure compostable packaging is certified as home or industrially compostable.
- Collection and recycling infrastructure: Regional variations in recycling facilities may impact material choices.
- Contamination: Prevent contamination during recycling to maintain recyclability.
- Cost and viability: Initial costs and logistical challenges may be offset by long-term benefits and improved consumer perception.

The progress made in sustainable packaging in the fashion industry is encouraging, but there is still much room for improvement. With growing consumer awareness and demands for environmentally friendly practices, fashion brands are expected to continue their journey towards more sustainable packaging solutions, contributing to a greener and more responsible fashion industry.

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SUSTAINABLE FOOD PACKAGING: EMPOWERING CONSUMERS WITH COLOR-CODED SUGAR CONTENT AWARENESS

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Original scientific paper
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Abstract: *The purpose of developing the color-coding system development serves a dual purpose: enhancing awareness of sugar content in foods and to promote sustainability. Our study focused on dairy products on the Slovenian market and addressed hidden sugars and associated health risks. By integrating sustainability, we aimed to raise awareness of sugar content through packaging design with a consistent labeling and coding approach. Our research included key questions to ensure labeling effectiveness and sustainability. We focused on creating an impartial labeling system, organizing the hierarchy and layout of food information, and integrating seamlessly with existing packaging. Critical to successful implementation was evaluating the impact of the information design on consumer behavior in the area of food packaging. Based on our discoveries, we developed several variants of a multicolor and one colour labeling system. These variants differed in key information graphics, color palettes, placement, and formats. To illustrate the application of the system, we designed packaging for a fictitious brand and implemented the code system accordingly. The final step was to embed the packaging design into 3D models for each food category. Consistent and coherent color-coded labels were integrated into the packaging, effectively attracting consumer attention while providing important information. With sustainability at the forefront, our design approach aims to promote environmentally friendly practices from production to disposal. This holistic strategy promotes environmental responsibility throughout the packaging process.*

Keywords: Sustainable food packaging; color coding system; sugar content awareness; consumer empowerment; packaging design

1 INTRODUCTION

Sugar consumption is ubiquitous in the modern diets and is present in almost all processed foods. It is important to distinguish between natural and added sugars, as they have different effects on health. Added sugar, while offering benefits, can lead to overconsumption and health problems. Therefore, it is important to closely examine the ingredients of products. While excessive sugar is known to be present in products such as sugary drinks and confectionery, even supposedly healthy options such as yogurt, milk, and cereal can contain hidden sugar, making it difficult for consumers to be aware (College of California, 2023). Efforts to clarify sugar content on labels have resulted in different formats worldwide. Research by Scapin et al. (2021) found that interpretive formats that combine sugar content in grams with colors, indicators such as "high sugar content," or percentage of daily value are most effective. Labeling strategies using textual warnings, health claims, and graphic representations with teaspoons were moderately effective. Erickson and Slavin (2015) examined consumer behavior in response to the new sugar guidelines, while Coyle et al. (2020) found that interpretive formats that conveyed information about sugar, particularly those that indicated high sugar content, improved consumer understanding and led to healthier food choices.

Uniform labeling systems, such as Slovenia's, are still poorly researched and absent from the marketplace. Challenges remain in the European Union due to inconsistent nutritional data and lack of knowledge about dietary habits (Eržen, 2014). Differing terminology for sugars-"added" versus "free"-contributes to confusion, which is exacerbated by incomplete sugar content labeling. Analysis of sugar content poses problems because different chemical methods, such as quantitative and chromatographic methods, are both unable to distinguish natural from added sugar (Goldfein et al., 2015). Consumer understanding is complicated by complex terminology. The ubiquity of sugar warrants nuanced differentiation on labels. Effective formats with color-coded indicators or percent daily value information facilitate understanding and healthier food choices. It remains difficult to create consistent labeling systems due to inconsistencies in terminology, measurement methods and consumer understanding. The study sought to enhance awareness regarding sugar content in dairy products and cereals using packaging design and to develop a consistent labeling system applicable to various products.

2 MATERIALS AND METHODS

The research adopted a systematic methodology comprising five sequential stages to assess sugar content in dairy products and subsequently integrate findings into 3D packaging arrangements. Furthermore, an innovative multi- and one color-coded labeling scheme were devised to enhance visual representation.

2. 1 Methods and sampling

The research encompassed five distinct steps:

1. Sugar content analysis covered a wide range of dairy products in the Slovenian market, classified based on the results.
2. Detailed graphic analysis and packaging hierarchy design for specific food groups (e.g., yogurt, milk, butter) were undertaken, considering variations like plastic cups, bottles, cartons, and boxes.
3. A comprehensive graphical analysis and global comparison of diverse labeling methods (symbols, colors, formats) in Slovenia and other countries led to the creation of multiple labeling versions with distinct symbols, colors, formats, and layouts.
4. Developed labeling systems were applied to conceptual packaging (labels) for an imaginary brand, aligning with the prior analysis.
5. Facilitating realistic representation, 3D packaging models were generated for each food group (yogurt, milk, butter), each showcasing two labeling variations and colours using program Blender (NeoGeo, USA).

2. 2 Analysis of sugar content in dairy products

The study included an extensive evaluation of dairy items present in the Slovenian market, encompassing a total of 47 samples from 12 distinct producers. The samples were thoughtfully chosen to ensure representation across diverse product categories. Across four food groups, multiple products were analyzed across various stores as outlined below:

- Yoghurt or milk bottles/bottles: 10 samples
- Butter packets: 12 samples
- Milk cartons: 10 samples
- Yoghurt containers: 15 samples

3 RESULTS

3. 1 Results of analysis of present sugar content in dairy products

Using samples that included natural, fruit, and protein yogurts, statistical frequency distribution methods were used to form classes by ascending sugar content in the products. These classes facilitated the subsequent development of a coherent color-coded scale that allowed different colors to be assigned to specific classes. For example, the blue color was assigned to the class with the lowest sugar content. Within the product spectrum, sugar content ranged from a minimum of 3.8 g to a maximum of 14.0 g. The levels or classes of sugar in food were created based on analyses of dairy and cereal products available on the Slovenian market. The sugar scale contains five classes ranging from the lowest to the highest sugar content (Table 1). In contrast to the middle three open intervals, the minimum and maximum classes have less than 3 g of sugar and more than 15.4 g of sugar, respectively.

Table 1. Ascending classes of amounts of sugar in grams.

Very low	***Low***	***Medium***	***High***	***Very high***
< 0.3	*– 7.9*	*8.0 – 10.4*	*10.5 – 12.9*	*> 15.4*

3. 2 Preparation and design of a coding system with colors and typography

The creation of a multi-hued scale was driven by the objective of swiftly and effortlessly recognizing sugar content in products. This color-coded approach facilitates a more lucid and succinct assessment of sugar levels, expediting the acquisition of desired information for customers. Classes have been associated with specific color codes, fostering an intuitive and rational link between sugar quantity and its corresponding color (Figure 1a and 1b). The scale presented in Figure 1a boasts a sleek, elongated rectangular design. Within this framework, the classes are segmented into smaller sections, demarcated by white stripes seamlessly blending into the backdrop. Each class features distinct primary and secondary information, separated by negative space that forms an arrow pointing towards the relevant data. The shapes' corners exhibit a subtle roundness, contributing to a welcoming yet uncluttered visual presentation. One solution would be for the colors on the scale to differ significantly in brightness, but this could prove inconsistent, unclear, or lacking in contrast with five different consecutive classes. Therefore, we also created black and white symbols to indicate the primary data and placed them on a scale (Figure 1c).

Besides the monochrome scale with symbols, we have also created the possibility of a monochrome scale that is not so illustrated, namely with simple patterns to mark the class (Figure 1d).

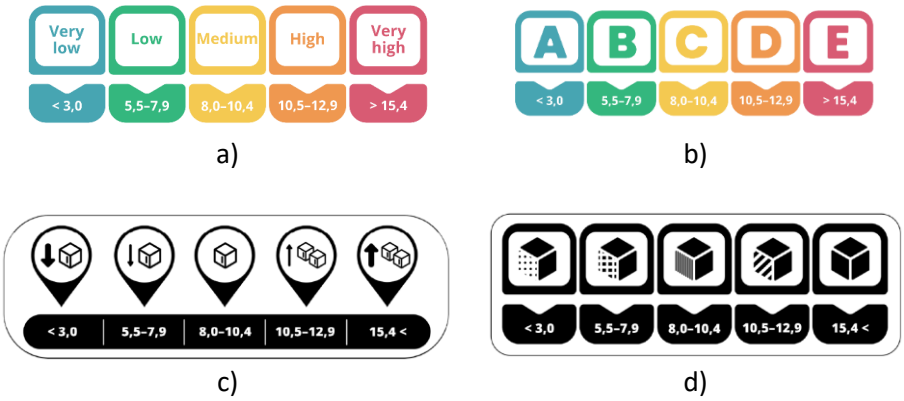

Figure 1. Variations of labelling for sugar content in dairy products: a) multi-coloured scale with words and sugar content, b) multi-coloured scale with lettering and sugar content, c) black-white coloured scale with figures and sugar content, d) monochrome scale

3. 3 Code placement on different dairy packaging products

Equally significant was the consideration of feasible scale placement on the packaging—ensuring logical positioning for swift recognition, while maintaining a non-disruptive coexistence with other food-related details. Presented in Figure 2 there are diverse scale placements on a product sample package for yogurt, milk and butter. Due to one and multi-colour labelling, both varionas are presented. With this innovative approach not only promotes eco-friendly practices but also equips consumers with the tools to make informed dietary choices. By intertwining sustainability and sugar awareness, this initiative fosters a more health-conscious and environmentally responsible future.

a)

b)

c)

Figure 2. Variations of multi colour and black-white code labelling for sugar content in dairy products: a) yogurt, b) butter and c) milk.

For easier presentation of the designed packaging and scales, we created 3D models of the packaging for each food group using the Blender software tool. We designed a model for a bottle with a label, a butter with a lid, a milk or yogurt carton. We designed the models using simpler modeling techniques. We made sure to model at a realistic scale so that the sizes of the packages were in proportion (Figure 3). Placements for black-white coding combinations could be on the same place as multi-coloured variation.

a)

b)

c)

Figure 3. 3D presentations of dairy products and colour labelling of sugar content on a) yogurt, b) milk and c) butter.

3 CONCLUSIONS

When evaluating the existing methods of nutrition labeling, it becomes clear that the Slovenian market lacks a uniform system for labeling sugar content. Consequently, our approach involved devising and contrasting diverse design solutions that vary in terms of format, colors, and interpretability (graphical visualizations). This led us to create different types of scales, differing in how they present primary information. We crafted a multi-color scale with word or letter

representation, alongside a single-color scale incorporating symbols or patterns in place of primary information.

Thoughtful contemplation was given to optimizing the scale placement on packaging, ensuring that sugar content information captures customers' attention without conflicting with the established visual identity. Drawing inspiration from our meticulous sample analysis, the visual aesthetics of our packaging evoke a sophisticated, natural, and subtly playful impression.

In our label design process, we also strategically considered the potential for adaptability, ensuring these labels can seamlessly find application across a diverse range of future food packaging scenarios.

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REVIEW OF GLOBAL PRODUCTION AND MARKET ANALYSIS OF BIOPLASTIC PACKAGING

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Professional paper
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Abstract: *Packaging generates environmental impact throughout its life cycle, so developing new packaging solutions is necessary to minimize environmental pollution. The rising environmental concerns owing to the increasing amount of plastic packaging waste across the globe, especially across developing economies, are driving the demand for bioplastic packaging. The bioplastic packaging market is predicted to increase significantly as a result of the strict regulatory environment, the worldwide environmental crisis, and other factors. Accordingly, the present review study deals with market size analysig, market share, growth factors as well as future forecasts in bioplastics packaging.*

Keywords: bioplastics, packaging, sustainability, environment, market analysis, CAGR

1 INTRODUCTION

Packaging development has become a great challenging task and of enormous responsibility for the manufacturers and the professionals involved (Bucci et al., 2007). Businesses are under pressure not only from consumers but also from governments to use eco-friendly packaging for their products (Nguyen et al., 2020).

More than 70% of the world's largest companies have committed themselves to reducing plastics pollution. It was recently concluded that the implementation of “circular innovations” for packaging on a global level is still low (Lisiecki et al., 2023). As a result of plastic waste, Earth’s ocean and freshwater biodiversity and ecosystems are being negatively affected. The magnitude of plastic pollution carried to sea has significantly multiplied over the past several decades. Oftentimes, wildlife is injured due to entanglement or ingestion of the plastics

found in the environment. For Procellariiformes such as the albatrosses, shearwaters, or petrels, the appearance of eroded plastic pieces are similar to many types of food they consume. Microplastics resemble phytoplankton which are eaten by fish and cetaceans. Ingested plastic debris has been found to reduce stomach capacity, hinder growth, cause internal injuries, and create intestinal blockage. Plastic entanglement with fishing nets or other ring-shaped materials can result in strangulation, reduction of feeding efficiency, and in some cases drowning (Sigler, 2014).

Growing concern about human health and environmental aspects has driven the focus more towards eco-friendly, biodegradable, and sustainable packaging materials (Surendren et al., 2022). In that sense, seeking new sustainable materials to replace petroleum-based plastics has led to the development of a new group of materials, termed bioplastics. The term bioplastic is mostly used to define plastics that can be either bio-based, biodegradable, or both (Shlush et al., 2022). Bioplastics are not just one single material. They comprise of whole family of materials with different properties and applications. The term 'biobased' means that the material or product is (partly) derived from biomass (plants). Biomass used for bioplastics stems from e.g. corn, sugarcane, or cellulose.

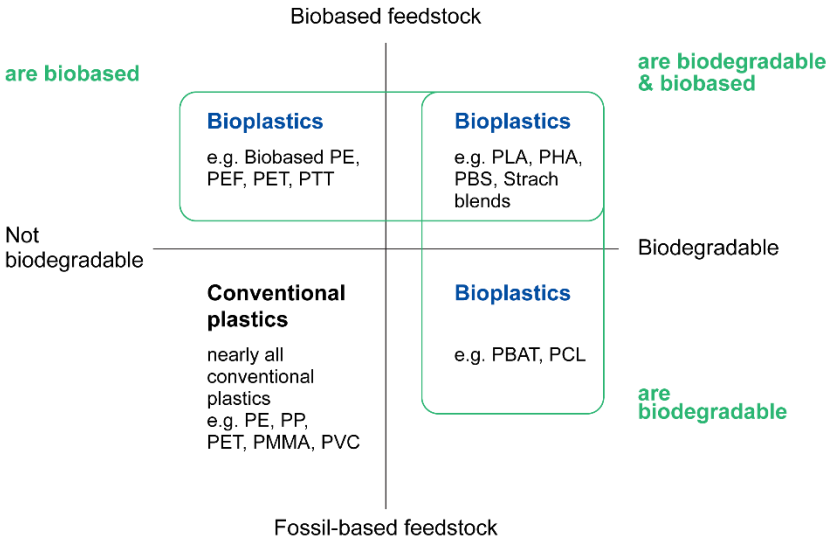

Figure 1. Material coordinate system for bioplastics (Bioplastics, 2023).

With respect to environmental impact, as opposed to their fossil- and petrol-based counterparts, polymers from natural sources significantly reduce the final product carbon footprint, the industry dependency on scarce resources and

leads to lower emission of greenhouse gas and other toxic compounds to the atmosphere (Shlush et al., 2022).

Bioplastics are gaining significant traction and they are suitable for a broad range of end-of-life options, including packaging. The expanding trend of sustainability in many packaging elements is driving the bioplastic packaging market. Due to the widespread use of packaging products and the rising aversion to plastic packaging with a high risk of contamination, the food and beverage sectors are recognized as the top consumers of bioplastic packaging. (Bioplastics Packaging Market, 2023).

This is owing to high consumer awareness, supportive government initiatives, and continuous innovation in biodegradable packaging in the market. Stringent regulations over conventional plastic use in food, beverage, and medical packaging has led to increasing adoption of these (Bioplastics Packaging Market, 2022).

2 MATERIAL AND METHODS

Market analysis is a comprehensive study of a specific market within an industry, including an examination of its various components, such as market size and trends, target audience, profitability and growth rate (Market Analysis, 2023). The aim of this review paper was to evaluate and understand bioplastic packaging market. The analysis is based on open-access market reports from 2022 to 2030.

2. 1 Global production of bioplastics

Currently, bioplastics still represent < 1% of the more than 390 million tonnes of plastic produced annually. After stagnating in 2020, mainly due to Covid-19, the overall global plastic production has been increasing again since 2021. This development is driven by rising demand combined with the emergence of more sophisticated applications and products.

According to the latest market data, the global bioplastics production capacities are set to increase from around 2.2 million tonnes in 2022 to approximately 6.3 million tonnes in 2027. Figure 2 shows the global production capacities of bioplastics in tones in period 2021-2027.

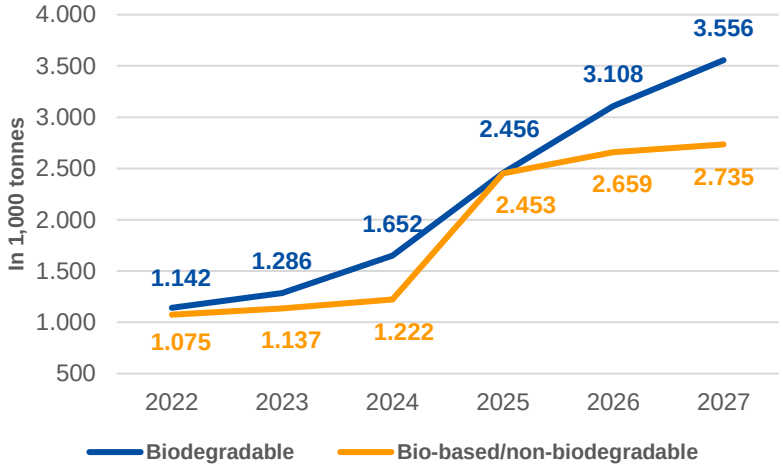

Figure 2. Global production capacities of bioplastics, 2022-2027.

Bioplastics are used in an increasing number of markets, from packaging, catering products, consumer electronics, automotive, agriculture/horticulture, and toys to textiles and several other segments. Packaging remains the largest market segment for bioplastics with 48% (almost 1.1 million tonnes) of the total bioplastics market in 2022. However, the portfolio of applications continues to diversify. Segments, such as automotives & transport or building & construction, remain on the rise with growing capacities of functional polymers.

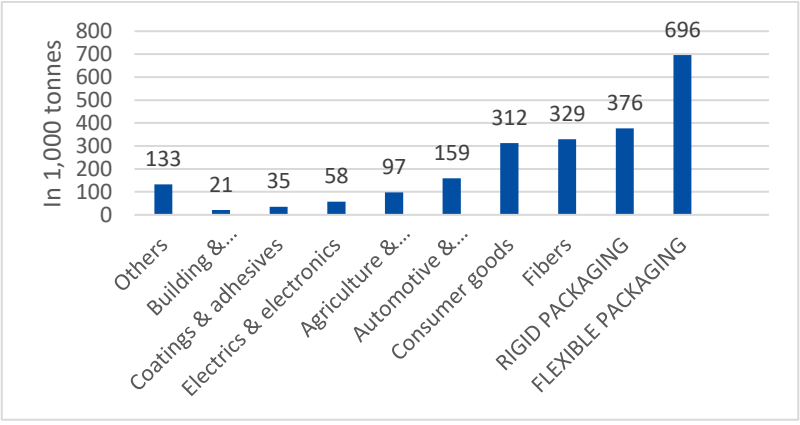

Figure 3. Global production capacities of bioplastics 2022 (by market segment).

With a view to regional capacity development, Asia further strengthened its position as major production hub with more than 41% of bioplastics currently being produced in the region. Presently, just over a quarter of the production capacity is still located in Europe. However, Europe's share and that off other

world regions will significantly decrease within the next five years. In contrast, Asia's production capacities are predicted to increase to almost 63% by 2027.

Figure 4. Global production capacities of bioplastics 2027 (by region) (Bioplastics, 2023, Ferreira et al., 2023).

2. 2 Market size and growth rate

Market size refers to the total sales generated in a specific period and provides insight into the current sales volume and future sales projections. Market size is influenced by market demand, and businesses can gather information on market size through surveys, government data, trade publications, and financial reports (Market Analysis, 2023).

The changed post Covid-19 business landscape, the global market for plastic packaging estimated at USD 702.4 Billion in the year 2022, is projected to reach a revised size of USD 944.3 Billion by 2030, growing at a CAGR (Compound Annual Growth Rate) of 3.8% over the analysis period 2022-2030.

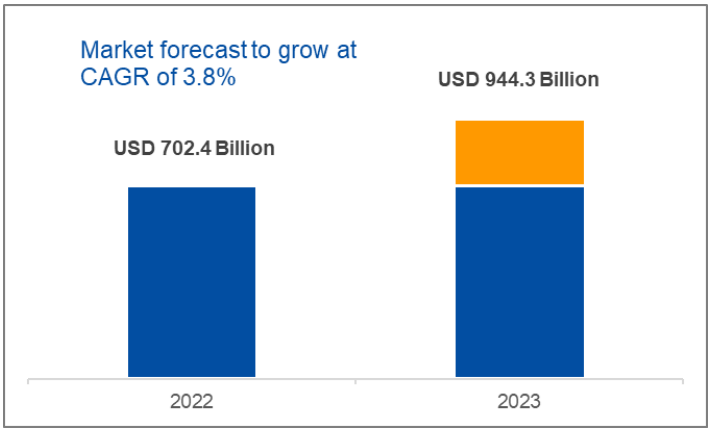

Figure 5. Global market for plastic packaging.

However, the increasing need for sustainable materials has developed a dynamic rise in bioplastics production in the upcoming years. The global bioplastic packaging market size was exhibited at USD 15.6 Billion in 2022 and is projected to attain around USD 58 Billion by 2032, growing at a CAGR of 14.02% during the forecast period 2023 to 2032.

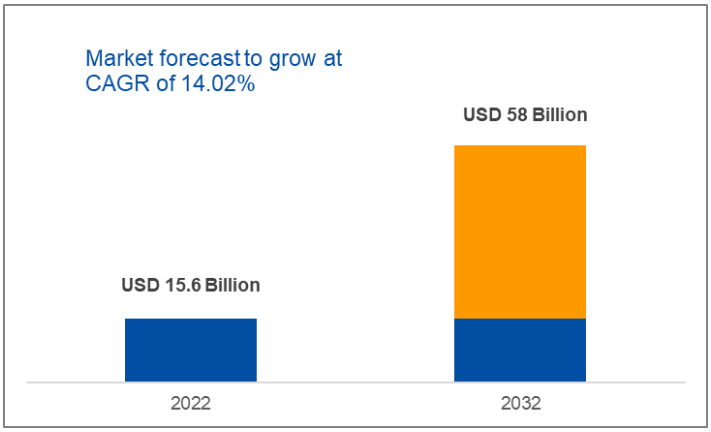

Figure 6. Global market for bioplastic packaging.

2. 3 Market share

The expanding trend of sustainability in many packaging elements is driving the bioplastic packaging market. Due to the widespread use of packaging products and the rising aversion to plastic packaging with a high risk of contamination, the food and beverage sectors are recognized as the top consumers of bioplastic packaging.

Regarding application, the food and beverage sector held a significant market share in 2022, accounting for 59% (Figure 7). The market is being driven by the increased prominence of quick-service restaurants and the demand for packaged food. The industry for flexible packaging will likely rise during the forecast period because manufacturers are expanding their production capacity in response to the rising demand for packaged goods.

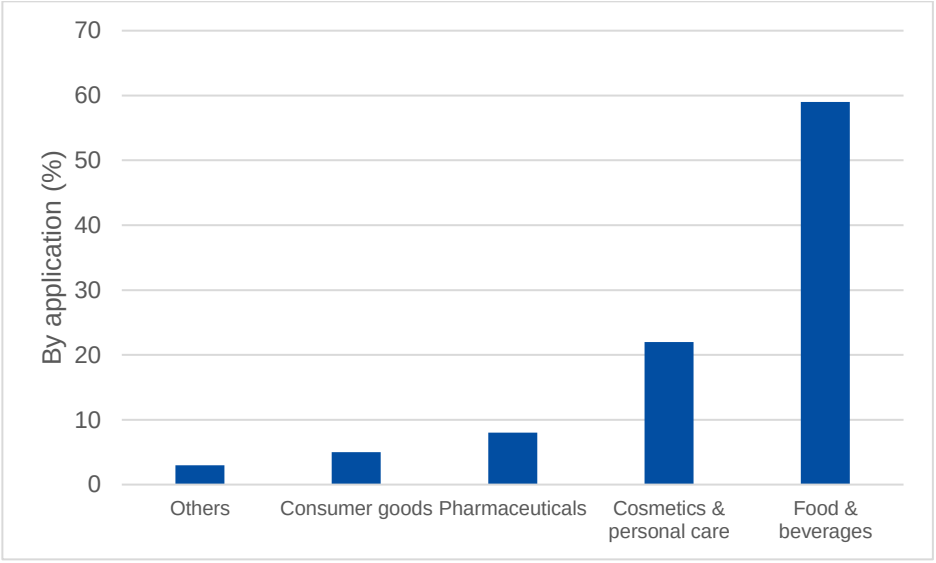

Figure 7. Bioplastic packaging market share, by application in 2022.

In terms of revenue, the bioplastics packaging market in Europe held the highest share 34% in 2022. Due to strict environmental legislation and rising consumer concern for the environment, the region will likely experience significant growth in the years to come.

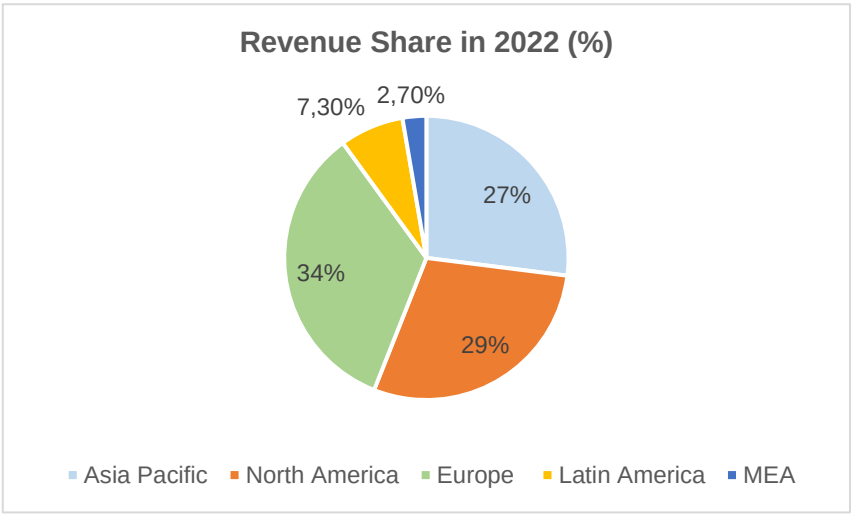

Figure 8. Bioplastic packaging market share, by region, 2022 (%).

Europe follows North America and the Asia Pacific region in terms of projected market expansion. The bioplastics packaging material market will likely grow significantly in Japan, the U.S., China, and Germany.

Government initiatives will also increase bioplastic demand over the evaluation period, such as the decision of the E.U. to lessen the widespread use of single-use plastic products. The European Parliament decided to ban single-use plastic products like cutlery and straws in 2019 as part of a comprehensive rule against plastic rubbish that damages beaches and pollutes waterways. In July 2021, a ban on single-use plastics was anticipated to go into effect (Bioplastics Packaging Market, 2023).

3 CONCLUSIONS

It is understood that one of the major benefits of going bioplastics packaging is the preservation and well-being of the environment we live in. Awareness and concerns about environmental issues are growing among consumers. Recent studies demonstrate that despite the economic crisis, consumers in developed countries affirm their wish for eco-friendly packaging more than ever before. Bioplastics are expected to displace conventional plastic in many industries due to the numerous benefits, especially in food and beverage packaging industry.

Acknowledgement: *The authors would like to acknowledge the financial support of Horizon Europe projects REMEDIES (GA 101093964) and UPSTREAM (GA 10112877).*

Abbreviations: *PE - Polyethylene; PEF – Polyethylene Furanoate; PET - Polyethylene terephthalate; PTT - poly trimethylene terephthalate; PLA - Poly Lactic Acid; PHA – Polyhydroxyalkanoate; PBS - Polybutylene succinate; PP - Polypropylene; PMMA - Polymethylmethacrylate Acrylic; PVC - Polyvinyl chloride; PBAT - Polybutylene adipate terephthalate; PCL – Polycaprolactone.*

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DESIGN FOR RECYCLING GUIDELINES OF PAPER-BASED PACKAGING – A REVIEW FOR PACKAGING DESIGNERS

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Professional paper
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Abstract: *Circular Economy requires products and material resources to be efficiently managed and used. For packaging, recycling is crucial to close the loop. Hence, packaging designers must balance pack performance, morphology, and communication to ensure its recyclability. This is particularly true for fibre-based packaging, which is the prevalent market packaging material, forecasted to increase its usage volumes. To help designers in their activities, several bodies provided Design for Recycling Guidelines (DGs). In this work, national and European DGs are discussed, providing shared design rules ranging from the substrate and its surface treatment to the packaging components. Such design rules can enable designers' creative process and enhance the exploration of new, efficient packaging solutions. Consequently, packaging designers may achieve a broader view and play an active role in extending fibre life time; hence, reducing landfilling or energy-recovery of valuable fibres.*

Keywords: Design for Recycling, Packaging, Design Guidelines, Circular Economy, Paper and board.

1 INTRODUCTION

Governments and institutions have been demanding industrial companies to innovate packaging materials and production systems due to, e.g., single-use plastics ban and reuse enforcing schemes. However, depending on the

application, packaging – specially paper-based packaging – may not be readily reusable or remanufactured, making recycling the most viable choice. Within Europe, paper and board packaging represents – with 40.9% – most of the packaging waste (Eurostat, 2020). However, looking at recent data, paper-based packaging recycling rate seemed to slightly decrease (EPRC, 2021, 2022). This might be associated to increasing multi-material paper-based packaging that is placed on the market; indeed, polymeric films, coatings, and components are generally non-cellullosic materials that end as rejects, reducing recycling yield. To guide the packaging designers in the Design for Recycling perspective, Design for Recycling Guidelines (DGs) were sometimes provided by recycling bodies as best practices to facilitate end-of-life material recovery. Such DGs represent the baseline for an aware packaging design, responding to "containment" needs, to valorise aesthetics, usability, and expressivity of packaging (Ciravegna, 2017; Giardina and Celaschi, 2020) without compromising the material recyclability. According to the specific application, packaging can impact on the Global Warming Potential more than the content itself (Licciardello, 2017). Aiming to sustain the recycling rate of paper-based packaging, in this study the authors analysed and systematised the white literature provided by the major European paper and cardboard recycling bodies, confederations, and associations. By doing so, this works aims to bridge industrial constraints and professionals' activities. Finally, common guidelines suitable for an EU-wide application were defined to help the design of packaging that eases the recycling process further helping recycling targets (European Parliament and Council, 2018).

2 MATERIAL AND METHODS

DGs were retrieved from European bodies involved in the paper-packaging recycling stream. Therefore, members of the PRO Europe (https://www.pro-e.org/) were – among others – investigated. In particular, documents covering six countries across Europe and three documents published by bodies referring to the European territory were retrieved (Ecodesign guidelines paper and board Packaging, no date; FostPlus, no date; ECOEMBES, 2017; Cepi, 2020; Marinelli, Santi and Del Curto, 2020; ARA, 2022; CEREC, 2022; CPI, 2022; FTI, 2022; 4evergreen, 2023). DGs were investigated to systematise recommendations according to several factors, as reported in Figure 1. A dual classification was followed, distinguishing between "Packaging Factors" and "Content Factors". Packaging factors refer to bulk substrate, surface of the substrate, and even to packaging accessories, whereas "Content Factors" affecting recyclability are essentially two: either the presence of residual content or surface contamination. DGs were filtered to refer to standard paper mills, which differ

from special paper mills since the latters are designed to cope with packaging that is more difficult to be recycled.

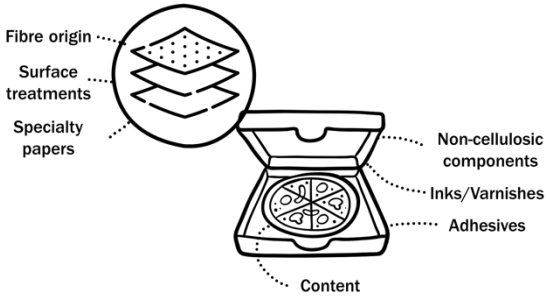

Figure 1. Main topics affecting recyclability.

3 RESULTS

Packaging designers' intrinsic role depends on designing formal, functional, as well as specific features like aesthetics, affordance, accessories, and possible barrier films and coatings. Such features can impact on migration, which can occur from the content to the packaging, from the packaging to the content or both ways. The topics covered by the retrieved DGs that should be addressed in the packaging design phase are reported in Figure 2. All the references discussed adhesives as well as inks and varnishes, followed by laminates, multi-layers, and non-cellulsoic components. On the contrary, only few DGs included topics such as fibre origin, contaminations, and specialty papers.

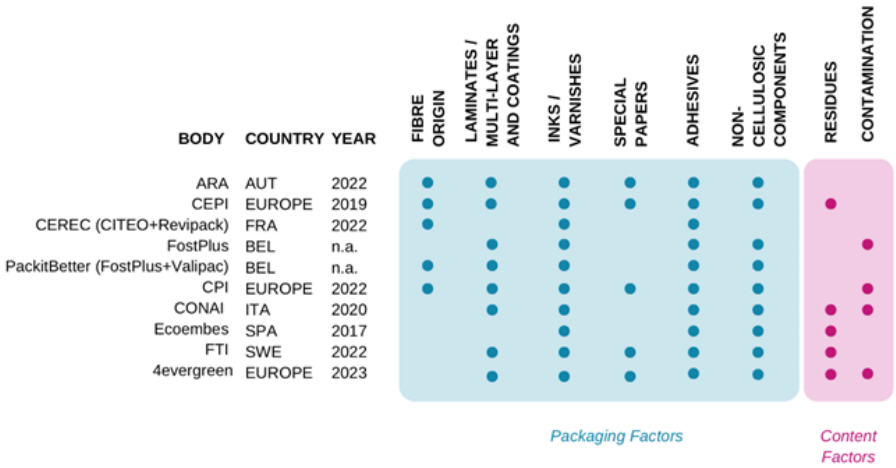

Figure 2. Topics covered by the Design for Recycling guidelines across different Institutional bodies.

3. 1 Results: Packaging factors

3. 1. 1 Fibre origin

The feedstock used to make paper is usually wood. However, some countries explored the use of different feedstocks (Laftah and Rahman, 2015). Fibres from different plant species differ in cellulose, hemicellulose, and lignin content, among other substances. Being cellulose the most important constituent of paper-based products, pulp feedstock affects possible chemical processing, mechanical processing, or a combination of the two to remove unneeded substances. Both the process and pulp feedstock determine fibre length, branching, colour, and mechanical properties. Therefore, depending on the use, the designer needs to clearly consider both the functional and aesthetic properties of the packaging to select the proper grade. DGs aren't univocal about such topic, yet a general guideline might be to prefer wood fibres against alternative sources, since the latters might not be readily recyclable or lead to poor Secondary Raw Material (SRM) quality. The use of non-wood fibres should be based on proven recyclability.

3. 1. 2 Surface treatments (Laminates, Multilayers, Coatings, and Transfer foil)

Packaging barrier is of highest concern when it comes to perishable goods such as food. To cope with paper's lower barrier properties to both gasses and liquid/oils, polymers and/or aluminium is generally used in film form and (co-) extruded or laminated (using adhesives) onto paper. Additionally, aqueous dispersion technology proved to be viable alternative, providing lower non-cellulosic content for similar barrier properties (Marinelli, Diamanti, *et al.*, 2023). Improved barrier is required due to food higher environmental burden compared to packaging one (Licciardello, 2017; Licciardello and Piergiovanni, 2020). Multiple layers might be used to sum single materials' barrier. Additionally, a polymeric layer may work as sealant for specific applications (Marinelli, Profaizer, *et al.*, 2023). Main lamination and extrusion coating materials are PE, PP, and PET. Recently, the use of biodegradable, compostable, and/or biobased polymers gained strong interest from both the industry and research (Khwaldia, Arab-Tehrany and Desobry, 2010; Peelman *et al.*, 2013), as well as nanomaterials (Li, Mascheroni and Piergiovanni, 2015; Herrera, Mathew and Oksman, 2017). The main issue with surface treatments is that they are generally insoluble non-cellulosic materials, hence they lower the overall quality of the SRMs if proper separation doesn't occur in the pulping stage. Therefore, given packaging's functionality, DGs agree on minimising polymeric content, as well as avoiding polymeric layers on both sides of the substrate−they prevent water from reaching packaging fibres, requiring higher temperature or processing times to countereffect recycling yield reduction. Things might change when considering

peelable solutions, which should be clearly communicated to the consumers for their call-to-action. Cepi harmonised European and UNI 11743 recyclability laboratory test methods request the packaging to produce minimum amounts of coarse and fine rejects. Many DGs agree that the maximum amount of non-fibrous material should be lower than 5% w/w.Finally, several DGs discuss foil transfer technology, whose covering area should be minimised to avoid scanning errors at the near-infrared selector at a sorting facility. About metallic layers, 4evergreen reports how metallised layer whose thickness is <1 μm do not affect recyclability.

3. 1. 3 Specialty papers

Specialty papers include silicone, wax, and bitumen papers, as well as cigarette and photography paper. Specialty papers can be produced using special chemicals in bulk or as a coating to implement properties in, e.g., release liners, grease-proof papers, and performant printable substrates. The main issue with specialty papers is that they are hardly recyclable; indeed, they usually need higher pulping time and temperatures to let defibring occur. Therefore, only special paper mills can recycle them, requiring specific collection and selection systems. Generally, DGs agree on limiting the use of specialty papers; in particular, they suggest avoiding the use of silicone and wax papers.

3. 1. 4 Adhesives

Adhesives lay in between layers of mono or multimaterial sandwiches. The nature and application parameters differentiate adhesives, i.e., hot-melt adhesives require heat before being applied, starch-based adhesives need water evaporation, whereas pressure-sensitive adhesives need pressure to adhere. Being non-cellulosic in nature and possibly leading to micro- and macro-stickies possibly machine downtime, their use is generally considered to be minimised. Generally, DGs stress on few, but broadely agreed factors: if hot-melt adhesives are used, it should be guaranteed that they do not fragment into pieces smaller than ~2 mm in diameter (4evergreen provides specific information depending on final application) so that mechanical screening can intercept them; additionally, particular attention should be given to their softening point, which should be generally higher than 70°C (although CONAI guidelines report 45°C as limit, and Ecoembes 65−80°C range). Emphasis is given to water-soluble adhesives, which are widely regarded as preferrable solutions. However, some pointed out that they might accumulate in the water circuit and increase Chemical Oxygen Demand (COD). Indeed, soluble content is considered in Cepi's European harmonised recycling lab test method. Finally, pressure-sensitive adhesives are generally regarded as avoidable since have higher persisting rate in the recycling facility.

3. 1. 5 Inks and varnishes

Inks are generally used to convey meaningful information to the user/consumer, to stand out once exposed on shelves (if applicable), and to comply to regulations and labelling requirements. EuPIA association provided information and guidelines about inks and their safety which are encouraged to be followed. Due to marketing reasons, several colours as well as heavily printed substrates are, unfortunately, common. Despite not affecting the recycling pocess *per se*, such artefacts reduce the optical homogeneity of the SRM. Indeed, heavily inked packaging should undergo a deinking process. Therefore, DGs agree on optimising – i.e., minimising – ink content. Additionally, it is broadly reported to avoid mineral oils since can migrate from recycled food packaging to food. Very thin varnish layers aren't usually used to improve barrier properties; on the contrary, they improve, e.g., printability, opacity, and roughness. UV-cured varnishes require a specific focus; indeed, they are not readily removed by conventional paper mills, possibly ending up in the SRM and causing flecking. Hence, UV varnishes should be avoided and used only if needed.

3. 1. 6 Non-cellulosic components

Paper-based packaging sometimes needs functional components that are polymeric. Examples are transparent windows that allow to see the content, caps, zippers, and sometimes handles and tape. Metallic accessories like grafts may be included, too. Despite cellulose-derivatives such as cellulose acetate − featuring optical transparency − were sometimes used, it should be considered that such material underwent chemical modification that do not allow a paper mill to recover fibres, since they exist no more. Moreover, the density of non-cellulosic components should not be in the 0.95÷1.15 g/cm^3 range, as reported by CPI. Non-cellulosic components increase coarse rejects, reducing paper mill recovery yield. Additionally, it is widely reported how such accessories, once they become waste, are often energy-recovered. Generally, DGs suggest their use should be limited, preferring peelable solutions. If peelable solutions are adopted, consumers' call-to-action must be clear.

3. 2 Results: Content factors

The content and the packaging interact each other. Issues related to the content that may affect the recyclability relate to the content migration on the substrate, as well as entrapped content residues in the packaging. This is especially true for food packaging application, as well as for other fields, e.g., packaging for powders and granules for industrial use. Solid residues increase reject fraction and might end in the SRM. Instead, water-soluble substances may impact on the, e.g., COD and filtering system, which are critical elements since paper mills generally operate in almost-closed water circuits.

DGs report how it is crucial designing packaging that optimises its emptying. Therefore, depending on the content nature, packaging designers should enable consumers and communicate them to easily empty the packaging from residues. However, contamination includes even stains, especially for food packaging. Stains are due to oil and grease. As a rule of thumb, light staining is still acceptable, though higher degrees might lead to microbial growth. Interestingly, CONAI reported that heavily stained food packaging (or with high amounts of food residues) should be designed to make it compostable – according to existing regulations – instead of recyclable in the paper stream.

4 DISCUSSION: THE DESIGNER CONTRIBUTION

Packaging functionalities include content protection, transportation, handling, and presentation to the consumer. However, there are several possible issues that reduce packaging recyclability and SRM quality. Monomaterial packaging – whether cellulosic or polymeric – should be preferred since it is easier to recycle and provides higher recycling yields. When this isn't possible, experienced designers with a broad overview of the recycling processes can design solutions implementing, e.g., material separation (Figure 3.a). Involving recycled content in the chosen substrate limits virgin material use, hence reduces felling operations. Additionally, recycled content could represent an interesting opportunity to explore new packaging aesthetics (Figure 3.b), playing with the texture to convey perceptual information.

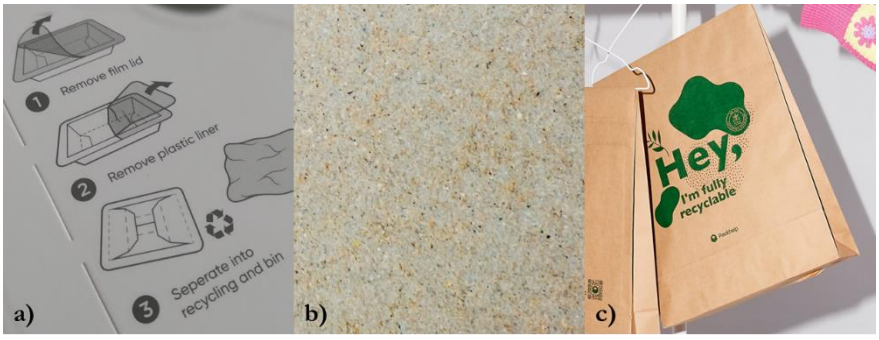

Figure 3. Communication and aesthetical properties of packaging. From left to right: a) Example of communication on how to confer peelable packaging; b) Recycled paper aesthetics; c) Paper bag graphic engaging customers attention on recyclability.

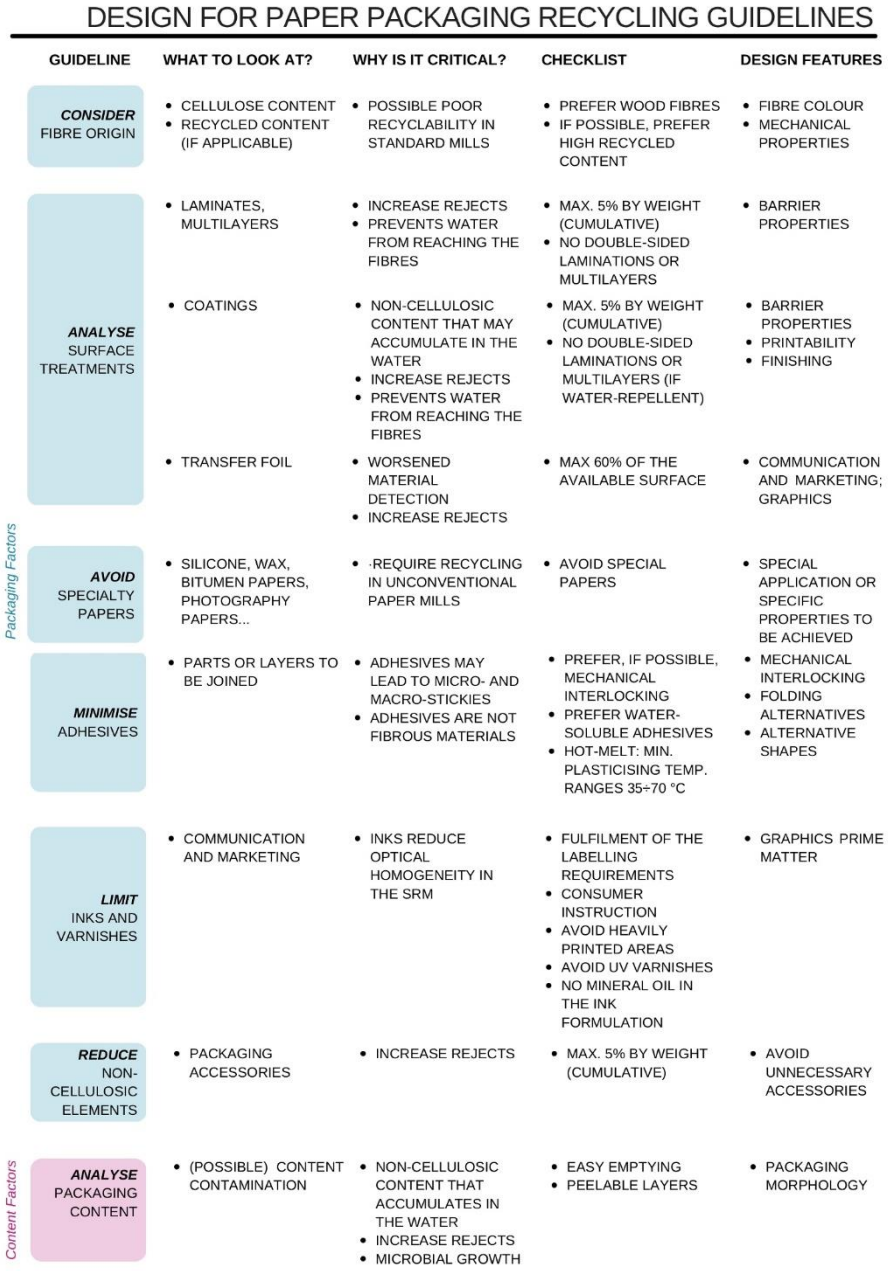

Figure 4. Design for Recycling guidelines and prompt to support paper-based packaging design.

It is worth to stress once again how the design process should consider each of the analysed topics, still including both the role of the end consumer, communication (Figure 3.c), and packaging affordance, striving for a holistic

approach. It is not the aim of the authors to include here a complete analysis of consumer behaviour on proper waste sorting. Nevertheless, correct consumer actions must be encouraged with clear instruction, otherwise all the previous argumentation is pointless. Therefore, environmental labelling and graphics should be carefully designed, too. Since packaging producers market generally crosses a single country's border and their packaging should adapt to different collection and recycling streams, the authors tried to systematise DGs to determine a comprehensive checklist of DGs to guide packaging designers to properly assess paper and cardboard projects entering the EU market in the recycling perspective (Figure 4). The provided tool merges the guidelines provided by the European bodies with the previous considerations, highlighting in the last column the features that packaging designers may undertake to develop new paper-based packaging that fosters material recyclability.

5 CONCLUSIONS

As designers are involved in packaging design, several factors should be considered, ranging from the substrate, up to the communication functions. Nothing should be left to chance, especially when it comes to recyclability. The tool here proposed may pave the ground for shared knowledge. On the one hand the guidelines set constraints, while on the other one they should be considered as stimuli to rethink the packaging. Therefore, packaging designers may become innovators embracing both aesthetic and functional features, yet being aware of the effects that any decision in the design process produces in the end-of-life of the product. Nevertheless, the packaging must ensure its functionality in protecting and enhancing the shelf life of the content, as well as conveying information to the consumer. Recycling must be evaluated with specific regulations, though it will not work if the consumer is not aware of its fundamental role, as well as the packaging designers in their activities. Future works on the topic could include integration of new literature, both white and scientific, to update and widen the DGs tool.

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COMPARISON OF FILM PRESS AND SPRAY APPLICATION OF BIOPOLYMER BARRIER COATINGS ON PAPER

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Preliminary report
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1 INTRODUCTION

Paper and board are well-established materials in packaging applications due to their excellent recyclability and biodegradability. Because of their hydrophilicity and porosity modifications are necessary to achieve the desired barrier properties. Especially in food packaging applications, barriers against gases, grease and/or oil are required. These barrier properties are often achieved by the application of layers made from non-renewable materials such as plastics or metal films.

However, these composite materials pose a significant problem for the environment and for the recyclability of fiber-based packaging materials. Naturally occurring biopolymers, such as alginate and chitosan, have shown to be good oxygen and grease barriers. The application of these biopolymers, however, poses several challenges to state-of-the-art paper coating equipment because of the difference in properties compared to conventionally applied paper coating materials. For instance, biopolymers often have a significantly higher viscosity already at low solids content, leading to lower dry application weights and therefore difficulties in reaching the needed film thickness to achieve the targeted barrier properties.

2 MATERIALS AND METHODS

Two commercial, sized base papers of different basis weights consisting of either virgin or recycled fibre materials were coated with alginate and chitosan solutions, which were prepared as aqueous solutions at a solids content of 5 wt%.

The application of the biopolymers onto the dry paper webs was performed either with a laboratory film press coating unit (Sumet Technologies) or a purpose-built web spray coating unit (see Figure 1).

Figure 1. Spray coating unit.

This spray coating unit consists of a paper web running through the machine and two standard air atomizing nozzles providing independent control of liquid and atomizing air pressure. After coating application, the paper web passes through an infrared drying section with a total of 18 kW drying capacity. Optionally, additional hot air drying is also installed in this spray coating unit. The most relevant machine parameters are liquid pressure, atomizing air pressure and machine speed and those are the ones we focused on in this research. All coating trials were performed to achieve an application weight of approximately 3 g/m² respectively 6 g/m².

The coated samples were tested regarding barrier properties such as air permeability, grease resistance and contact angle.

3 RESULTS AND DISCUSSION

The results of these trials show that the application of biopolymers poses several challenges both to the conventional film press and to the alternative coating method. The dry application weight of both biopolymers using a laboratory film press is limited by the low solids content due to the high viscosity of the biopolymers. To obtain higher application weights necessary to a achieve the desired barrier properties a second coating layer with a drying step in between is required. In the spray coating unit, the application weight is not limited by the high viscosity of the biopolymers as for film press application. There, the limiting factor at higher application weight seems to be the rewetting of the paper

substrate because of the low solids content of the coating material and the high drying energy needed after the coating. The spray application of the biopolymers results in similar barrier properties as the film press application if the parameters are chosen correctly. The atomizing air pressure must be high enough to guarantee good atomization and therefore small droplets. But the increase in atomizing air pressure is limited by increasing material losses due to misting leading to a significant amount of the biopolymers no longer to land on the substrate. This in turn causes the need for lower machine speeds to achieve the desired application weight. Another option is to increase the liquid pressure which in turn also necessitates a significant increase in the atomizing air pressure.

In upcoming research, the optimization of the spray application is intended by changing the properties of the paper substrates or of the aqueous biopolymer solutions to promote wetting of the paper surface and film formation in order to increase the barrier properties of the spray coatings.

MOISTURE AND OIL RETENTION IN COATED PAPERS FOR FLEXIBLE FOOD PACKAGING: A STUDY ON BARRIER PROPERTIES AND SURFACE CHARACTERISTICS

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Original scientific paper
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Abstract: *Coated paper exhibits promising potential for application in flexible food packaging due to its positive sustainability perception among consumers, recyclability potential, good formability, and printability. One crucial aspect of food packaging is its ability to retain moisture in food items such as fruits/vegetables and prepared meals, as well as to prevent the loss of oil in products with high oil content. Additionally, maintaining a low humidity environment is important for preserving the crispness of dry foods, such as cookies and spices. In its natural state, paper possesses weak barriers against moisture and oil. Therefore, the coating applied to the paper must offer adequate barrier properties against water vapor, water, and oil to meet these requirements and ensure sufficient shelf life for the food items. Within the framework of the CORNET-TETRA project HBC.2021.0288 REPAC², a total of 15 commercially available coated papers were selected based on their production process, composition, and performance characteristics such as heat sealability, as well as permeability to oxygen gas and water vapor. To assess moisture and oil retention, water vapor permeability was measured at 23°C and 85% relative humidity, and Cobb water and oil absorption were evaluated after 1800 seconds. Additionally, water and oil contact angles were measured to assess the polarity of the coated surface. Notably, the water vapor permeability values, which are crucial for preserving dry foods, exhibited high variation among the different coated papers,*

ranging from 0.2 g/m²/d to immeasurably high values. The Cobb water and oil absorption values, important for respectively preserving moist and oily foods, showed a slightly lesser extent of variation, ranging from 0.5 to 95 g/m² for water and 0.8 to 46 g/m² for oil. In conclusion, this study provides valuable insights into the relationship between the barrier properties and physical surface properties of coated papers utilized in flexible food packaging.

Keywords: Flexible food packaging, coated paper, Cobb absorption, water vapor permeability, surface characterization

1 INTRODUCTION

The European Green Deal sets important policy objectives to further advance the sustainable transition of the packaging value chain. One key objective is to ensure the reusability or recyclability, in an economically viable manner, of all packaging in the EU market (European commission, 2022). Given the long history of mechanical recycling of paper, the consumer preference for paper over plastic, and the renewable nature of paper fibers, a transition from plastic to coated paper is being considered in many primary flexible food applications. An increasing number of brand owners are widely promoting their shift to paper in the media to demonstrate their commitment to a sustainable transition.

However, uncoated paper exhibits low barrier properties, which necessitates the application of a functional coating. The transition to coated paper introduces additional considerations for food companies. Specifically, the barrier properties play a critical role in determining product shelf life (Adibi et al., 2023). Moisture absorption from the surrounding environment can lead to a loss of crispness in dry products, while liquid leakage may result in packaging stains, rendering it unappealing to consumers.

Within the context of the CORNET-TETRA REPAC² project (HBC.2021.0288), commercially available materials for primary food applications were utilized, and their barrier and surface properties were evaluated (UHasselt, 2022). This study aims to investigate potential correlations between the obtained results, aiming to gain comprehensive insights into the relationship between the barrier properties and the physical surface properties. Such insights can contribute to enhancing flexible packaging of food products, thereby ensuring and maintaining their quality and safety standards.

2 MATERIAL AND METHODS

2. 1 Materials

During the REPAC project, 15 food-grade and heat-sealable materials were selected, each differing in various aspects such as barrier properties, production process, and polymer origin in the coating. To maintain confidentiality, which is inherent to this type of research project involving commercial materials, exclusively descriptions, as supplied by the companies, were used. Out of the 15 materials, 12 were coated with a dispersion coating, 2 with an extrusion coating, and 1 with a wax coating. Thirteen materials were supplied as commercially available packaging papers, while two materials ('Dispersion 3' and 'Dispersion 11' in Table 1) were coated in the laboratory.

2. 2 Surface characterization

Contact angles were measured using static droplets of 3 µl water and sunflower oil, using a microsyringe, on the seal coating of each sample. Measurements were done on an OCA 50 contact angle device (Dataphysics Instruments GmbH, Filderstadt, Germany) and fitting of the droplet geometry by a tangent procedure averaging left and right contact angle. Samples are attached to a microscope slide. An average of 10 measurements was taken for each material.

The roughness of the sealing sides, which come into contact with the food product, an average of 10 measurements with the air leak method was taken for each sample, following ISO 8791:2, using the L&W Bendtsen tester and through a visual assessment of the arithmetical mean height (Sa), taken an average of two measurements for each sample, following ISO 25178, using Keyence 3D topographical imaging with magnification lens 20x. These results are expressed in mL/min and µm, respectively.

The main component of the seal-side is identified through attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) by fitting the spectra with a dedicated database. This analytical approach serves to elucidate the components as described by the companies and may yield a more precise nomenclature for said components. Furthermore, this test has the potential to unveil novel components if the previously described components were absent within the seal-side of the paper.

2. 3 Barrier characterization

There are two types of barriers tested in this study:

i.) Barrier against liquids, specifically sunflower oil and water, determined by weighing the absorbed mass after an exposure of 1800 s, taken an average of five measurements for each sample, following ISO 535, using the Rycolab Semiautomatic Cobb water and oil absorption tester;

ii.) Barrier against water vapor, determined using a Modulated Infrared Sensor with single measurements, following ASTM F1249, using the Permatran-W model 3/33 MG, where the outer side is exposed to 23°C and a relative humidity of 85% and the carrier gas is at the seal side.

3 RESULTS AND DISCUSSION

The table presented below provides grammages the ATR-FTIR main identified components of the seal-sides, and outcomes of all coated papers. Among the 15 samples, 4 samples showed an extremely high Water Vapor Transmission Rate (WVTR), which could not be accurately measured. As a result, a value of 1000 g/m²/d was assigned to these samples for the purpose of facilitating statistical analysis. It should be noted that this assigned value underestimates the true WVTR value. Based on the unsatisfactory barrier performance and relatively large standard deviations, it can be inferred that the coated papers produced under laboratory conditions, 'dispersion 3' and 'dispersion 11', are likely of inferior quality compared to most of the coated papers manufactured under industrial conditions. Additionally, 'dispersion 2' and the wax-coated paper also exhibited poor barrier properties, suggesting a similar deficiency in the coating process used for these materials. This deficiency in coating quality is substantiated by the FTIR results. In three out of the four materials exhibiting the lowest performance in terms of WVTR, cellulose is identified as the primary component. Cellulose is a material which is not heat sealable in its natural state (Bamps et al., 2023), which suggests that the infrared radiation directly impinges upon the paper surface or a cellulose layer, where seal coating should ideally be present if the paper were uniformly coated. The extremely low WVTR-values of 'dispersion 1' and 'extrusion 1' are respectively better as or comparable to a 25 µm film of polyethylene or polypropylene (1 - 4 g/m²/d), which are polymer types known for its excellent water vapor barrier properties. In both coated papers, polyethylene was identified within the sealing layer, which is well-known for its excellent moisture barrier properties. With such low WVTR, it is possible, disregarding other nutritional requirements such as oxygen content, to consider the coated paper for extremely moisture-sensitive products that are at risk of losing crispness, such as cookies, crackers, and potato chips (Robertson, 2013).

The results of the Cobb tests conducted with water and sunflower oil under extended exposure of 1800 seconds, provide indications of the ability of the coated papers to retain water and oil within the packaging, simulating a significant shelf life limiting factor for food products with high moist and oil content. As evident from the table, the previously mentioned 'dispersion 1' and 'extrusion 1', but also 'extrusion 2' can be considered for moist food applications. For oil-rich food products, there are multiple coated papers that may be suitable. 'Dispersion 4' stands out positively with a relatively low oil absorption rate of 0.8 g/m². Due to the unclear spectra, potentially resulting from a blend within the sealing layer, the identification of a primary component that could account for the low oil absorption value was not achievable. The relatively favorable values mentioned above demonstrate the potential of these coated papers to retain liquids. However, due to the lack of scientific literature providing $Cobb_{1800s}$ results in relation to shelf lifes of various food categories, it is not possible to discuss a one-on-one relation with shelf life.

Table 1. Average values and standard deviations of surface and barrier characteristics (water contact angle (WCA), oil contact angle (OCA), Bendtsen rougness, surface roughness (Sa), Cobb water and oil absorptions, water vapor transmission rate (WVTR)).

Name - grammage (g/m²) – description (ATR-FTIR identified main component)	***WCA (°)***	***OCA (°)***	***Bendtsen roughness (mL/min)***	***Sa (µm)***	***$Cobb_{1800s}$ water (g/m²)***	***$Cobb_{1800s}$ oil (g/m²)***	***WVTR (g/m²/d)***
Dispersion 1 - 67 – ethylene, metacrylic acid, acrylate copolymer	*97.0 ± 3.7*	*20.2 ± 1.2*	*31.3 ± 0.1*	*0.60 ± 0.07*	*1.8 ± 0.2*	*3.0 ± 0.4*	*0.2*
Dispersion 2 – 45 – acrylic, polyethylene vinyl acetate copolymer	*15.0**	*34.4 ± 2.5*	*430.9 ± 1.9*	*4.13 ± 0.08*	*59.6 ± 1.2*	*25.0 ± 1.5*	*1000*
Dispersion 3 – 103 – cellulose nanocrystals	*53.1 ± 4.3*	*44.8 ± 6.3*	*900.4 ± 0.5*	*4.33 ± 0.04*	*95.1 ± 4.7*	*46.0 ± 1.1*	*1000*
Dispersion 4 – 71 – proprietary vegetable wax	*119.2 ± 3.1*	*56.6 ± 4.8*	*399.4 ± 0.1*	*3.29 ± 0.23*	*39.8 ± 20.6*	*0.8 ± 0.4*	*794.1*
Dispersion 5 – 45 – polyvinylalcohol	*104.0 ± 1.0*	*51.8 ± 1.5*	*26.4 ± 0.0*	*1.41 ± 0.17*	*22.9 ± 0.2*	*2.7 ± 0.1*	*85.1*
Dispersion 6 – 80 – proprietary polymeric component	*42.2 ± 2.5*	*54.8 ± 6.1*	*104.7 ± 0.0*	*1.52 ± 0.08*	*24.4 ± 0.2*	*2.9 ± 0.6*	*141.1*
Dispersion 7 – 69 – acrylic copolymer	*103.6 ± 1.0*	*50.1*	*129.6 ± 0.0*	*2.72*	*16.9 ± 1.0*	*6.0 ± 1.0*	*105.7*

		± 0.8		± 0.42			
Dispersion 8 – 71 – vacuum metalized	*92.1 ± 2.0*	*47.4 ± 2.3*	*686.8 ± 0.0*	*4.03 ± 0.05*	*61.5 ± 3.3*	*3.0 ± 0.6*	*167.6*
Dispersion 9 – 55 – vacuum metallized	*97.9 ± 3.5*	*52.9 ± 1.2*	*160.2 ± 0.0*	*2.04 ± 0.17*	*40.0 ± 0.4*	*10.2 ± 0.4*	*64.0*
Dispersion 10 – 65 – polyolefin	*97.5 ± 2.5*	*54.3 ± 1.9*	*45.2 ± 0.0*	*1.10 ± 0.28*	*42.7 ± 0.4*	*2.7 ± 0.6*	*124.8*
Dispersion 11 – 41 – polyvinylalcohol	*46.5 ± 4.1*	*30.3 ± 6.1*	*466.1 ± 0.6*	*3.06 ± 0.89*	*32.9 ± 1.2*	*15.9 ± 0.9*	*1000*
Dispersion 12 – 102 – acrylic acid copolymer	*91.1 ± 2.4*	*19.1 ± 4.2*	*33.1 ± 0.0*	*1.17 ± 0.04*	*20.0 ± 4.1*	*3.1 ± 0.6*	*146.4*
Extrusion 1 – 98 – polyethylene	*97.7 ± 2.2*	*37.2 ± 3.8*	*76.7 ± 0.0*	*3.40 ± 0.76*	*0.6 ± 0.2*	*3.4 ± 0.6*	*4.2*
Extrusion 2 – 100 – polyolefin	*93.2 ± 3.2*	*35.6 ± 8.2*	*441.8 ± 0.0*	*4.27 ± 0.21*	*3.2 ± 0.3*	*3.6 ± 0.5*	*23.8*
Wax – 44 - – ethylene copolymer and wax	*101.4 ± 4.5*	*65.2 ± 2.5*	*485.2 ± 0.7*	*2.62 ± 0.09*	*29.3 ± 1.5*	*9.2 ± 1.5*	*1000*

** Complete absorption of droplet upon contact*

An overview of the relation between contact angles of oil and water for the different coating grades is shown in Figure 1. It indicates that the present selection of industrial coatings includes grades that either can provide sufficient oleophobicity, hydrophobicity and/or a combination of both depending on the coating type.

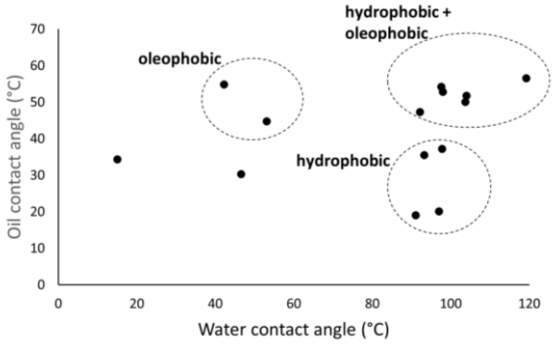

Figure 1. Relation between water contact angle and oil contact angle for different coating grades, prodiving a selection tool for papers with oleophobic and/or hydrophobic barrier properties.

Due to the uncertainty regarding the existence of linear relationships between contact angles, roughness and barrier properties, an investigation into monotonic correlations is conducted by calculating Spearman coefficients and p-values of the variables. The findings are presented in Table 2. The strongest significant relationship, within a 95% confidence interval, is observed between Bendtsen roughness and surface roughness. Additionally, there are significant correlations, highlighted in Table 2, between oil and water contact angles, WVTR and Bendtsen roughness, Cobb water absorption and Bendtsen roughness, Cobb water absorption and WVTR, Cobb oil absorption and Bendtsen roughness, and Cobb oil absorption and surface roughness. There are no significant correlations with grammage (not shown in table).

Although relationships between contact angles and barrier properties have been discussed in the literature (Rastogi et al., 2015) (Tambe et al., 2016), no correlation was found between the different sets of results in this study. Rastogi et al. mentions that hydrophobicity is a primary requirement for the creation of a barrier layer on papers. Tambe et al. discusses that it is not surprising that Cobb water absorptions and water contact angles are inversely correlated. Possibly, the absence of correlation between contact angles and barrier properties can be explained by a lack of quality of some of the coatings.

However, several correlations were found between roughness of coated surface and barrier properties of coated paper, a relationship that has been previously mentioned in the literature (Thitsartarn et al. 2020) (Lee et al. 2021). Thitsartarn et al. refers to authors who report that increasing surface roughness generally enhances hydrophobicity. Other authors are cited who state that for hydrophilic surfaces, greater surface roughness leads to increased wettability. Hydrophobicity and particle size are utilized in the discussion to relate low Cobb absorptions, albeit conducted at much lower exposure times, to the effective filling of the porous structure of paper-based materials to prevent water absorption. Lee et al. discussed the WVTR values by positively relating them to surface roughness.

Table 2. Spearman coefficients and p-values of variables.

Variable	***By Variable***	***Spearman ρ***	***p-value***
Surface roughness Sa	*Bendtsen roughness*	*0.779*	***0.001***
Water contact angle	*Bendtsen roughness*	*-0.286*	*0.302*
Water contact angle	*Surface roughness Sa*	*-0.246*	*0.376*
Oil contact angle	*Bendtsen roughness*	*0.118*	*0.676*
Oil contact angle	*Surface roughness Sa*	*-0.096*	*0.733*
Oil contact angle	*Water contact angle*	*0.525*	***0.045***
WVTR	*Bendtsen roughness*	*0.652*	***0.008***
WVTR	*Surface roughness Sa*	*0.368*	*0.178*

WVTR	*Water contact angle*	*-0.360*	*0.187*
WVTR	*Oil contact angle*	*0.142*	*0.613*
Cobb water absorption	*Bendtsen roughness*	*0.579*	***0.024***
Cobb water absorption	*Surface roughness Sa*	*0.321*	*0.243*
Cobb water absorption	*Water contact angle*	*-0.282*	*0.308*
Cobb water absorption	*Oil contact angle*	*0.279*	*0.315*
Cobb water absorption	*WVTR*	*0.697*	***0.004***
Cobb oil absorption	*Bendtsen roughness*	*0.600*	***0.018***
Cobb oil absorption	*Surface roughness Sa*	*0.539*	***0.038***
Cobb oil absorption	*Water contact angle*	*-0.414*	*0.125*
Cobb oil absorption	*Oil contact angle*	*-0.339*	*0.216*
Cobb oil absorption	*WVTR*	*0.384*	*0.158*
Cobb oil absorption	*Cobb water absorption*	*0.243*	*0.383*

To visualize the correlations between the roughness (Sa, Bendtsen) and barrier (Cobb water + oil, WVTR) variables, Figure 2 displays three XY-scatterplots. In all three graphs, the relationship appears to be asymptotic, with high absorption or permeability levels at high roughness values. It is also interesting to focus on the outliers, characterized by high roughness and low absorption and permeability. Two such outliers that appear in all three graphs are the two extrusion coated papers, exhibiting high surface roughness values of 3.4 and 4.27 µm, as well as low liquid absorptions and WVTR. Presumably, the melt-processing during extrusion helps and limits defects through which liquids and/or gases can penetrate. In addition to surface roughness, material properties of the coating are also important. The FTIR results reveal that these two outliers are coated with polyethylene, a polymer widely recognized for its excellent moisture barrier properties.

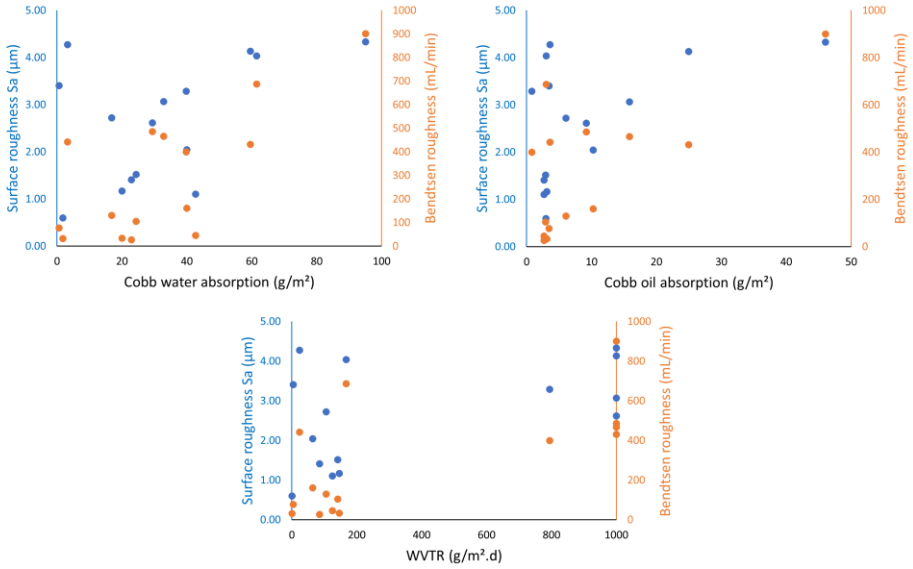

Figure 2. XY-scatterplots of roughness (Sa, Bendtsen) and barrier (Cobb water + oil absorptions, WVTR) variables.

4 CONCLUSION

This study emphasizes the importance of a smooth surface coating to achieve good barrier performance. However, this is only one of the factors influencing barrier properties, as evidenced by the deviating results of the extrusion-coated papers in the study, which achieved good barrier properties despite having high roughness, and by material properties, such as the excellent moisture barrier of polyethylene. Further research would be valuable to explore other aspects in detail, such as more details on the chemical composition of the coating as well as the nature and porosity of the underlying paper. In conclusion, this study provides an overview of the variations in surface characteristics and barrier properties among coated papers available in the market for primary food applications.

Acknowledgments: *This research was conducted as part of the CORNET project titled "REPAC²: Functional & recyclable coated paper packaging for food products". The funding for this research was provided by the Flemish Government through the grant number HBC.2021.0288, administered by the Agency for Innovation and Entrepreneurship (VLAIO-TETRA). We thank Kelly Vannitsen, Phil Rosenow and Arne Derluyn for technical assistance.*

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BIODEGRADABLE FILMS BASED ON PHBV/PBAT BLENDS AND HEMP FIBERS FOR FOOD PACKAGING APPLICATIONS

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Abstract: *Among the food packaging industry requirements, rigid hydrophobic materials are highly demanded. These materials enable the preservation of food products, preventing weight loss while maintaining the package integrity. Research focusing on using biodegradable polymers has increased in light of the growing awareness of environmental pollution and the need to replace conventional plastics by more sustainable materials. A specific area of concern is the selection of materials used in the production of food packaging products, as commonly used plastics contribute significantly to daily waste generation (Moreno et al. 2020).*

Biodegradable polymers are widely considered as an alternative to conventional plastic-based materials, as these materials would significantly reduce waste accumulation in the environment. For example, the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) has attracted significant interest due to its advantageous performance characteristics and relatively lower cost compared to other polymers within the polyhydroxyalkanoates (PHAs) family (Pal et al. 2020; Gupta et al. 2022). The synthesis of PHBV involves incorporating poly(3-hydroxyvalerate) (PHV) into the PHB molecule (Pal et al. 2020; Gupta et al. 2022; Meereboer et al. 2020). Blending PHBV with other materials can improve the mechanical properties and price of the final product. For instance, a low-cost biodegradable copolymer that can be used in polymeric matrices is the polybutylene adipate terephthalate (PBAT) that is an amorphous copolyester with an aliphatic-aromatic chain formed through polycondensation of 1,4-butanediol with adipic and terephthalic acids (Pal et al. 2020; Jian et al. 2020).

PBAT can be incorporated into polymer blends to promote stiffening and improve elongation at break (Larsson et al. 2016). Although PBAT is not a natural polymer, its biodegradable capability makes it a viable alternative for producing environmentally friendly materials.

Additionally, natural fibers are renewable, cheap and eco-friendly materials widely available from various vegetal biomasses, such as, wood fibers, jute, miscanthus, sisal, hemp, and flax (Pal et al, 2020; Wu et al, 2018), that can be used to develop biodegradable packaging materials. Hemp fiber (Cannabis sativa), is a natural fiber with crystalline cellulose fibrils, is an interesting under-exploited biomass to be used as a source of natural lignocellulosic fibers acting as fillers in polymeric formulation (Promhuad et al. 2022). Extensively grown in Latin America, Europe, and China, hemp fiber possesses a notable content of crystalline cellulose (55-72%), lignin (2-5%), and hemicellulose (8-19%), rendering it highly appealing as a reinforcement material in polymers (Wu et al. 2018; Promhuad et al. 2022).

This study aimed to produce biodegradable composites focused on the highest possible amount of hemp fibers, which is a low-value residue, and blending it with different concentrations of the biodegradable polymers PHBV and PBAT. With the goal of improve the processability and the hydrophobicity of the composites, natural waxes (beeswax or carnauba wax) were added. The formulations were produced by melt compounding, and films were prepared by compression molding. The concentration of the polymers used showed to be an important element to choose the hemp fiber concentration to be employed. With the waxes addition in the biocomposites, the water vapor barrier properties were improved, and also their hydrophobicity improved by up to 41% in the contact angles results. The methodology employed in this study to produce a biocomposite using a mixture of PHBV, PBAT, and the higher possible incorporation of HF has proven to be effective, generating an environmentally friendly material, with good cost-effective and desirable traits that may be suitable for utilization in food packaging.

Keywords: Biodegradability, films, food packing

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INVESTIGATING THE AGING STABILITY AND THERMAL PROPERTIES OF CHITOSAN-COATED PAPER FOR SUSTAINABLE PACKAGING APPLICATIONS

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Original scientific paper
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Abstract: *Paper is a valuable material in important areas such as printing, packaging, healthcare, food and agriculture. Its ageing process is influenced by storage conditions, microbiological factors and chemical composition. Chitosan, which is compatible with cellulose, is widely used as an additive and coating in paper manufacturing. Understanding the ageing stability of chitosan-coated paper is crucial from a scientific and practical point of view. The aim of this study was to investigate the thermal stability of chitosan-coated woodfree wrapping paper. Pulp and four paper samples were investigated, with three samples coated with different amounts of chitosan. Accelerated thermal ageing at 105°C for 72 hours was performed, along with dynamic thermogravimetric analysis (TGA) and evaluation of colour changes. The results showed that higher chitosan coating improved the ageing stability due to improved cross-linking with the paper substrate, resulting in higher strength. Thermogravimetric analysis showed thermal stability improved by 2.6°C with higher chitosan coating. The surface of the coated paper samples appeared more uniform and the barrier properties were improved. The chitosan coating had a positive effect on the ageing stability and thermal properties of wood-free wrapping paper. Its potential as an effective additive and coating in paper production was highlighted. Understanding the relationship between the amount of chitosan, ageing stability and performance characteristics is crucial for the development of sustainable and high-performance paper products in various fields.*

Keywords: bio-based polymers; stability; packaging paper; thermogravimetric analysis

1 INTRODUCTION

The European Green Deal (European Grean Deal, 2023) emphasises sustainability, and in this context, paper is an excellent choice for various applications such as packaging, printing and hygiene products thanks to its multiple properties, being recyclable, biodegradable, lightweight and having commendable mechanical properties. However, due to its porous and fibrous structure and limited barrier properties, especially low resistance to oil and grease, challenges arise in packaging (Wang et. al, 2022). Attempts have been made to modify the surface with waxes and polymeric coatings, but their impact on the environment raises concerns. To ensure the shelf life of products and prevent contamination during storage and transportation, the integration of antibacterial properties into medical and food packaging is essential. Given the need for environmentally friendly solutions under the European Green Deal, the demand for renewable polysaccharide-based composites is key as they enable packaging improvement, reduce hazardous by-products and promote recycling. Polysaccharides such as cellulose, chitosan, starch etc. play an important role in improving paper coatings. Chitosan, which is derived from chitin, offers beneficial properties such as biodegradability, biocompatibility and non-toxicity, so it is often used as a coating, food additive and antibacterial agent in packaging (Azmana et. al., 2021). Chitosan-coated paper improves mechanical, barrier and antimicrobial properties and is a potential replacement for fossil-based packaging (Tanpitchai et al., 2019; Gatto et al., 2019). Namely it fills the pores of paper, reduces water vapour permeability and increases stiffness, strength and toughness (Fernandes et. al, 2011; Verma et al., 2019). In addition, researchers have explored chitosan-coated paper for antimicrobial packaging applications (Morin-Crini et al., 2019; Egil et al., 2022). The sensitivity of chitosan to degradation, particularly thermal degradation at temperatures above 200–220°C, has been investigated and plasticisers such as glycerol, xylitol and sorbitol have been explored to mitigate this problem. Important thermal analyses, especially TGA, help to understand and control the processing and working conditions of chitosan-based materials (Xing et al., 2020). Advances in chitosan-based materials include composite and multilayer coatings that combine the mechanical strength of paper with barrier properties (Ezati & Rhim., 2020). This study focuses on investigating the thermal stability of paper coatings with bio-based chitosan and provides valuable insights into the ageing of paper with such coatings as packaging material. The experiment aims to produce chitosan-coated wood-free wrapping paper with different amounts of chitosan and to investigate

its strength and thermal stability over time, contributing to the development of sustainable packaging solutions.

2 MATERIAL AND METHODS

2. 1 Paper samples

Initially, cellulose mixtures for paper samples were produced from bleached wood-free kraft pulp purchased from Svenska Cellulosa Aktiebolaget (SCA), Sweden, and Svilosa AD, Bulgaria. Pulp grinding was carried out with a laboratory valley beater according to ISO 5264-1:1979. The result was an 80:20 pulp blend with a 30 °SR (Schopper Riegler value) grind according to ISO 5267-1/ AC:2004. The experimental setup included a pure pulp sample, a base paper sample and three chitosan coated paper samples. The base paper was produced using wet chemical additives, including alkyl ketene dimer sizing agents and cationic retention additives. A Rapid-Koethen laboratory paper machine according to ISO 5269-2:2005 with a basis weight of 50 g/m^2 was used to simulate paper production. The wet paper samples were dried at 95°C and −90 kPa pressure for 7 minutes.

2. 2 Coating procedure

The chitosan coating was prepared using Fluka Crayfish Chitosan 28191 dissolved in 1% aqueous acetic acid. The solution was stirred at 300 rpm for 24 hours until the chitosan had completely dissolved and a viscosity of 300 mPa·s was reached. The laboratory base paper samples were coated with chitosan solution and dried in a vacuum dryer at 50°C and 0.08 MPa until completely dry. The coatings obtained had grammages of 0.5 g/m^2, 1 g/m^2 and 2 g/m^2 (Table 1). The coating was applied using the K Control Coater laboratory coating machine, which is equipped with standard wire rods for uniform and repeatable coating application. A stainless steel K-rod with a wire diameter of 1.52 mm was used for wet coating.

Table 1. Samples and used coatings.

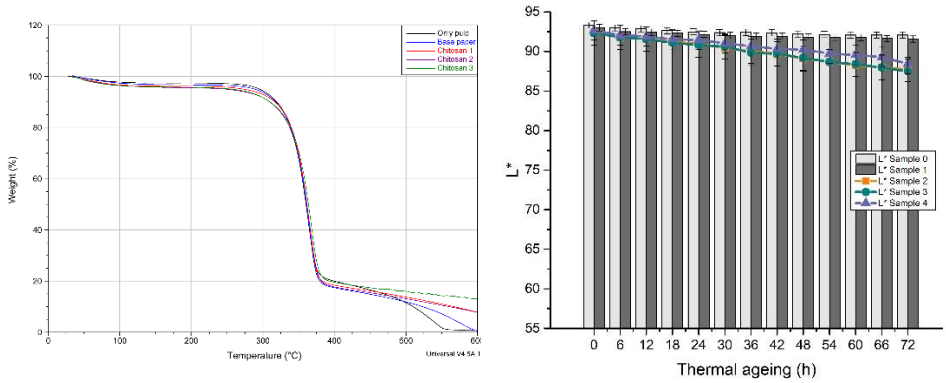
Sample	***General characteristics***
0	*Only pulp*
1	*Base paper*
2	*Base paper + 0.5 g/m^2 chitosan*
3	*Base paper + 1 g/m^2 chitosan*
4	*Base paper + 2 g/m^2 chitosan*

3 RESULTS

The smoothness of paper plays a crucial role in achieving an effective surface-coating process and reflects any modifications in the paper surface structure. Based on the data in Table 2, the addition of hydrophobic agent and retention additive does not impact paper surface smoothness (comparing sample 0 to sample 1). The coated paper samples exhibit a denser structure, which increases proportionally with the grammage of the chitosan coating.

Table 2. Sample characteristics of the used materials and coatings.

Paper properties	***Testing method***	***Sample***				
		0	***1***	***2***	***3***	***4***
Grammage (g/m^2)	*ISO 536:2012*	*50.89±2*	*50.96±2*	*50.48±3*	*49.68±3*	*49.95±3*
Thickness (mm)	*ISO 534:2011*	*0.081±0.01*	*0.081±0.01*	*0.080±0.01*	*0.078±0.02*	*0.079±0.02*
Porosity (%)	*ISO 534:2011*	*57.6±0.5*	*58.06±0.6*	*57.93±0.8*	*55.84±0.9*	*55.60±0.9*
Smoothness (Bekk, top side) (s)	*ISO 5627:1995*	*10.98±1.12*	*10.96±1.19*	*12.27±1.24*	*14.56±1.36*	*16.42±1.93*



a) b)

Figure 1. a) TGA analysis and b) Lightness of the paper samples without and with chitosan-coating during 72 h thermal aging.

The thermal degradation patterns of all studied samples, including the cellulose sample, base paper, and chitosan-coated paper samples, appear identical (Figure 1a). However, sample 3 (base paper + 2 g/m^2 chitosan) shows a different deviation in weight change, likely attributed to the uneven distribution of chitosan coating, owing to its higher amount relative to the low base paper weight of only 50 g/m^2.

As seen from Figure 1b, the color coordinate (L*) of the examined paper samples decreases as expected over time. Small differences between cellulose-only (sample 0) and base paper (sample 1) are observed, but with a comparatively low color parameter variation over time, most pronounced in the first 24 hours of accelerated thermal aging. Adding chitosan-coating slightly darkens the paper but remains close to the base paper. Increasing chitosan-coating from 0.5 g/m^2 to 2 g/m^2 and extending thermal aging darkens the paper samples and increases the color difference. The curves' location does not correspond directly to the chitosan-coating amount. Noticeably, paper with 2 g/m^2 of chitosan-coating (sample 4) exhibits higher whiteness than the other two coated samples (sample 2 and sample 3). This result is likely due to uneven coating distribution and additional cross-linking processes occurring in the chitosan-coating at 105°C. Despite the high temperature during accelerated aging, the lightness reversion from 0 to 72 hours for the three coated papers ranges from 92 to 87, which is relatively low.

The strength properties of paper serve as essential indicators, reflecting its ability to withstand various processing conditions and determining the load resistance of the resulting products. In this reserach, we focus on describing the tensile index and tear index, which are important parameters in assessing the paper's strength characteristics.

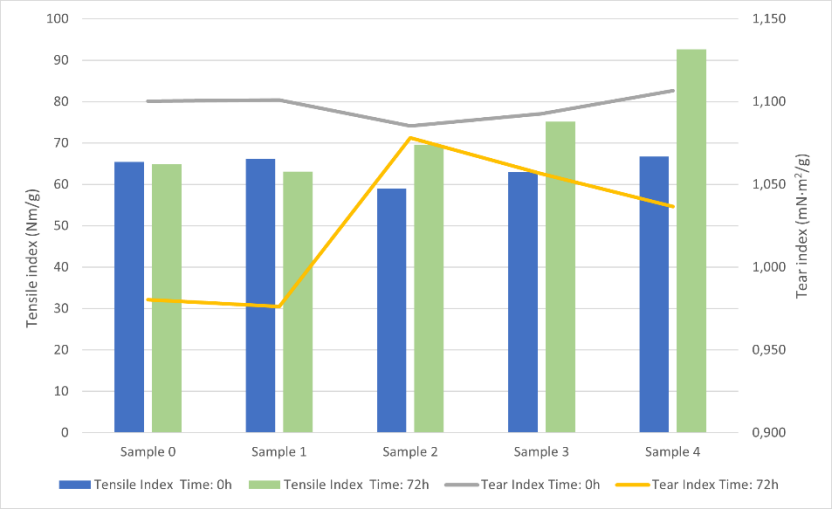


Figure 2. Tensile and tear index of analysed samples.

Figure 2 shows the strength properties, indicating that the addition of "wet-end" chemical additives has a positive impact. However, the chitosan coating has a negative effect on the tensile index, likely due to reduced elasticity and plasticity of the base paper. Instead of observing a reduction in tensile index, an increase

of approximately 46.75% is measured with 2 g/m^2 chitosan coating compared to the base paper, and a 10.30% increase is observed with the lowest chitosan coating (0.5 g/m^2). With the increase in chitosan coating on paper from 0.5 g/m^2 to 2 g/m^2, the strength indicators show significant improvement at both 0 hours and 72 hours of thermal aging. This enhancement can be attributed not only to the larger coating layer but also to the improved adhesion between the base paper and chitosan layer. Additionally, the crosslinking effect of chitosan at higher thermal aging temperatures is visibly contributing to the observed effect.

4 CONCLUSIONS

Chitosan coating has proven to be a highly effective method for enhancing paper properties and expanding its applications. In our experiments, we tested uncoated and chitosan-coated paper samples made from bleached soft- and hardwood pulp in an 80:20 ratio. The results showed that the coated papers exhibited good strength and thermal stability during 72 hours of accelerated thermal aging. The weight loss of chitosan-coated paper samples was slightly lower than the uncoated base paper. Moreover, the maximum weight loss temperature increased with higher chitosan coating amounts. Interestingly, after aging, an increase of about 46.75% in tensile index at 2 g/m^2 chitosan coating compared to the base paper and 10.30% at the lowest chitosan coating (0.5 g/m^2) was observed. These findings demonstrate the significant benefits of chitosan coating in improving paper properties and suggest its potential for various applications.

Acknowledgments: *This research was funded by Bulgarian Science Fund, grant number 920 (KP-06-H49/1) — "Investigation of new possibilities for obtaining multifunctional properties of paper".*

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SLOT-DIE COATING OF CELLULOSE NANOCRYSTALS AND CHITOSAN FOR AN IMPROVED BARRIER PROPERTIES OF PAPER

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Original scientific paper
doi: 10.5281/zenodo.10007963
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Abstract. *Nanocellulose and chitosan (Cht) are the two most abundant naturally produced biopolymers and are being extensively studied as candidates for renewable oxygen and water vapour barrier films used in food packaging. However, rare studies have been performed by using a scalable, inexpensive, and relatively fast continuous coating processes. In this work, the feasibility of cellulose nanocrystal (CNC) and Cht coating, as an individual or a hybrid mixture in a single or bi-layer process, was studied by using a slot-die technique. The effect of CNC/Cht solid content and the coating parameters (injection/coating speed and wet thickness applied) on the quantity (dry weight, g/m^2), homogeneity, wettability and barrier properties of the paper is studied by evaluating its thickness, whiteness, air and water-vapour permeabilities.*

Keywords: Barrier properties, nanocellulose, chitosan, slot-die coating, paper.

1 INTRODUCTION

Besides of nanocellulose, the most abundant biopolymer in nature, other polysaccharides such as chitosan, starch, pectin and alginate, have been extensively studied as candidates for the preparation of biodegradable and renewable films and coatings, able of exerting a barrier effect to oxygen and

water vapour (Grimaldi et al. 2022), following the circular economy and sustainability (Kumar et al. 2021).

The combination of CNCs as reinforcement and filler with polysaccharides have shown to significantly lowers oxygen permeability of the films due to the formation of a network that connects via hydrogen bonds (Saxena et al. 2010). It has also been observed that the addition of CNC in chitosan (Cht) influences on water vapour permeability, which decrease with increasing CNC content (Khan et al. 2012). Many coating techniques, including filtration, rod/barrier coating, blade coating, spray coating and tear-off coating (Lavoine et al. 2014; Mazhari Mousavi et al. 2017 & 2018, Juhant 2021) on paper substrates, have been performed to improve their resistance and barrier effect (Tayeb et al. 2022; Wang et al. 2018). Although these techniques are efficient with good coating deposition, the low solids content of highly viscous solutions often requires multiple layers of deposition to achieve good barrier effects (Cranston et al. 2008; Satam et al. 2018).

Slot-die coating is a scalable, continuous, inexpensive and relatively fast (up to several m/sec) continuous deposition technique, that enables an uniform and controlled deposition of thin layer coatings over the entire surface of a moving substrate. Both low and high viscosity solutions, including nanocellulose suspensions (Kumar et al. 2018), can be used, and a wide range of thicknesses (from 20 nm up to few 100 µm) can be deposited by modulating the process parameters (such as coating speed, flow rate, slot-gap), solution properties (surface tension, water retention, viscosity) and drying temperature.

In this work, slot-die deposition technique was used to apply CNC suspension and Cht solution onto plain/un-modified paper substrate in order to improve their barrier properties, focusing on wettability (contact angle), air permeability and moisture transport. The effect of the established coating parameters (injection speed and wet tickness) in a single (monolayer) and bi-layer deposition was investigated by coating quantity (g/m^2), thickness (µm) and homogeneity (whiteness) of the applied coating.

2 MATERIALS AND METHODS

2. 1 Materials

Chitosan (MW: 310,000-375,00; Deacetylation grade >75%) and acetic acid (HOAc, ACS grade) were purchased from Sigma-Aldrich (St Louis, MO, USA). CNC (containing 253.5±7.5 mmol/kg of sulphate groups) was purchased from CelluForce (Canada, production #2015-011) in the form of a fine powder. The

plane uncoated paper (44±2 g/m^2, 65±2 µm) from industrial production was used.

2. 2 Preparation of suspensions

Three water-based suspensions with different total solid contents of CNC vs. Cht were prepared: 11 wt% CNC (50 dPas), 2 wt% Cht solution prepared with 1 % of acetic acid (52 dPas), and mixture of 5.5 wt% CNC and 1 wt % Cht (25 dPas). To all suspensions, 20 wt/wt % sorbitol was added as plasticizer.

2. 3 Slot-die coating

The Challanger 175, semi-pilot & automated S2S coating unit (Norbert Schläfli nsm AG, Switzerland) with inline integrated 190 mm wide slot-die module (TSE Troller AG, Switzerland) and NIR drying station (NIR252-125 Adphos GmbH, Germany) was used to controll the speed of the substrate, the flow rate of injected solutions, and the drying power/time. The slot-die shim of 180 µm thickness was used, while the distance between the substrate and the slot was 75 µm. The injection/flow speed of the suspension/soltion was set in the range between 5 and 80 mL/min (corresponding to the substrate speed between 0.3 and 2.4 m/min), depending on the viscosity of the suspension/solution, while the thickness of the wet deposited layer were in the range between 5 and 12.5 µm. The drying was performed at 5 m/min using 6x1.2 kW emitter power.

2. 4 Characterization

Water retention properties of the suspensions/solution and the paper were evaluated with the updated method of (Abo Akademi, 1989). The paper thickness (gouge metter) and weight increase (gravimetrically), air (Bendtsen, ISO 5636-3:2014) and water vapor permeability (WVP at 23±2°C and 50±5% RH; MultiPerme srl, ISO 15106-2), CIE whiteness (ISO 11475:2004) and surface wetting (contact angle, OCA 15EC, DataPhysics Instruments, ASTM D5725-99) were determited.

3 RESULTS AND DISCUSION

As seen from the Figure 1, the paper thickness increased slightly with injection speed for all wet-thickness settings, and was the most significant for CNC+Cht (5.5+1 wt%) mixture resulting to an increse from 27.6% (at 19 mL/min injection speed) to 39.3 % (38 mL/min) at 5 to 10 µm wet thickness setting (0.323-0.489 g/m^2 dry weigh applied), that reduced the air permeability from around 30 to 7 mL/min. In the case of 11 wt% CNC suspension, the air permeability of the paper

was depended (decreasing) primarily on the wet thickness setting and secondarily on the injection speed; the air pemeability thus reduced from 51.8 to 25.3 mL/min at 7.5 µm wet thickness (0.827 g/m^2 dry weigh), and from 8.47 to 0.013 mL/min at 10 µm wet thickness (1.150 g/m^2 dry weigh) by increasing the injection speed from 21.4 to 35.6 mL/min and from 28.5 to 76 mL/min, respectively. However, similary low air permeability (3 mL/min) was obtained for pure 2 wt% Cht solution at much lower solid applied (up to 0.323 g/m^2) resulting to a slightly incresed (2-14%) paper thickness.

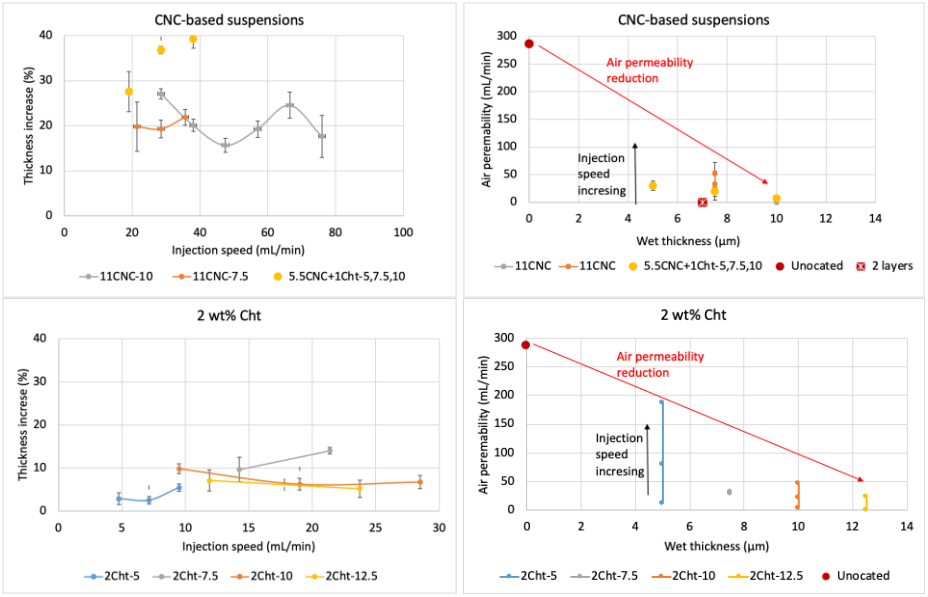

Figure 1. Effect of slot-die coating of different CNC-based suspensions and Cht solution on increasing dry paper thickness and air permeability, depending on the coating parameter setting (injection speed (ml/min) and wet thickness (µm)).

The dewatering is an important aspect of a coating process, influeneces on both the runnability/coatability and the drying originate from the interaction between the base paper and the water phase of the coating suspension/solution. As seen from the results collected in Table 1, the water retention of 2 wt% Cht solution is much higher (749 g/m^2) compared to 11 wt% CNC suspension (152 g/m^2) and is almost compeletly retained by the paper when applied on it. While the increase of paper thickness (Figure 1) for all Cht coated samples was generaly much lower (between 2-14%) as compared to the CNC coated ones (17-25%), this mean that the Cht solution penetrating better into the bulk structure of the paper while CNC remained mainly on its surface; The Cht coated paper also required longer time to dry (even up to 6 passes have been required for NIR drying). Relatively lower water retention (213 g/m^2) of half-less concentrated mixture of CNC+Cht (5.5+1 wt%) can thus be due to electrostatic interactions

between negatively charged/sulhonated CNC and positive/aminated Cht, resulting to its networking and deposition mainly on the outer surface of the paper.

These conclusions are supported by barrier and wetting properties of the coated paper. The uncoated paper was highly permeable for water vapour, so WVTR tests failed, althouth the CA was relatively high (85°) as compared to the CNC coated samples (CA is reduced up to 39° by incresing the coating speed), confirming the retention of highly hydrophilic CNC mainly on the surface, while reducing the air permeability (from 51.8 to 0.01 mL/min) and increasing the whiteness by better distribution of CNC over the paper surface. On the other hand, as expected, the more diply penetrating Cht increased the hydrophobicity of the paper (102°), while also reducing the air permeability (3 mL/min). The mixture of CNC and Cht did not have a significant effect on any of the properties, probably due to low solid content and inadequate weight ratio between them. In the opposite, the 2-layer coated sample (CNC applied before the Cht) thus resulted to CA of 93° and no air permeability. It can be concluded that both CNC and Cht contribute to the air permeability reduction, where CNC generating a highly H-bonded network with the paper, while eletrostatic interaction with the Cht applied on top, reducing the paper surface wettability.

The deviation in the WVTR may also be explained from the decreased uniformity of both the paper and the coated layer leading to pores or defects on the measured surface.

*Table 1. Whiteness, contact angle, water-vapour and air permeability of paper after slot-die coating of different suspensions/solution. *Sample was too permeable, could not me measured.*

Suspension/ solution Water retention of susp./sol. & the paper (g/m²)	***Coating parameters seting***	***Coated dry weight (g/m²)***	***Whiteness CIE***	***Contact angle / CA (°)***	***WVTR (g/m²d)***	***Air permeability (mL/min)***
Uncoated	*/*	*0*	*77.94*	*85.00*	***	*287.2*
11CNC (50 dPas) 152 & 13 g/m² Δ=139 g/m²	*21.38 mL/min 7.5 µm*	*0.827*	*90.78*	*51.73*	*n.d.*	*51.8*
	35.63 mL/min 7.5 µm		*92.71*	*48.36*	*n.d.*	*25.3*
	28.5 mL/min 10 µm	*1.150*	*92.27*	*50.28*	*n.d.*	*8.47*
	38 mL/min 10 µm		*n.d.*	*n.d.*	*n.d.*	*1.1*
	76 mL/min 10 µm		*93.87*	*39.83*	*45.98*	*0.013*
	19 mL/min	*0.323*	*n.d.*	*n.d.*	*n.d.*	*29.94*

5.5CNC+1Cht (25 dPas) 213 & 19 g/m² Δ=194 g/m²	*5 µm*					
	28.5 mL/min 7.5 µm	*0.489*	*76.52*	*85.60*	*67.55*	*19.7*
2Cht (52 dPas) 749 & 10 g/m² Δ=739 g/m²	*9.5 mL/min 10 µm*	*0.226*	*79.61*	*101.8*	*50.42*	*3.0*
11CNC/2Cht-5	*CNC: 38 mL/min - 10 µm Cht: 20 mL/min - 5/7.5 µm*	*1.15 + 1.35*	*75.36*	*74.24*	*70.26*	*0*
11CNC/2Cht-7.5			*75.36*	*93.38*	*71.16*	*0*

4 CONCLUSIONS

A homogenous thin layer deposition of CNC (1.15 g/m^2) and Cht (1.35 g/m^2) were formed on paper substrate by slot-die coating, resulted to no air permeability compared to the untreated sample at 2-layer deposited sample. The surface wettability was also reduced (CA 93°) and the moisture permeability decreases to around 70 g/m^{2}d. This investigation shows that the barrier properties of a plane/untreted paper after a thin-layer deposition of CNC and Cht can be significantly improved, opening a way for the production of a paper with biodegradable coatings based on natural materials.

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THE INFLUENCE OF PROCESS PARAMETERS ON THE MECHANICAL PROPERTIES OF BIOPOLYMER MATERIALS BASED ON CAMELINA OIL CAKE

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Original scientific paper
doi: 10.5281/zenodo.10008039
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Abstract: *Recently, the field of biopolymer materials finds its expansion, both at the level of scientific research and on the market itself. Biopolymer materials could substitute commercial synthetic polymer materials because synthetic polymers are obtained from non-renewable sources, along being endanger the environment by their disposal. There are numerous sources for biopolymer materials synthesis. This work is a contribution to the valorization of agro-industrial waste through the synthesis of biopolymer materials. the advantage of using agro-industrial waste (e.g. straws, cakes, peels...) is the synthesis of composite materials. Used substrate was Camelina seed cake, which was obtained as a by-product of cold-pressed camelina oil production using a single screw press. The remaining cake was then milled and prepared for further analysis. Different process parameters were varied in the optimization procedure. In this paper, the influence of the process parameter pH on the mechanical properties (thickness, tensile strength, elongation at break) of the obtained materials was examined. The results showed that new biopolymer materials can be obtained at different pH values. Mechanical characteristics of the synthetized materials are in the range of mechanical characteristics of other composite materials.*

Keywords: biopolymers, camelina oil cake, pH, mechanical properties

1 INTRODUCTION

The world population increase leads to an increase in the use of different packaging materials and packaging, among which, over the years, the largest increase in market has been recorded in plastic (polymer) packaging. Due to good physical-mechanical and barrier characteristics against external environmental factors (moisture, oxygen, radiation, microorganisms, etc.), polymer packaging materials are leading in the food industry where they are used independently, as monomaterials or as multilayer and/or combined materials, in various packaging forms (Lazić and Novaković, 2010). The problem with the use of plastic packaging begins with the raw material, which is non-renewable in origin. Also, bearing in mind that the environment is affected by the entire life cycle of the packaging, the very use and eventual disposal of the used packaging contribute to a negative impact on the environment, because packaging waste accumulates.

Research into the possibility of applying more environmentally acceptable packaging materials and packaging goes in the direction of the development of natural biodegradable polymer materials. These materials doubly solve the problem of the burden on the environment caused by the use of conventional plastics - biopolymer materials come from natural, renewable raw materials and in most cases are biodegradable (Lazić and Popović, 2015). In this way, the usage of non-renewable sources and energy, whose prices are on the rise, is reduced, and non-degradable polymers are replaced by biodegradable ones, which have positive effects on the environment (Lazić and Gvozdenović, 2007).

Biopolymers have numerous advantages, and due to their biodegradability, they are increasingly finding practical use in food packaging and extending its shelf life (Basumatary et al., 2022), but also in the pharmaceutical industry and others (Udayakumar et al., 2021). Contrary to conventional polymers, biopolymer films can also be edible (Suhag et al., 2020), so they can be consumed along with the food product; can protect food from the growth of microorganisms, extening its shelf life (Hasan et al., 202); or prevent loss of moisture and impairment of the sensory characteristics of the product (De Pilli, 2020).

In recent years, the production of biodegradable packaging materials obtained from agro-industrial waste has been expanding. From an economic and ecological point of view, composite films obtained directly from secondary products of agro-industry - cake, sawdust, flour, straw, etc. are particularly interesting. The high protein, fiber, and carbohydrate content of cakes and pellets make them suitable raw materials for the production of edible biopolymer packaging materials (Popović et al., 2020), because precisely these macromolecules are more prevalent as a source for obtaining biodegradable

films and coatings. In this way, the problem of disposing and depositing waste is solved, by converting renewables into useful products, without additional energy consumption, due to the use of secondary products in their native form, without subsequent modifications.

In the Republic of Serbia, oilseeds such as sunflower, soybean, flax and pumpkin are widely represented. After the production of edible unrefined oils, a highly nutritious side product is left behind - cake, which makes up about 50% of the initial seed mass. Considering the remained quantities and the rich nutritional composition, there is a clear tendency towards the valorization of these secondary products. Potential solutions are mainly focused on the production of biofuels and animal feed, as well as the extraction of biologically valuable components (proteins, polysaccharides, phenols, etc.). However, the direction of utilization through the production of biopolymer films is also confirmed by the conducted studies, where biodegradable composite films with excellent potential for packaging food products were produced from pumpkin oil cake (Popović, 2013) and sunflower oil cake (Šuput et al., 2018).

Camelina (*Camelina sativa* (L.) Crantz) is a rediscovered protein and oilseed crop belonging to the *Brassicaceae* family, which was cultivated in the distant past (2000 BCE) in South-eastern Europe and Southwest Asia. It was grown sporadically in Europe as a conventional crop until the mid-20th century when it was replaced with more productive species like oilseed rape and sunflower (Zubr, 2010; Berti, Gesch, Eynck, Anderson & Cermak, 2016; Joudka et al., 2022). However, camelina has regained more attention in the last decade due to its numerous applications and agrotechnical and industrial benefits. Camelina may have many applications in biofuel production, cosmetology, agrochemicals, food and feed industry, etc. (Mondor & Hernández‐Álvarez, 2022).

Camelina is cultivated due to its high content of protein, fat and valuable bioactive compounds, which deliver numerous beneficial effects on health. Its seed contains approximately 24-35% of crude proteins and 36% oil consist-ing of 40-60% polyunsaturated fatty acids, of which 35-40% is an α-linolenic fatty acid (Raczyk, Popis, Kruszewski, Ratusz & Rudzińska, 2016; Juodka et al., 2022). Unusually high levels of n-3 fatty acids and their health benefits and relative stability make camelina oil suitable for human consumption as a part of functional foods (Berhow, Vaughn, Moser, Belenli & Polat, 2014). The extraction of oil from the seed with different solvents or by mechanical pressing results in a large number of by-products (cake and meal). These by-products are regarded as valuable sources of proteins and bioactive compounds (Ilić et al., 2022).

In this paper, the possibility of valorisation of Camelina oil cake (COC) as raw material for biopolymer materials production was examined. Also, the influence of the process parameter pH on the mechanical properties (thickness, tensile strength, elongation at break) of the obtained materials was examined

2 MATERIAL AND METHODS

2. 1 Materials

The grounded hull-less Camelina Sativa oil cake (COC) was kindly provided by Institute of Field and Vegetable Crops (Novi Sad, Serbia). All other reagents used in this study were of analytical grade.

2. 2 Preparation of film solutions and film formation

Biofilms based on Camelina oil cake (COC) were prepared using the casting method. Filmogenic solution was prepared by dissolving COC (10%, w/v) in distilled water. Glycerol, as a plasticizer, was added in a concentration of 0.4 g/g oil cake. pH was adjusted to 2, 4 and 6 by addition of HCl solution and to 8, 10 and 12 by addition of NaOH solution. The resulting mixture was incubated in a water bath at 90°C for 20 min. After thermal treatment, the solution was filtered through a nylon filter, and the filtrate was used for further use. All solutions were poured (50g each) into Petri plates lined with Teflon and dried in room conditions.

2. 3 Mechanical properties

Film thickness was surveyed with 1 μm sensitivity micrometer. Eight replicates were carried out on each sample.

Tensile strength (TS) and elongation at break (EB) of films were measured on the Instron Universal Testing Instrument Model No. 4301 (Instron Engineering Corp., Canton, MA) according to standard method EN ISO 527-3:2018. A rectangular film strip of 90 mm in length and 15 mm in width was used. The initial grip separation was set at 50 mm, and crosshead speed was set at 50 mm/min. The TS and EB of the strips were measured in controlled chamber, at 25°C and 75–80% relative humidity.

TS (MPa) was calculated by dividing the peak load given by the cross-sectional area of the film.

EB (%) was calculated as the percent of change by dividing film elongation at the moment of rupture by initial gage length of the specimen (50 mm) and multiplying by 100 (EN ISO 527-3:2018).

TS and EB measurements for each type of film were repeated at least five times.

3 RESULTS AND DISCUSSION

To examine the effect of pH on film formation, COC film-forming solutions were prepared, varying pH in the range from 2 to 12. In the whole pH range, COC was filmogenuos, except at pH=4.0. The inability to form films at pH=4 is due to the insolubility of the protein at the specified value of pH, which represents the isoelectric point (IEP) of camellia seed protein (Ngo & Shahidi, 2021). The obtained films have very similar visual characteristics: they are dark, yellow-brown in color, non-transparent, tough and flexible. Color gradation is observed depending on the change in pH, in the sense that the films synthesized at pH values closer to the isoelectric point are lighter, and as the pH values become more extreme, the films also become darker. The different color of the films can also be a consequence of the influence of IPE, i.e. insolubility. During the preparation of films near the IEP, a smaller amount of proteins and other extractables are dissolved, and the films are probably lighter because of this. Moving away from the IEP, the extraction of filmogenic macromolecules (proteins) is greater and the color is more intense. Within each group of samples, a characteristic odor originating from the raw material is noticeable.

Films synthesized at pH 4 were not formed in the sense that they could not be dried and peeled of the non-adhesive Petri dish. The surface of the films remains moist and sticky. Therefore, the results of the characterization of these films are not presented in the paper.

3. 1 Film thickness

The obtained films had a thickness of up 193.71±8.76 to 179.22±3.42, and with increasing pH value, the thickness of the films decreased.

Table 1. Film thickness (µm).

	pH2	***pH6***	***pH8***	***pH10***	***pH12***
d (µm)	*193.71±8.76*	*192.0±7.45*	*183.36±8.70*	*181.22±9.27*	*179.22±3.42*

3. 2 Mechanical properties

The effects of pH on the mechanical properties of COC films are showed in Fig 1 and 2. The best mechanical properties have the films prepared at pH=12, TS is 2.12 MPa, and EB is 16.66%.

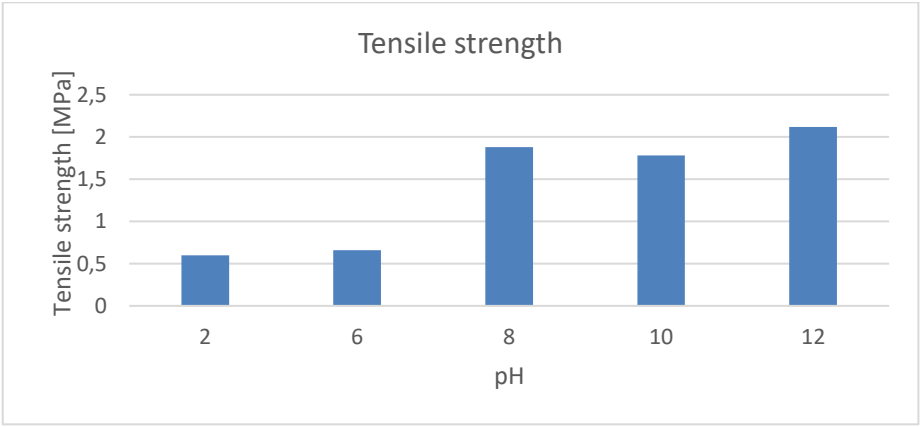

Figure 1. Tensile strength (MPa).

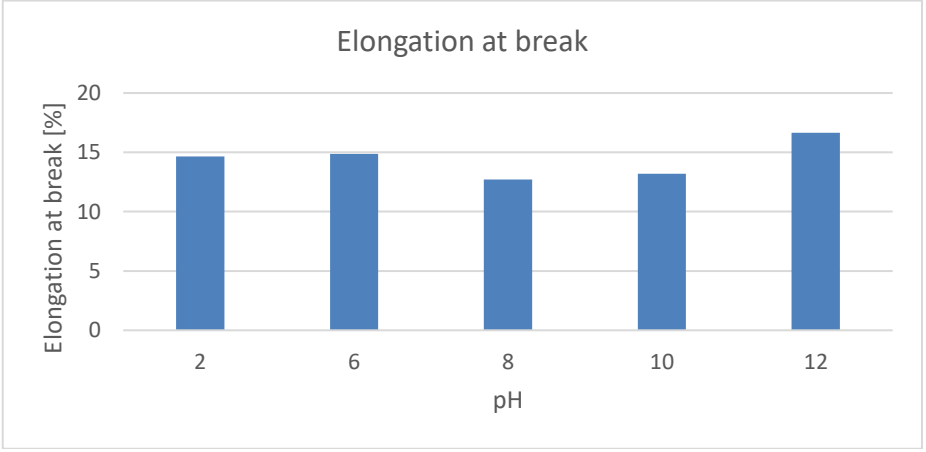

Figure 2. Elongation at break (%).

The results displayed that TS and EB of the COC films are influenced by the applied pH, and film with the best mechanical characteristics was prepared at pH=12. Films prepared at lower f values have a lower value of tensile strength, probably due to a smaller amount of extracted proteins, while this dependence is less pronounced regarding elongation at break.

4 CONCLUSION

COC was successfully employed to produce novel edible cast films. The impact of pH of the film solution was observed on the both TS and EB. The best properties were shown by the film prepared at pH=12, probably due to the applied extreme value of pH, with the highest extraction of filmogenic macromolecules, but also the highest IEP distance.

It is necessary to focus further research on the optimization of other process parameters (temperature, type and amount of plasticizer, etc.) in order to optimize the properties of COC films or use as a packaging material.

Acknowledgments: *This paper is a result of the project „Production and application of bio-packaging obtained from agro-industrial waste“ („Proizvodnja i primena bio-ambalaže dobijene iz agroindustrijskog otpada“), Project number 142-451-3059/2023-01/02, financed by the Provincial Secretariat for high education and scientific research activity, Autonomous Province of Vojvodina, Republic of Serbia.*

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POLYLACTIC ACID (PLA) AND SODIUM ALGINATE FILM PRODUCTION AND USAGE IN ACTIVE PACKAGING FOR TOMATO PRESERVATION

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Original scientific paper
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Abstract: *Increasing food needs and decreasing food sources have made it necessary to protect food from pathogens and keep it fresh for a longer period. Active packages are used to increase the shelf life of food. Interest in biopolymeric film and edible antibacterial agents is increasing day by day due to migration in the active packaging system. Biopolymers are organic molecules that do not have a problem in contact with food. Polylactic acid, polyglycolic acid, polyvinyl alcohol, carrageenan, and starch are the most widely used biopolymers. Nanoparticles and metal contents as antimicrobial additives are being replaced by natural origin antimicrobial agents today. These include aromatic oils such as peppermint oil, cinnamon oil, and products of natural origin such a sodium alginate, nisin, chitosan. The aim of this study is to produce active packaging film to extend the shelf life of tomatoes by using sodium alginate and polylactic acid. In this study, films were produced by solvent casting method by adding 0, 1, 2.5, and 5% sodium alginate into 10% polylactic acid solution. The chemical structure of the produced films was determined by ATR-FTIR, transparency by visiually, color properties by spectrophotometer, contact angle and surface energy by goniometer. In addition, the elongation tests of the produced films were carried out. Decomposition characteristics of tomatoes packed with the obtained films were determined at room temperature. As a result, it has been determined that the produced films have mechanical and surface properties that can be used in food packaging and extend the shelf life of tomatoes. It was concluded that as the amount of sodium alginate increases, the shelf life of tomatoes increases.*

Keywords: active packaging, sodium alginate, polylactic acid, food shelf life

1 INTRODUCTION

The effort to provide taste, texture, aroma, stability and perhaps most importantly, compliance with the palate in the foods that human beings have to consume in order to survive is a process that goes back to ancient times and continues increasingly today. The diversification of products with new production techniques, the increase in consumer demands and consumption rate, the increase of shelf life in perishable and risky foods, the necessity of production in seasonal products within a certain time interval have made it necessary to use different preservation methods and food additives. However, the determination of the negative effects of food additives on human health has led researchers to studies to increase the shelf life of foods without using additives (Shim et al., 2011). At this point, the most appropriate approach is to protect the shelf life of the food by means of the food packaging surrounding it and to keep the quality and freshness at the desired standards throughout the shelf life. The basic functions of a food packaging; to preserve the integrity of the food at every stage of the chain from production to consumption, to protect the food against the parameters that threaten quality and safety, to inform the consumer on issues such as product content and storage conditions. While the packaging that fulfills these functions was accepted in the past, it is insufficient to meet the changing consumer demands today. This situation leads manufacturers to new generation technologies such as modified atmosphere packaging, active and smart packaging (Kruijf et al., 2002).

Active packaging; it is the interaction of the packaging with both the foodstuff and its environment in order to extend the shelf life or ensure safety while maintaining the quality of the foodstuff. While active packaging systems are basically designed to provide microbial safety, they find a wide variety of uses due to their oxygen scavenger, ethylene remover and carbon dioxide absorber properties. Biodegradable polymers or plastics are used as packaging material in antimicrobial packaging. Considering environmental concerns, biodegradable composites such as chitosan, starch, gluten, or poly (lactic acid) come to the fore. The main function of a food packaging is to ensure the quality and safety of food during storage and transportation and to prevent factors and conditions such as pathogenic microorganisms, air, light, oxygen, and humidity from spoiling the food (Rhim et al., 2013). Food packaging should not absorb moisture into the product and should prevent moisture loss from the product. It should protect the food from microbial contamination and act as a barrier against the passage of other volatile compounds such as water vapor, oxygen, carbon dioxide and

flavors into the food (Han, 2005; Mauriello et al., 2005; Tornuk et al., 2015). Microbial spoilage, which shortens the shelf life of foods and makes them unusable, mostly occurs on the surface of the food and poses a significant threat to human health (Ayana & Turhan, 2010). In order to prevent these deteriorations, antimicrobial agents are used in the form of spraying, dipping or coating the food surface. However, these substances can quickly transition into food or become neutralized in food. For this reason, its usefulness in food is limited (Coma et al., 2002; Outtara et al., 2000). As consumers become much more conscious, the interest in food packaging systems has increased, where all these negativities are not experienced, and better quality and safe food preservation is possible. All these problems have made it inevitable to increase the tendency towards new generation food packaging materials and technologies such as bioplastic material technologies, edible film and coating materials, modified atmosphere packaging systems, active and smart packaging systems. Food safety is always among the priority areas and antimicrobial packaging systems play a very important role in ensuring quality and safety in food. The basic principle of antimicrobial packaging with traditional preservation methods is to prevent microbial growth. There are 3 ways to add antimicrobial additives to the packaging system or to gain antimicrobial function by using antimicrobial polymer material; release, absorption, and immobilization (Han, 2003). In the release, microorganism growth is inhibited by the migration of the antimicrobial agent into the food or into the headspace of the package. In absorption, essential factors for microbial growth are removed from the food system. In immobilization, there is no antimicrobial agent release, but growth is suppressed by contact with the surface. Immobilization is more effective in liquid foods than solids.

Poly(lactic acid)s are rigid thermoplastic and aliphatic polymers with semi-crystalline or amorphous structure. This polymer has a unique feature in that it has both polyethylene terephthalate (PET) characteristics and exhibits polypropylene (PP) feature (Henton et al., 2005). Another feature of polylactic acid is that it is a biodegradable polymer produced from starch-rich plant sources such as corn, sugar cane and wheat. In addition to these features, PLA has features such as environmental friendliness and biocompatibility; It provides potential use in plastic applications, packaging, agricultural products, disposable products, and medical field (Gupta et al., 2007).

Sodium alginates are components that have been used in the food industry for many years as a thickener, gelling agent, and colloidal stabilizer, as well as for the distribution and/or retention of various proteins and cells. Sodium alginates are a polyuronic saccharide produced as an extracellular matrix by certain soil bacteria (Azotobacter vinelandii and Pseudomonas aeruginosa) isolated from the

cell walls of brown seaweed species (Phaeophyceae). Sodium alginate is a low-cost, biocompatible, and biodegradable polymer that can be separated into functional components such as β-D-mannuronic acid (M) and α-L-gluonic acid (G). It is coded as a food additive with the code E400. The solubility of sodium alginates in water depends on the pH of the solvent, the ionic strength of the medium, and the presence of gelling ions in the solvent. While alginic acid and calcium alginate are insoluble in water, ammonium alginate, potassium alginate and sodium alginate are soluble in water. For them to become soluble, protonated carboxylic acid groups and pH must be kept above certain critical values. It is used as an antibacterial in flour and pastry products (Kandirmaz, 2020). In this study, it was aimed to produce active packaging film and to determine its properties to extend the shelf life of tomatoes.

2 MATERIAL AND METHODS

2. 1 Materials

Polylactic acid (PLA), all other solvents, HCl and NaOH and sodium alginate were purchased from Sigma Aldrich Chemical Co. (St. Louis, MO, USA).

2. 2 Methods

For the preparation of active film, firstly 10% polylactic acid solution was prepared in chloroform. Sodium alginate was added to the prepared solution in the ratios in Table 1 and mixed rapidly, and film formulations were prepared.

Table 1. Active film formulations.

Formulation	***%10 PLA solution (%)***	***Sodium Alginate (%)***
F0	*100*	*0*
F1	*99*	*1*
F2	*97.5*	*2.5*
F3	*95*	*5*

The resulting equal volumes of film mixtures were poured into the Teflon mold and set in 10 minutes at room temperature. A standard mold made of PTFE with a thickness of 5 mm and dimensions of 1500 mm x 1500 mm was used in film casting processes.

2. 3 Characterization

Chemical characterization of the films obtained was done with Perkin Elmer Spectrum100 ATR-FTIR spectrophotometer. The surface properties of the films were determined with a Leica optical microscope. Thickness of the films was

measured using a digital micrometer (Mitotuyo 7327, Tokyo, Japan). The mean value was taken from ten replications across each film sample. Tensile tests of the produced films were determined standard tensile stress-strain tests to measure modules, ultimate tensile strength, and elongation at break. Standard tensile stress-strain experiments were performed at room temperature on a Materials Testing Machine Z010/TN2S, using a crosshead speed of 10 mm/min.

The wettability of active films was determined using the contact angle with the sessile water droplet method. The characteristics of surfaces were determined with contact angle (TAPPI T 458). Distilled water was used as standard wetting fluid in a Pocket Goniometer Model PG-X, (FIBRO Systems AB, Sweden), which was measured as a function of time. The program is of version 3.4. Images of water droplets were then recorded by using a CCD video camera. Surface energies were calculated on the contact angle by ASTM D5946 standard test method.

The color measurements of obtained films were made by CIEL*a*b* method using X-Rite eXact spectrophotometer according to ISO 12647-2: 2013 standard. The measurement conditions of the spectrophotometer are determined as polarization filter with 0°/ 45° geometry with 2 observer angle with D50 light source in the range of 400-700 nm. The difference between the colors of the different films were calculated according to formula 1 according to the CIE ΔE 2000 ISO 13655 standard.

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \qquad (1)$$

The obtained films were wrapped on tomatoes and the related tomatoes were kept at room temperature. The deterioration of tomatoes was evaluated visually and colorimetrically.

3 RESULTS

Films containing sodium alginate have been produced successfully. Chemical illumination of the produced films was done with ATR-FTIR. ATR-FTIR spectra of the films are given in Figure 1. When the ATR-FTIR spectra of Polylactic acid without sodium alginate (F0) is examined, carbonyl stretches at 1750 cm and C-O-C stretch bands at 1200 cm are clearly seen (Mele et al., 2019). It is clearly visible that the characteristic bands of Polylactic Acid are shown in all spectra of F1, F2, F3 films. Main peaks of sodium alginate, only the signal of C = O stretching at 1630 cm observed in composite films. These results suggest the successful

combination of sodium alginate in polylactic acid films. The results are consistent with the literature (Mortalo et al., 2023).

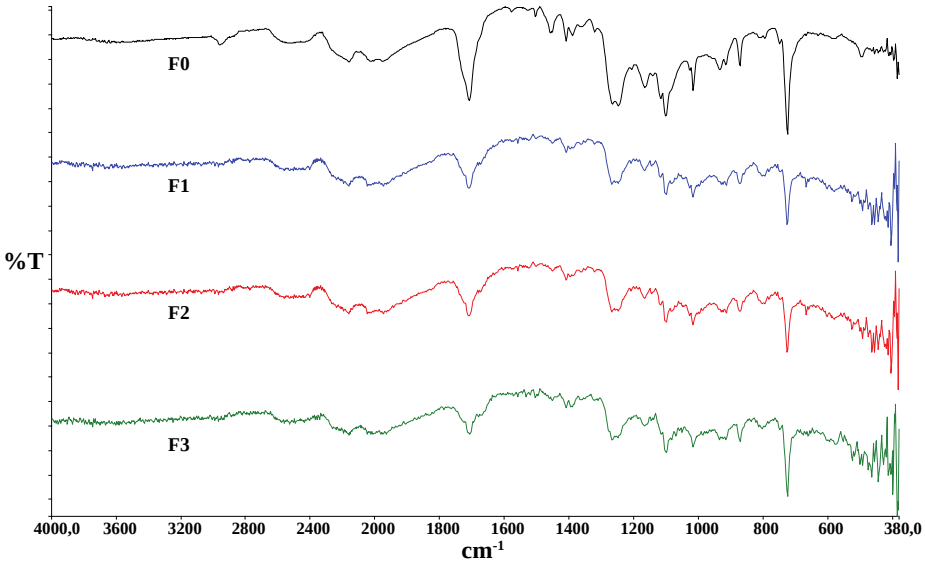

Figure 1. ATR-FTIR spectrums of active films.

SEM images of the obtained films were photographed and examined. It was determined that the surfaces of the films in all compositions had smooth and homogeneous distribution. Figure 2 shows the SEM image of the film containing the highest sodium alginate.

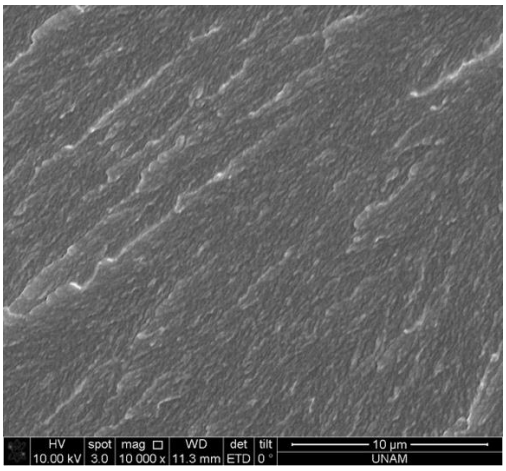

Figure 2. SEM images of F3 film.

The contact angles of the obtained films were measured, and the surface energies were calculated accordingly and given in Figure 3. When the figure is examined, the contact angle of F0 (the film containing only pollactic acid) is 73.8.

With the addition of sodium alginate into the film, the contact angle decreased and reached a maximum of 71.7. The reason for this is due to the hydrophilic groups of sodium alginate. As the number of hydroxyl groups in the environment increases (i.e., as the amount of sodium alginate increases), the contact angle decreases. The results are in line with the literature (Bhasney et al., 2017). As the contact angle of the films decreased, the surface energies increased. This is an expected result.

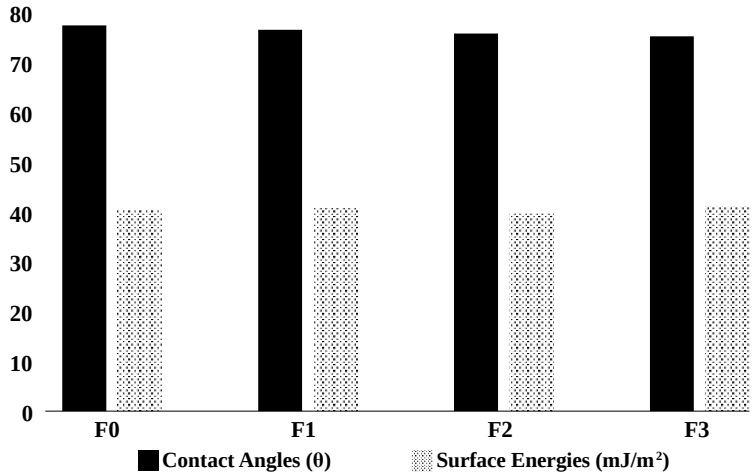

Figure 3. Contact angles of active films.

When Figure 4 is examined, the tensile properties of active films are shown. When the pure polylactic acid film is examined, it is seen that it has the highest tensile strength. With the addition of sodium alginate into the film, there was a noticeable decrease in tensile strength due to the increase in the crystalline structure. It is known that this is due to the polymorphism feature between PLA and sodium alginate (Zhang et al., 2008). For this purpose, it can be concluded that the polymeric film should contain minimum sodium alginate in order to be used in food packaging.

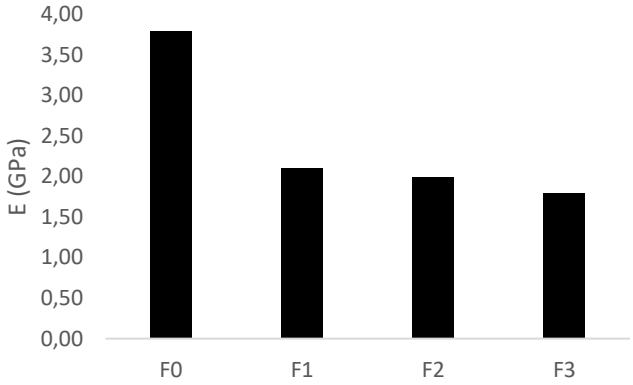

Figure 4. Tensile strength of active films.

The color and gloss properties of the obtained films were examined (Table 2) and it was determined that the films without sodium alginate were white and visually semi-permeable. With the addition of sodium alginate, the film colors shifted significantly towards yellow. As the amount of sodium alginate increased, as can be seen from the color difference, the yellow shift reached advanced levels. The gloss, on the other hand, increased slightly with the addition of sodium alginate, and then the gloss decreased depending on the surface roughness as the amount of sodium alginate added increased. In addition, the transparency remained visually semi-permeable.

Table 2. Active films color and gloss properties.

Sample	***L****	***a****	***b****	ΔE	***Gloss***
F0	*87.09*	*0.57*	*-1.55*		*7.1*
F1	*72.24*	*1.86*	*10.65*	*14.55*	*7.9*
F2	*71.85*	*8.94*	*26.27*	*20.37*	*3.8*
F3	*78.99*	*6.90*	*28.76*	*21.15*	*1.9*

Tomatoes were wrapped with F0, F3, and market film, and the freshness of the tomatoes was visually evaluated at 24°C for 15 days. In the evaluations, it was determined that the tomato in the market film visually shriveled, softened and deteriorated on the sixth day, the same deterioration rate was reached on the seventh day of the tomato wrapped in the F0 film, and the tomato wrapped in the F3 film reached the eleventh day. It was found that the resulting active film helped the tomato maintain its freshness for twice as long.

4 CONCLUSIONS

In this study, active films were successfully produced using PLA and sodium alginate. The chemical structure of the produced films was clarified with ATR-

FTIR. The surface was examined by SEM, and it was determined that it had a homogeneous and smooth structure. The contact angle and surface energies of the obtained films were examined, and it was determined that the films were capable of printing with solvent-based flexo ink. The tensile strength of the films obtained was measured and it was determined that the tensile strength of the films decreased as sodium alginate was added. The addition of sodium alginate significantly shifted the color to yellow and reduced the gloss. All the active films obtained increased the shelf life of tomatoes, and it was determined that the film containing the most sodium alginate increased the shelf life of tomatoes approximately twice.

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AN ECO-FRIENDLY SMART PACKAGING FILM WITH CARREGENAAN AND ANTHOCYANIN

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Original scientific paper
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Abstract: *The basic functions of a packaging; convenience, protection, containment, and communication. While protecting the product in the package against external environmental conditions, it should also provide information about the product with the information and design on it. Research on active and smart packaging, which extends shelf life with decreasing food resources or informs when any change in food structure occurs, attracts more and more attention. The use of natural resources in food traceability (in smart packaging) is very beneficial for health. The fact that polylactic acid is a material of natural origin and its use in food and medicine by the U.S. FDA suggests that it is a very good raw material for the smart packaging industry. Anthocyanins are a naturally sourced material that changes color with pH obtained from plants such as grape skin, red cabbage, strawberries, and turnips. When foods spoil, they release amine derivatives into the environment, which causes shifts in the packaging towards the base. In this study, anthocyanins were extracted from natural sources and carregenaan's films containing these anthocyanins was prepared by solvent casting method. The color properties of the prepared films were determined by both color spectrophotometer and UV spectrophotometer. The surface morphologies of smart films were examined using SEM. The swelling ratio, re-release in water, optical, and mechanical properties were determined. The use of the obtained films as smart films was determined on chicken. As a result, smart films have been produced successfully. The resulting smart films turn red-violet in acidic conditions and blue-green in basic conditions. It has been determined that the film, which changes color with deterioration, can be used as a smart packaging material.*

Keywords: smart packaging, anthocyanin, carregenaan, colorimetric indicators, food quality

1 INTRODUCTION

The deterioration of chicken meat depends on the microorganism activities that reproduce on it. As a result of these activities, permanent and undesirable changes occur in the structure of chicken meat, these changes are called "deterioration". The most important factor that increases the deterioration rate of chicken meat from the production to the end consumer is the temperature conditions during storage. Because microorganisms operating on chicken meat can survive at certain temperature values. For this reason, chicken meat is kept in the cold chain and the deterioration time is extended. However, breaks in the cold chain will cause the meat to deteriorate before the expiration date (Petruzzi et al., 2017). For this reason, many studies have been carried out on active and smart packaging in recent years. In traditional packaging, the primary purpose is to make the product act as a barrier to protect it from moisture, light, air, impurities, and physical damage. Active packaging provides the extension of shelf life with chemical modifications made in conventional packaging materials. Smart packaging, on the other hand, does not have an effect on extending the shelf life of the product, but they are markers that can show the changes in the product environment and the structure of the product with color changes (Park et al., 2013). As an example of smart packaging; lactic acid-based time-temperature indicators (Hidayat et al., 2017), binary color indicators (Chen et al., 2017), salmonella biosensors (Rukchon et al., 2014), colorimetric mixed-pH dye-based indicators (Brizio and Prentice, 2014), photochromic time-temperature indicators (Saliu and Della Pergola, 2018), carbon dioxide indicators (Quested et al., 2011) can be displayed.

The main function of traditional food packaging includes reducing food spoilage (thus extending shelf life), maintaining quality and safety, and reducing/eliminating physical damage to food. Packaging serves to protect the contents from factors such as heat, light, humidity, pressure, oxygen, enzymes, microorganisms, odours, insects, dust, and dirt. The traditional secondary function of food packaging is the marketing of the product. In recent years, it has increasingly demonstrated the importance of packaging as a natural part of marketing. Although it performs a secondary function, this aspect of food packaging has a direct impact on the sales of the product. However, a significant problem of food waste and increasing consumer demands for lightly preserved, fresh-tasting, convenient foods as well as changing retail practices (i.e., the globalization of food distribution) are beginning to emerge (Butler, 2001)

Although the potential advantages of smart packaging are numerous, there are concerns about the use of smart packaging. At a time when consumers are becoming more aware of the environmental impacts from the use of excessive non-biodegradable plastics, concerns have been expressed about the increased amount of packaging that may be required for the widespread use of smart packaging (Taoukis et al., 1999). One of the most convenient ways to incorporate smart packaging technologies into food and beverage packaging is with smart labels. The functionality of smart tags is typically in the form of inks that are chemically formulated to interact with the surrounding environment. The working principle of smart labels is mechanical, chemical, enzymatic or microbiological irreversible change, usually expressed as a visible response in the form of mechanical deformation, color development or color movement (Zhao et al., 2017). Chemical or physical reactions are caused by chemical reactions or acid base reactions, melting, polymerization etc. It is based on physical changes such as time and temperature. The color-based pH indicator is a promising indicator to be used in the detection of microbial metabolites of food freshness. This method is used as a label on the package to monitor food freshness. These labels work based on pH changes because the total volatile basic nitrogen (TVBN) produced during food spoilage inside the package cavity causes a pH increase resulting in the indicator color changing and easily detectable with the naked eye. Smart packaging techniques, which have been increasingly used in recent years, are systems that show the conditions that packaged foods are exposed to during transportation and storage, and they are used as an indicator of inside and outside the packaging, especially during distribution and storage, to protect the quality characteristics of the food and to ensure food safety.

Anthocyanins are an important type of water-soluble flavonoid pigment that gives the roots, leaves, seeds, stems, flowers, fruits, and other organs of various plants a wide range of distinctive colors from purple, blue, pink and red. These colorants, which have low toxicity, are frequently used in the pharmaceutical, food and cosmetic industries (Çoruhli, 2013). Anthocyanins, water-soluble polar compounds, are highly sensitive molecules sensitive to some factors. For this reason, their stability and color change in the presence of those factors. These include sulfur dioxide, oxygen, metallic ions, copigments, ascorbic acid, protein, sugar, light, heat, and pH (Ersus and Yurdagel, 2007). Most anthocyanins turn blue under low basic condition and red under acidic condition. The use of anthocyanins as acid-base indicators is based on these properties. Anthocyanins have been found in fruits such as blueberry, blackberry, cherry, raspberry, blood orange, red grape, apple, peach, strawberry, watermelon, carrot, cabbage, purple onion, red bean, pepper, tomato, and similar colored vegetables (Lila, 2004).

In this study, it was aimed to develop a natural freshness indicator label that can indicate the deterioration of chicken meat over time based on volatile ammonia and biochemical amine type compounds formed from chicken meat, and therefore pH change.

2 MATERIAL AND METHODS

2. 1 Materials

Black carrot was obtained from a local market. Carregenaan, acid, base, and solvents were purchased from Sigma Aldrich Chemical Co. (St. Louis, MO, USA).

2. 2 Methods

Obtaining anthocyanin from black carrot was done according to the literature (Ağçam and Akyildiz, 2015). 5g samples were taken from the homogenized black carrot pulp, transferred to a 50 mL Teflon tube, and 20 mL of distile was added as an extraction solution, mixed, and kept at room conditions for 5 min. Following this, the mixture in the tube was vortexed at high speed for 30 seconds and then centrifuged (4000 rpm, 4°C, 10 min). The clear part obtained after centrifugation was transferred to a 50 mL flask and the pulp residue was extracted a second time under the same conditions. The clear portions were combined and made up to the volume of the balloon with the same extraction solution. The clear colored solutions obtained were removed from their solvents in the evaporator and dried in a vacuum oven at room temperature.

The color properties of the obtained anthocyanins were investigated by shimadzu UV spectrophotometer at different pHs. Smart tag films were created by using the obtained anthocyanins and carregenaan in the ratios in Table 1.

For the preparation of smart film, firstly 10% carregenaan solution was prepared in water. Obtained anthocyanin was added to the prepared solution in the ratios in Table 1 and mixed rapidly, and film formulations were prepared.

Table 1. Smart label formulations.

Chemical structure	***%10 Carregenaan solution (%)***	***Anthocyanin (%)***
F0	*100*	*0*
F1	*99*	*1*
F2	*97.5*	*2.5*
F3	*95*	*5*

The resulting equal volumes of film mixtures were poured into the Teflon mold and set in 10 minutes at room temperature in vacuum oven.

2. 3 Characterization

The color character of the anthocyanin was determined by Shimadzu UV-2450 model UV-VIS spectrophotometer. The surface properties of the films were determined with Philips XL30 ESEM-FEG/EDAX. Thickness of the films was measured using a digital micrometer (Mitotuyo 7327, Tokyo, Japan). The mean value was taken from ten replications across each film sample. Tensile tests of the produced films were determined standard tensile stress-strain tests to measure modules, ultimate tensile strength, and elongation at break. Standard tensile stress-strain experiments were performed at room temperature on a Materials Testing Machine Z010/TN2S, using a crosshead speed of 10 mm/min.

The color measurements of obtained films were made by CIEL*a*b* method using X-Rite eXact spectrophotometer according to ISO 12647-2:2013 standard. The measurement conditions of the spectrophotometer are determined as polarization filter with 0°/45° geometry with 2 observer angle with D50 light source in the range of 400-700 nm. The difference between the colors of the different films were calculated according to formula 1 according to the CIE ΔE 2000 ISO 13655 standard.

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \qquad (1)$$

The obtained films were wrapped on tomatoes and the related tomatoes were kept at room temperature. The deterioration of tomatoes was evaluated visually and colorimetrically.

3 RESULTS

Anthocyanins were successfully extracted from black carrots. The color of the obtained anthocyanin solutions at different pHs is given in Figure 1. When foods such as chicken decompose, they release nitrogen-containing compounds into the environment, which causes the pH to shift to the basic environment around the food. When the anthocyanins extracted in this study were examined at different pHs (Figure 1), it was observed that the color turned pink at acidic pHs, purple-blue at basic pHs, and gray-green in extremely basic conditions.

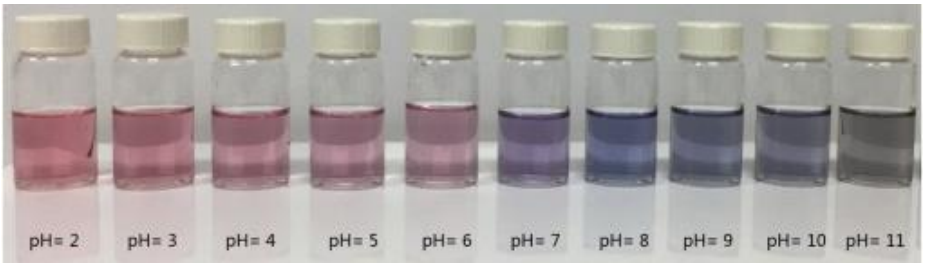

Figure 1. Color change of extracted anthocyanin.

The color characters of the obtained extracts were examined by UV spectroscopy at pH'1-2-5-7-8 and are given in Figure 2. When the pHs obtained are in acidic condition, a broad anthocyanin peak is observed around 520 nm. However, this peak disappears as the pH shifts towards the base. The results obtained are compatible with the literature (Kammerer et al., 2004).

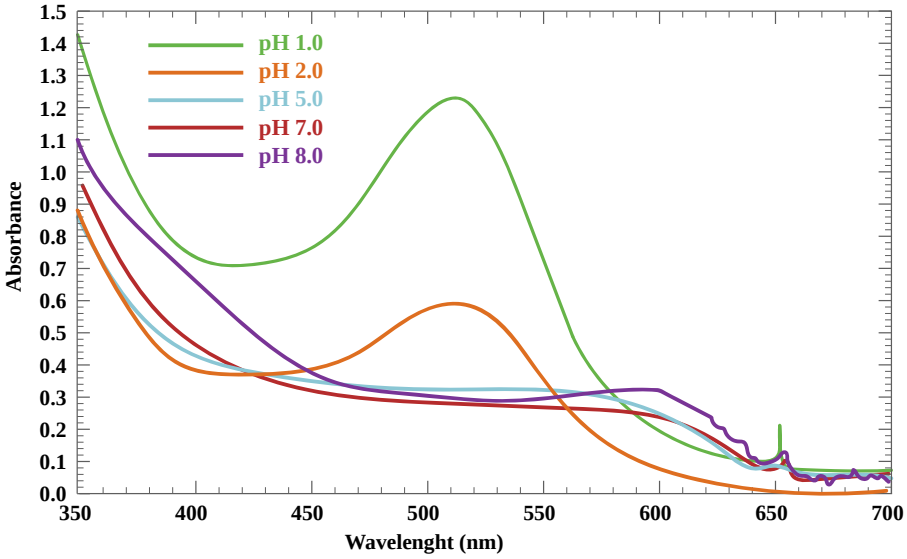

Figure 2. UV spectrums of anthocyanin in different pH.

Caragennan binder biofilms were produced by using the obtained extract at different rates. The films produced were placed in a petri dish with chicken bought from the local market and kept at +4 C. At the end of 4 days, the change in color was measured with x-rite spectrophotometer and the results are given in Table 2. When the table was examined, it was determined that the label color changed from pink-red to purple-blue at the end of 4 days. When the color properties were examined, it was determined that the shift to b in the basic case confirmed the blue shift. The fact that the difference between the two colors

obtained is above 3 in ΔE indicates that the color difference is at a perceptible level. the films that show values higher gloss values.

Table 2. Optical characteristic of smart labels due to chicken spoilage.

	L*	***a****	***b****	ΔE	***Gloss***
Color before decay	*30*	*15*	*5*	*-*	*15.30*
Color after decay	*23*	*7*	*-1*	*9.48*	*15.20*

The surface properties of the films obtained were determined by SEM (Figure 3). When the SEM photograph is examined, it is seen that the films have a smooth surface and are homogeneous.

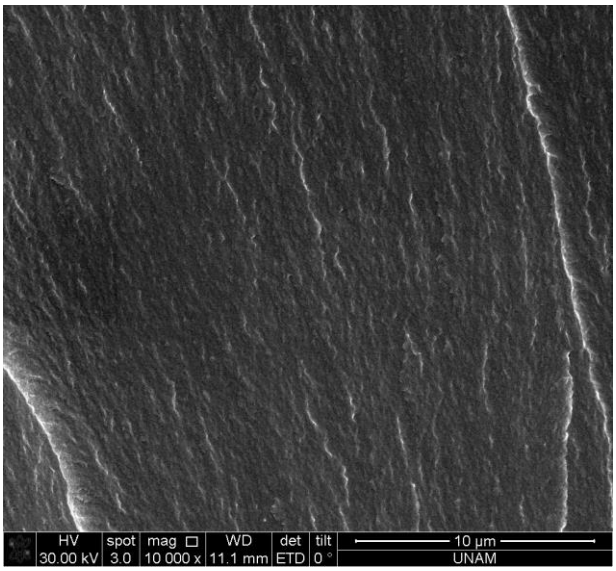

Figure 3. SEM image of anthocyanin-carregenaan film.

Carregenaan films were immersed in water for 24 h at 25°C. Swollen films were then putted between two dry papers to remove residual liquids from the smart label surface, after that weighed, dried in a vacuum oven, and reweighed. The water contents of smart labels were calculated using eq. (2).

$$\text{Water content (\%)} = (Ws-Wd)/Ws \times 100 \qquad (2)$$

where Ws: weights of swollen films and Wd: vacuum-dried films.

The swelling characteristics of the films obtained were examined and it was determined that 15% swelling occurred in the films due to the hydrophilic structure of carregenaan. However, with this swelling, the anthocyanin

molecules did not pass into the water sample and fulfilled the smart label function.

Carregenaan films were weighed after vacuum-drying, then immersed in a water for 24h. The samples taken from the water were examined by UV spectroscopy and it was investigated whether the anthocyanin peak at 520nm exists or not, whether the film releases the active substance or not. According to the data obtained, it was determined that there was no back-release in contact with water for 24 hours. Results are line with literature (Roh and Shin, 2006).

The thickness of the produced films was determined as 0.178 ± 0.02mm. In addition, the tensile strength was determined as 3.150 ± 0.15 kg/mm^2.This results shows that carregenaan film is stronger.

4 CONCLUSIONS

Anthocyanin was successfully extracted and films containing carregenaan were stably prepared. The films obtained have good mechanical properties and no re-release in water occurred from the film for 24 hours. The films proved that they can be used to determine chicken degradation colorimetrically depending on the pH, with the color change from pink to purple.

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MODIFICATION OF PLA-BASED BIO-NANOCOMPOSITE WITH NCC

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Original scientific paper
doi: 10.5281/zenodo.10008103
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Abstract: *In this article, the properties of bio-nanocomposite with poly(lactic acid) (PLA)/polycarbonate (PC)/ bled, prepared with reactive extrusion, are described. For good dispersion of nanocrystalline cellulose (NCC) mixture of two compatibilizers was used, without surface treatment of NCC. To enhance the miscibility of the bio-nanocomposite two compounding cycles were performed. To enable the crystallization during the cooling of PLA, CaCO3 was added in all series. A mixture of PLA/PC with all additives and without NCC was used as a reference. The addition of NCC enhanced stiffness, strength, and elongation at break, showing good interfacial interaction between thermoplastic matrix and NCC due to proper compatibilizer mixtures. At lower NCC loading the mechanical properties were enhanced also beyond the glass transition temperature. The crystal moieties formation was characterized by Flash DSC. At 1 % and 2 wt.% NCC loading the time for crystal formation is min. 600 s, at 5 wt.% NCC loading time is min. 100 s. The toughness was enhanced except for the sample with 5 wt.% NCC and second compounding cycle due to the PLA and NCC degradation. With the material, the design jars were produced. Production was possible due to the material modification, with plain PLA production via injection molding not possible due to the negative angle. Modified bio-nanocomposite is suitable for the production of design injection molded parts.*

Keywords: PLA, bio-nanocomposite, compatibilizer, reactive extrusion

1 INTRODUCTION

Biopolymers, biopolymer blends and biocomposites are becoming more and more interesting for research and industry because they pollute the environment

less. Researchers are working hard to avoid the disadvantages of biopolymers. Environmentally friendly materials, especially biodegradable ones such as PLA, poly(3-hydroxybutyrate) (PHB), poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBA) and PBAT, are attracting great interest from researchers and industry (Ma, 2011). The properties of PLA together with its ability to be processed on conventional equipment make it possible to replace conventional petroleum-based thermoplastics (Zeng, Li and Du, 2015; Murariu and Dubois, 2016). There are numerous research efforts in the field of reactive modification of biopolymers using various reactive agents such as organic peroxides and multifunctional crosslinking modifying agents (Dluzneski, 2001; Tolinski, 2009; Kruželák, Sýkora and Hudec, 2017). Researchers reported the degradation of PLA in combination with crosslinking by modifying PLA with peroxides (Takamura *et al.*, 2008, 2010; Rytlewski, Zenkiewicz and Malinowski, 2011; Signori *et al.*, 2015). Reactive compatibilisation is a very cost-effective processing technology, an environmentally friendly process as it does not contain solvents, does not require special equipment and can be easily converted to industrial production (Formela *et al.*, 2018). In microcellulose and nanocellulose, the cellulose surface is chemically modified to improve the surface interaction of the cellulose with the polymer matrix, usually by esterification and silanisation or by plasma and corona surface treatment, which is also required in the case of PLA matrix (Singha *et al.*, 2019). Unmodified bacterial cellulose nanomatrices were incorporated into the PLA matrix by electrospinning, followed by incorporation of the nanostructured fibres into the PLA matrix by melt blending. The stiffness and strength were increased while the ductility remained at the level of pure PLA (Martínez-Sanz, Lopez-Rubio and Lagaron, 2012). Major research efforts have been made to improve the reactive compatibility of PLA, including petroleum-based polymers. Chain extenders have been used for the PLA/PC blend to increase toughness (Zhao *et al.*, 2020). A stiffer PLA base blend was mixed with PC, a hydrogenated styrene-butadiene-styrene block copolymer and a reactive compatibiliser, poly(ethylene-co-glycidyl methacrylate). Thermal stability and excellent toughness were achieved (Hashima, Nishitsuji and Inoue, 2010).

2 MATERIAL AND METHODS

2. 1 Sample

Commercially available PLA with the trade name Ingeo 4043D was provided by Plastika Trček, Slovenia. Commercially available polycarbonate with the trade name Lexan 243 R was obtained from Sabic, Austria. NCC was donated by the company Navitas, Slovenia. Commercially available SEBS-g- MA with the trade name FG 1901 GT was purchased from Kraton, Germany. Commercially available

TPU copolymer with the trade name Kuramiron U TU -S5265 was purchased from Kuraray, Germany. Commercially available CaCO3 with the trade name Calplex Extra was donated by Calcit, Slovenia. Reactive compounding was performed twice. The composition of the samples is listed in Table 1.

Table 1. Composition of the samples of the third series and number of comounding cycles.

Sample	***PLA (wt.%)***	***PC (wt.%)***	***SEBS (wt.%)***	***TPU (wt.%)***	***$CaCO_3$ (wt.%)***	***NCC (wt.%)***	***Compounding cycles***
PLAPC	*42*	*40*	*10*	*5*	*3*	*0*	*1*
PLAPC 1NCC-1	*41*	*40*	*10*	*5*	*3*	*1*	*1*
PLAPC 1NCC-2	*41*	*40*	*10*	*5*	*3*	*1*	*2*
PLAPC 2NCC-1	*40*	*40*	*10*	*5*	*3*	*2*	*1*
PLAPC 2NCC-2	*40*	*40*	*10*	*5*	*3*	*2*	*2*
PLAPC 5NCC-1	*37*	*40*	*10*	*5*	*3*	*5*	*1*
PLAPC 5NCC-2	*37*	*40*	*10*	*5*	*3*	*5*	*2*

2. 2 Reactive compounding

For the first reactive extrusion cycle, the materials were mixed separately and extruded on the Labtech LTE 20-44 twin screw extruder. The screw diameter was 20 mm, the L/D ratio was 44:1 and the screw speed was 600 rpm. The temperature profile for the PLAPC samples increased from the hopper (165°C) to the die (200°C). Vacuum extraction was performed during reactive extrusion to remove the volatile gaseous products of reactive extrusion. The vacuum was set to 50 mbar. After compounding, the two produced filaments with a diameter of 3 mm were cooled in a water bath and formed into pellets with a length of about 5 mm and a diameter of 3 mm. In the second reactive extrusion cycles, the produced pellets of bio-nanocomposites were extruded on the same extruder with identical extruder settings.

2. 3 Injection moulding

The injection moulding was carried out on a Krauss Maffei 50-180 CX injection moulding machine with a screw diameter of 30 mm and a clamping force of 500 kN. The cold runner mould was used to produce the samples. The mould had two cavities, one with a dumbbell-shaped mould of type 1BA (ISO 527-1), the second with a cuboid-shaped mould (ISO 178/ ISO 179). The temperature was increased from the hopper (185°C) to the die (200°C), the injection speed was set to 60 mm/min and the mould temperature to 30°C, and the cooling time was set to 10 s. The mould was then cooled down to a temperature of 10°C. During plasticising, the back pressure was set to 150 bar and the screw speed to 50 rpm. The low screw speed was used to prevent thermal degradation of the bio-nanocomposite

melt and to minimise shear during processing due to the higher processing temperature.

2. 4 Methods for characteriaztion of the bio-nanocomposites

The tensile tests were carried out with the Shimadzu AG -X plus according to ISO 527-1. Five measurements were taken for each sample. In the tensile tests, tensile stiffness (E_t), tensile strength (σ_m), tensile yield strain(ε_m) and elongation at break (ε_{tb}) were determined. The thermomechanical properties were investigated using a Perkin Elmer DMA 8000 dynamic mechanical analyser. The viscoelastic properties of the samples were analysed by recording the storage modulus (E') and loss factor (tan δ) as a function of temperature. The viscoelastic analyses were performed on samples with dimensions of approximately 42 x 5 x 2 mm. The samples were heated at 2°C/min from room temperature (23°C) to 180°C in an air atmosphere. A frequency of 1 Hz and an amplitude of 20 µm were used in dual- cantilever mode. Thermal measurements were performed with a differential scanning calorimeter (DSC 2, Mettler Toledo) under a nitrogen atmosphere (20 mL/min). The temperature of the samples was raised from 0 to 200°C at a heating rate of 10°C/min and held in the molten state for 5 minutes to quench the thermal history. After cooling at 10°C/min, the samples were reheated to 200°C at 10°C/min. The crystallisation temperature (T_c), crystallisation enthalpy (ΔH_c), glass transition temperature (T_g), cold crystallisation temperature (T_{cc}), cold crystallisation enthalpy (ΔH_{cc}), melting temperature (T_m) and melting enthalpy (ΔH_m) were determined from the cooling scan and the second heating scan. The crystallisation behaviour of the samples was determined using the Mettler Toledo Flash DSC 1 with Huber intercooler TC45 and nitrogen purge gas (50 ml/min). Samples were cooled from melt (200°C) to the desired temperature, rapidly heated to the ageing temperature (90°C for 100 s), rapidly cooled to 15°C, reheated to 120°C and then cold crystallised at 120°C for various times (from 0.1 s to 2,400 s). All cooling and heating segments were rapidly cooled and heated (500°C/s) to prevent crystallisation during cooling and heating. The first heating run was from 15°C to 200°C. For the evaluation of the heating section, segment No. 12 was taken and the melting temperature and melting enthalpy were characterised. The mass of the samples was determined from the normalised change in specific heat capacity at the glass transition based on the evaluation of the DSC 2 measurements.

3 RESULTS AND DISCUSSION

3. 1 Mechanical properties

The results of the tensile strength are shown in Table 2. Compared to the reference, the mixtures with the addition of 1 % NCC showed higher stiffness, strength, and elongation at break. Further addition of NCC increases the tensile stiffness at the first mixing cycle but decreases the strength and elongation at break. The addition of 5% NCC reduces stiffness, strength, and elongation. An additional mixing cycle with the addition of 1 % NCC increases tensile stiffness and strength and maintains elongation at break. An additional mixing cycle with 2 % NCC addition reduces tensile stiffness while maintaining tensile strength and elongation at break. An additional mixing cycle with 5 % NCC additive reduces the stiffness, strength, and elongation. It can be concluded that the mixing conditions of the reaction ensure a good interfacial interaction between the thermoplastic matrix and the NCC and ensure a good dispersion of the NCC in the thermoplastic matrix at NCC concentrations below 5 %. The comparison of the first and second reaction mixture suggests that with an additional cycle of the reaction mixture with the addition of 2 % and 5 % NCC, the degradation of PLA and possibly also of NCC is already taking place. This is evidenced by the decrease in tensile strength and elongation, which in the case of the PLAPC matrix is a good indicator of the onset of degradation of the PLA matrix, and the lower stiffness is an indicator of the onset of degradation of the NCC. The reaction mixing of PLA and PC in the presence of a combination of two compatibilisers and a filler provides good mixing of PLA and PC while ensuring good interfacial interactions and dispersion of NCC in the thermoplastic matrix at NCC concentrations below 2%.

Table 2. Summarized results from the tensile tests.

	Tensile test results		
Sample	***E_t (GPa)***	***σ_m (MPa)***	***ε_{tb} (%)***
PLAPC	*2.17 ± 0.16*	*31.6 ± 0.3*	*4.8 ± 0.6*
PLAPC 1NCC-1	*2.37 ± 0.31*	*40.5 ± 0.2*	*9.6 ± 0.4*
PLAPC 1NCC-2	*2.44 ± 0.24*	*40.7 ± 0.4*	*9.5 ± 0.8*
PLAPC 2NCC-1	*2.38 ± 0.27*	*37.4 ± 0.2*	*8.7 ± 0.9*
PLAPC 2NCC-2	*2.33 ± 0.11*	*37.3 ± 0.4*	*8.8 ± 1.0*
PLAPC 5NCC-1	*2.23 ± 0.07*	*36.6 ± 0.5*	*8.6 ± 0.6*
PLAPC 5NCC-2	*2.01 ± 0.13*	*31.5 ± 0.6*	*4.6 ± 0.3*

3. 2 Thermo-mechanical properties

The storage modulus curves (Figures 1 and 2) show the first drop in glass transition temperature for PLA. The storage modulus is higher in this range (75°C

to 100°C) with higher NCC content. Above 100°C, the storage modulus increases due to cold crystallisation of the material. The lowest temperature peak during cold crystallisation was observed in the PLAPC sample (114°C) and the highest peak in the PLAPC 1NCC-2 sample (119°C). The addition of NCC to PLA-based compounds inhibits the cold crystallisation of PLA. At low NCC loading (1 wt%), NCC acts as a reinforcement for the PLA-based compound; at higher loadings (2 wt% and 5 wt%), the stiffness of the nanocomposites drops below that of the neat matrix. The dissipation factor curve shows two sharp peaks at 69°C and 160°C (Figures 1 and 2) for the PLA and PC matrices. The height of the first peak is lowest for the PLAPC 1NCC sample and highest for the PLAPC sample. The height of the second peak is lowest for the PLAPC sample and highest for the PLAPC 1NCC sample. In the second mixing cycle, the peak heights are higher, indicating the start of matrix degradation. The PLAPC 1NCC sample shows the most elastic behaviour after the first mixing cycle. The good surface interaction of the NCC with the matrix due to the compatibiliser in the PLAPC 1NCC sample increases the storage modulus, keeps the storage modulus at a high level and reduces the peak height of the loss factor for PLA. The higher peak loss factor for the PC sample is due to the highest cold crystallisation temperature for the PLAPC 1NCC sample and thus the overlap between the glass transition temperature of PC and the onset of melting of PLA. The DMA results show that reactive extrusion is a suitable technology for processing bio-nanocomposites even without surface modification of the natural fibres.

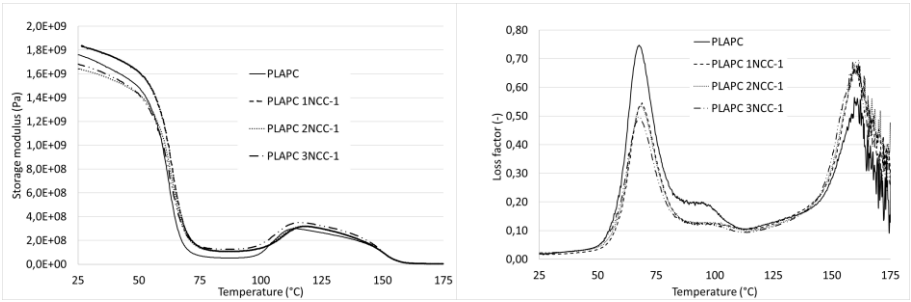

Figure 1. Summarized results of storage modulus (left) and loss factor (right) for the first compounding cycle.

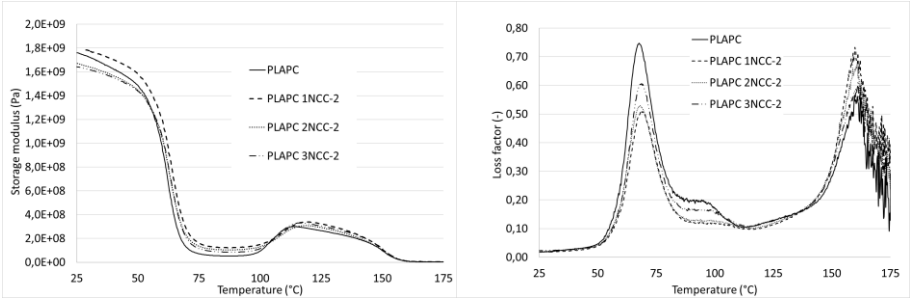

Figure 2. Summarized results of storage modulus (left) and loss factor (right) for the second compounding cycle.

3. 3 Thermal properties

The results of the DSC evaluation are shown in Table 3. During the first mixing cycle, the cold crystallisation temperature, melting temperature and crystallinity were increased for all bio-nanocomposite samples compared to the PLAPC reference. During the second mixing cycle, the cold crystallisation temperatures decreased and the crystallinity increased. The higher crystallinity indicates a good homogeneity of the bio-nanocomposites.

Table 3. Summarized results from the 2nd heating from DSC tests.

Sample	***T_g (°C)***	***ΔC_p (J/gK)***	***T_{cc} (°C)***	***ΔH_{cc} (J/g)***	***T_m (°C)***	***ΔH_m (J/g)***	***Diff. ΔH_m (J/g)***
PLAPC	*59.8*	*0.11*	*123.6*	*5.35*	*152.0*	*5.37*	*0.02*
PLAPC 1NCC-1	*60.8*	*0.09*	*133.3*	*0.32*	*152.2*	*0.37*	*0.05*
PLAPC 1NCC-2	*60.6*	*0.09*	*128.3*	*0.04*	*152.2*	*0.33*	*0.29*
PLAPC 2NCC-1	*61.1*	*0.08*	*133.4*	*0.13*	*152.4*	*0.31*	*0.18*
PLAPC 2NCC-2	*60.7*	*0.09*	*131.6*	*0.18*	*152.8*	*0.52*	*0.34*
PLAPC 5NCC-1	*61.1*	*0.06*	*130.4*	*0.24*	*153.2*	*0.48*	*0.24*
PLAPC 5NCC-2	*60.1*	*0.08*	*128.4*	*1.28*	*152.9*	*1.67*	*0.39*

The kinetics of crystallisation were characterised by Flash DSC (Figure 3). The onset of formation of crystal units was at 90°C for 100 s after ageing and at 120°C for 100 s after ageing for all samples. A shorter time is not sufficient for the formation of crystalline units. The higher NCC loading promoted the formation of crystalline units as did the second mixing cycle. The fastest and largest increase in crystalline segments was observed in the PLAPC 5NCC-2 sample up to a cold crystallisation time of 600 s and thereafter in the PLAPC 1NCC-2 sample. It can be concluded that NCC inhibits cold crystallisation at shorter times and increases cold crystallisation at longer times at elevated temperatures. The mobility of PLA chains at elevated temperatures reaches the threshold for the formation of crystalline units after 600 s at NCC loading of 1 wt% and 2 wt%. At an NCC loading of 5 wt%, 100 s is sufficient due to the higher amount of NCC particles in the

matrix. The results also indicate that NCC agglomeration occurs to a lesser extent and increases with increasing NCC content.

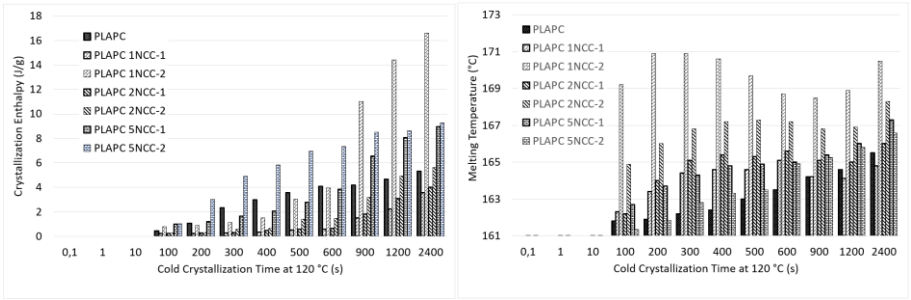

Figure 3. Summarized results of crystallization enthalpy (left) and melting temperature (right) of the samples after aging at 90°C for 100 s and various cold crystallization times at 120°C.

4 CONCLUSIONS

The evaluation of the mechanical properties showed that new properties were obtained by the addition of NCC. The mixture was able to achieve high temperature stability due to the addition of PC. The produced bio-nanocomposites showed good miscibility of PLA and PC and good surface interaction between the thermoplastic matrix and the natural fibres, although the surface of the natural fibres was not changed. Furthermore, the DSC results showed an altered morphological behaviour of the PLAPC 1NCC-2 bionanocomposite. Longer residence time at elevated temperature accelerates crystallisation as a result of degradation of PLA and NCC due to shorter PLA chains and smaller NCC particles, which serve as nuclei for the initiation of heterogeneous PLA crystallisation. At the same time, it can be observed that NCC is well distributed in the thermoplastic matrix due to the increasing crystallinity. Good surface interaction between the thermoplastic matrix and narurium fibres was achieved by suitable compatibilisers and loading. The suitability of the reaction mixture was evaluated by the simultaneous increase in stiffness and elongation at break in tensile test, change in storage modulus and loss factor in DMA, change in cold crystallisation temperature and crystallinity in DSC. The produced bio-nanocomposites showed a stiffer behaviour with high stiffness and strength at the same time. The addition of NCC also affected the morphology of the bio-nanocomposites, which can be controlled by the processing parameters. A second cycle of reactive mixing at 1% NCC loading showed that recycling of the new bio-nanocomposites can be performed without significant effects on the properties of the recycled products. The present work shows that existing polymer processing equipment is suitable for the production of bio-

nanocomposites and their recycling. To characterise the dependence on the amount of added NCC in bio(nano)composites, further studies should investigate the addition of less than 1 wt% NCC to PLA-based bio(nano)composite blends.

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MECHANICAL RECYCLING OF PRE-CONSUMER POLYETHYLENE TEREPHTHALATE (PET) WASTE

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Original scientific paper
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Abstract: *The exponential rise in plastic waste, particularly polyesters such as polyethylene terephthalate (PET), polylactic acid (PLA) and other packaging materials, has become a pressing environmental concern on a global scale. To tackle this issue, mechanical recycling has emerged as a promising solution. Mechanical recycling of PET, such as any other polymer, involves a series of crucial steps, including collection, sorting, cleaning, size reduction, and reprocessing. These steps aim to convert polymer waste into high-quality recycled materials suitable for diverse applications, however they come with challenges that need to be addressed, the most significant risks are represented by contamination and degradation. The main advantages of the are reduced energy consumption, carbon emissions compared to the production of virgin PET and conservation of valuable resources by decreasing the demand for raw materials. In the paper prospect of pre-consumer recycled PET (rPET) for mechanical recycling is studied by evaluating the influence of multiple cycles of mechanical recycling on the thermal and mechanical properties. The results show that rPET can be mechanically recycled up to 7 times starting from regrind material, before losing its processability. However, the properties after 7 cycles of mechanical recycling are still acceptable for less demanding applications, since PET retain moduli quite well, strength on the other hand decreases more noticeable. Thermal properties do not change significantly, only small decreases in degradation temperatures were recorded and crystallization behaviour shifted to higher temperature.*

Keywords: mechanical recycling, regrind materials, pre-consumer waste, polyethylene terephthalate, reuse

1 INTRODUCTION

There is no need to emphasize that the exponential growth of plastic waste has become one of the most critical environmental challenges of our time. Among various plastic materials, polyethylene terephthalate (PET) stands out due to its widespread use in packaging applications, especially in the food and beverage industry (Hopewell, Dvorak and Kosior, 2009; Association of Plastic Manufacturers (Organization), 2020). To combat the environmental repercussions of PET waste, mechanical recycling has emerged as a promising and sustainable solution. Mechanical recycling involves the collection, sorting, cleaning, size reduction, and reprocessing of post-consumer and pre-consumer pet waste, transforming it into high-quality recycled materials suitable for a wide range of applications. By diverting PET waste from landfills and incineration, mechanical recycling significantly reduces the burden on the environment and conserves valuable resources (Volfand, 2019; Schyns and Shaver, 2021; Benyathiar *et al.*, 2022).

Mechanical recycling offers a promising solution to address the challenges of PET waste. By incorporating circular economy principles, recycling aims to close the loop in the life cycle of PET products. The process starts with the collection of PET waste, including both post-consumer and pre-consumer sources. Pre-consumer PET waste, also known as industrial or manufacturing waste, originates production of PET-based products and is usually not contaminated. Recycling pre-consumer waste presents an opportunity to intercept plastic waste before it reaches the consumer. Despite its potential, mechanical recycling faces certain challenges, particularly when dealing with post-consumer PET waste. Contamination from additives, processing residues, and incompatible polymers can affect the quality and purity of recycled pet materials. Additionally, mechanical recycling processes may induce thermal and mechanical degradation in the polymer, leading to a decline in performance attributes of the recycled PET. However, by avoiding main challenges of contamination and difficulties with separation of gathered waste the effectiveness of pre-consumer waste recycling is very prospective (Hopewell, Dvorak and Kosior, 2009; Volfand, 2019; Schyns and Shaver, 2021; Benyathiar *et al.*, 2022).

This study focuses on evaluating the prospects of utilizing pre-consumer PET for mechanical recycling. The study aims to assess the influence of multiple recycling cycles its thermal and mechanical properties. Understanding the possibilities of mechanical recycling for pre-consumer PET waste is crucial for promotion of such praxis in the industry and decrease in significant share of waste.

2 MATERIAL AND METHODS

2. 1 Sample preparation

Ground PET pre-consumer bottles were supplied by Stramex PET d.o.o. (Podplat, SLO. The ground material consisted of various particle shapes and sizes ranging from fine dust to 3 mm in diameter, with the average shifted towards the upper limit.

The ground PET was dried in the Memmert 100-800 hot-air drying oven until the moisture content, determined with the Mettler Toledo HX204 moisture analyser, was below 0.025 % before injection moulding (Arburg Allrounder 320 C 500-100 Golden Edition with a screw diameter of 20 mm) into test specimens with the shape according to the standards ISO 527 (type 1BA), ISO 178 and ISO 179. The temperature profile was set to decrease from 290°C on the die to 270°C at the hopper, the screw rotated at 100 rpm^{-1} at a backpressure of 30 bar, the injection speed was 50 mm/s, the holding pressure was set to 320 bar for 5 s, and the cooling was set to 25°C for 20 s. Last forty samples from each series were analysed for their properties, while the rest were milled using the Wanner C13.20 s mill for thermoplastics, and re-injected. Mechanical recycling, consisting of milling and injection moulding, was repeated until PET retained the processability which was 7 cycles since at the beginning of 8^{th} cycle melt was already to degraded for it to be plasticized for injection.

2. 2 Characterization

The thermal and mechanical properties of the specimens were evaluated after each processing cycle. For thermal properties, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed. Samples for DSC (DSC 2, Mettler Toledo) weighing between 5 mg and 10 mg were prepared in aluminium crucibles. The temperature regime of the analysis consisted of a 5 min isothermal section at 0°C followed by heating from 0°C to 280°C at 10°C/min, at 280°C there was a 5 min isothermal section followed by cooling at 10°C/min, in two cycles, and the entire measurement was performed in nitrogen atmosphere with a gas flow of 20 mL/min. TGA analyses were performed using a Mettler Toledo TGA/DSC 3+. Samples of approximately 10 mg prepared in an alumina crucible were heated from 40°C to 600°C in a nitrogen atmosphere with a gas flow of 20 mL/min, followed by heating from 600°C to 700°C at 10°C/min in an oxygen atmosphere (20 mL/min). Dynamic mechanical analysis (DMA) was performed using a Perkin Elmer DMA 8000 dynamic mechanical analyser in dual cantilever mode. Samples were heated at 2°C/min from room temperature to

170°C in an air atmosphere and dynamically loaded at a frequency of 1 Hz and an amplitude of 20 µm.

Mechanical evaluation included tensile, flexural, and impact tests on notched specimens using the Charpy method. Tensile and flexural properties were determined using the Shimadzu AG-X plus universal testing machine equipped with a 10 kN load cell and an optical strain gauge. The tensile test was performed according to ISO 527-1 and the flexural test according to ISO 178. Impact strength was tested according to ISO 179 standard using Dongguan Liyi LY-JJD5 impact strength tester. Notched specimens were tested using a 1 J pendulum. The results of tensile and flexural tests represent the average of 5 specimen measurements each, while 10 specimens were submitted to impact toughness testing.

3 RESULTS AND DISSCUSION

The thermal behaviour of rPET during multiple processing cycles was investigated using DSC, results of second heating are presented in Table 1. Throughout the processing cycles, the glass transition temperature (Tg) of the rPET remained relatively stable, with only minor fluctuations observed. The observed T_g values ranged from approximately 75.43°C to 80.76°C. On the other hand, melting points (T_m) and enthalpies of melting are indicating slightly increasing trends, corresponding to eased crystallization of PET subjected to more processing cycles due to shortening of polymer chains.

Table 5. DSC results of second heating of injection moulded samples.

Processing cycle	***T_g (°C)***	***Cp (J/gK)***	***T_{m1} (°C)***	***T_{m2} (°C)***	***ΔH_m (J/g)***
1	*80.76*	*0.075*	*241.58*	*248.16*	*34.98*
2	*80.01*	*0.065*	*241.57*	*247.74*	*35.20*
3	*80.62*	*0.030*	*243.80*	*248.01*	*37.27*
4	*75.43*	*0.026*	*244.53*	*249.50*	*39.37*
5	*79.81*	*0.043*	*244.80*	*249.50*	*41.57*
6	*79.67*	*0.029*	*245.28*	*249.99*	*41.51*
7	*79.75*	*0.030*	*246.37*	*250.44*	*41.84*

For insight in thermal stability TGA was employed. Degradation temperatures in dependence of processing cycles are presented in Figure 1. The most noticeable drop in degradation temperature was recorded from 2nd to 3rd reprocessing, but was still less than 5°C. Following reprocessing did not affect thermal stability in sense of degradation temperature since no further drop was recorded.

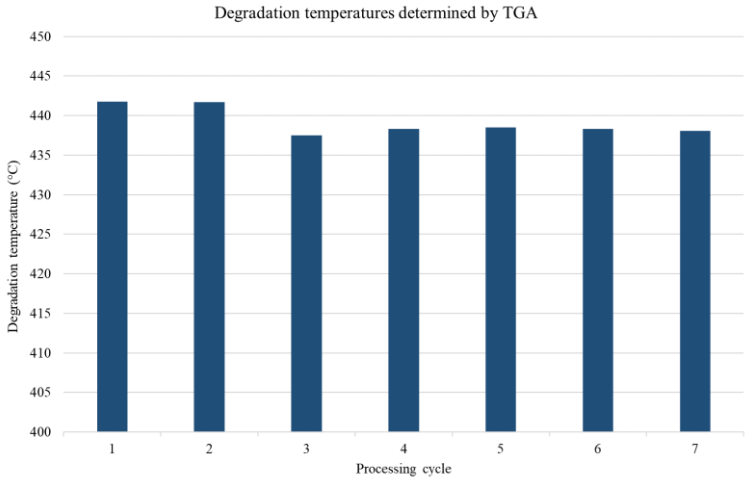

Figure 6. Degradation temperatures of samples determined by TGA.

Figure 2 presents determined tensile modulus in dependence of processing cycle. Significant decrease was recorded from 1st to 2nd reprocessing while further reprocessing did not affect it significantly since all the values remained in range of standard deviations indicating that material do not suffer significant decreases in stiffness due to multiple mechanical recycling.

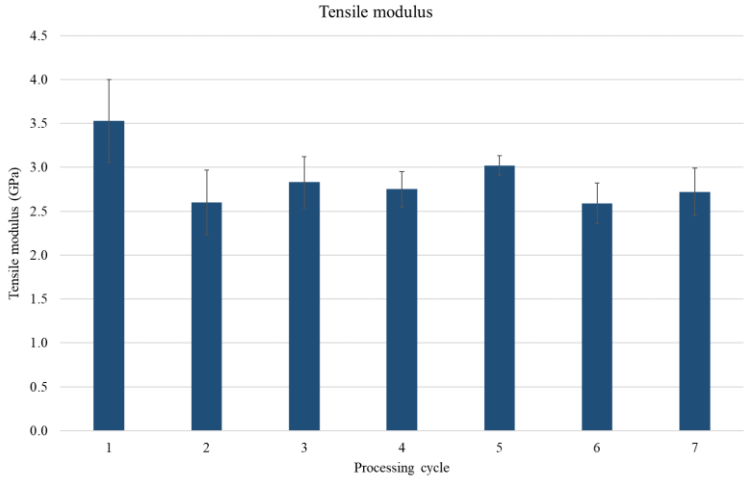

Figure 2. Tensile modulus in dependence of processing cycles.

Flexural modulus was also evaluated, results are presented in Figure 3. Results are indicating slightly increasing trend in flexural stiffness with more processing cycles presumably due to recorded increase in crystalline domains due to chain shortening and corresponding enabling more compact packing of polymer chains.

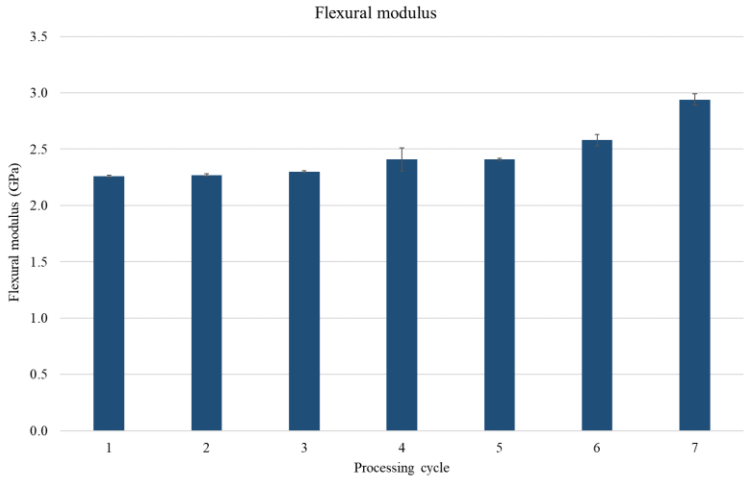

Figure 3. Flexural modulus in dependence of processing cycles.

Tensile strength initially does not seem to be negatively affected by reprocessing, as can be seen in Figure 4. Significant decrease was recorded from 5th cycle onwards. This trend points to complex microstructure behaviour of rPET during reprocessing, while also indicating the material's potential for multiple cycles of mechanical recycling.

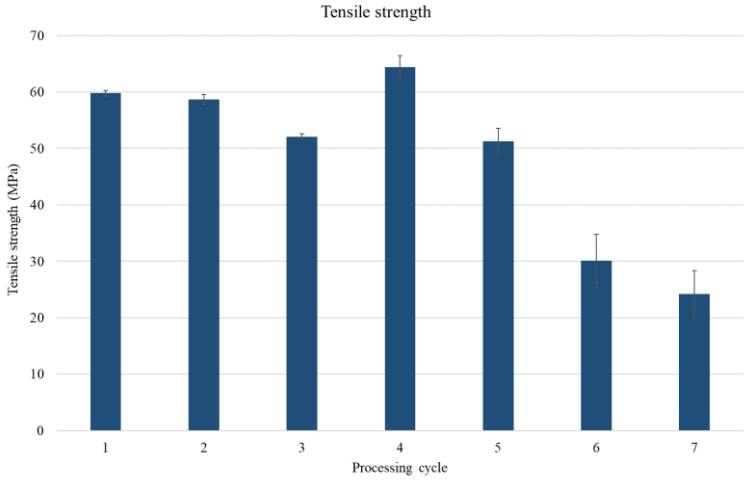

Figure 4. Tensile strength in dependence of processing cycles.

Figure 5 presents graphical representation of the determined flexural strengths. The results exhibit the same trend, as was observed with tensile strengths, reinforcing the significance of observed trend and suggests that pre-consumer rPET can be mechanically recycled at least up to five times while still retaining good mechanical performance.

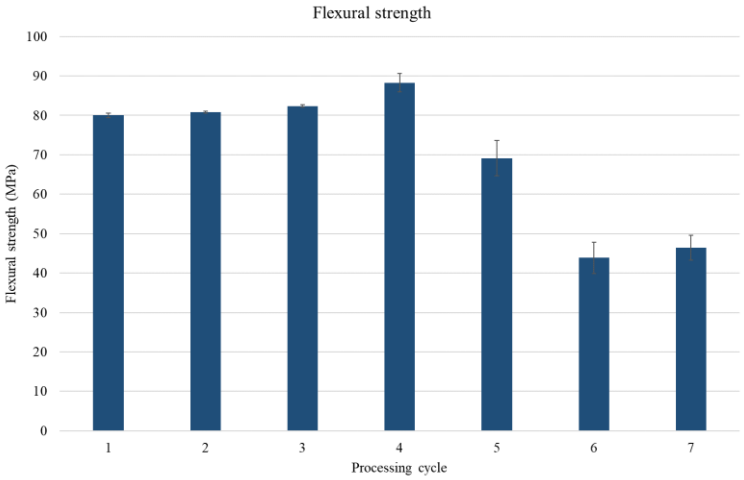

Figure 5. Flexural strength in dependence of processing cycles.

The storage modulus, determined by DMA offers further insight into material's behaviour. Figure 6 presents the determined storage modulus of samples at 30°C. The storage modulus values show significant decrease with each reprocessing up to 5th cycle, where trend reverses and storage modulus gradually returns to initial values. The initial decrease is indicating enhanced molecular mobility due to chain scission, while the subsequent increases could be explained by chain scission reaching a point where chains are able to pack themselves more efficiently.

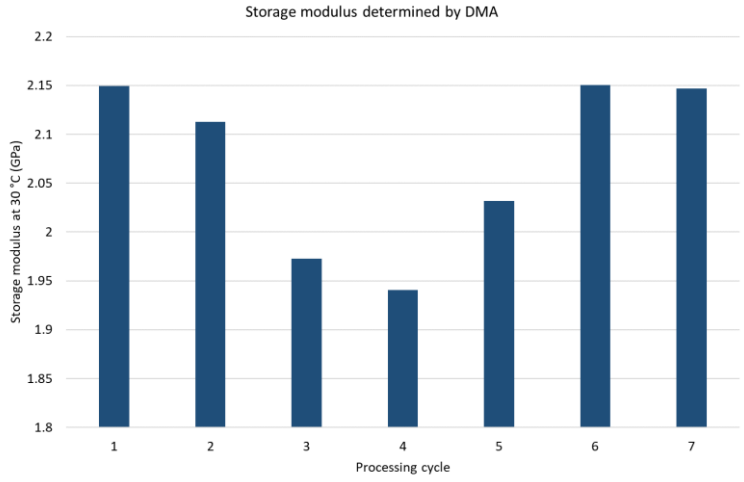

Figure 6. Storage modulus at 30°C determined by DMA.

Figure 7 presents the loss factors values determined with DMA at its peak. The trend exhibits a decrease with more processing cycles indicating a reduction in

the material's damping ability and stiffer response with its subjection to more reprocessing. The values remain comparable up to 3rd reprocessing, after which the most significant decrease occurs followed by steady declines in each subsequent cycle.

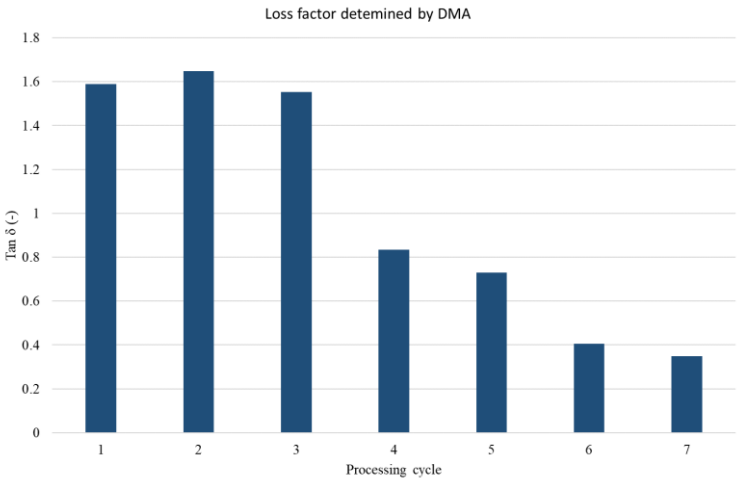

Figure 7. Loss factor determined by DMA.

4 CONCLUSIONS

In conclusion, the rising issue of plastic waste, particularly polyesters such as PET, necessitates the adoption of effective recycling strategies. Mechanical recycling has emerged as a promising solution, offering reduced energy consumption, lower carbon emissions, and the conservation of valuable resources compared to the production of virgin PET. This article has focused on the prospects of utilizing pre-consumer PET for mechanical recycling, specifically evaluating its thermal and mechanical properties after multiple recycling cycles.

The observed trends reveal the dynamic nature of rPET's response to reprocessing and highlighting its potential for mechanical recycling. The study findings indicate that rPET can undergo mechanical recycling up to seven times starting from virgin material before experiencing a loss in processability. Furthermore, suggests that while initial cycles of reprocessing do not significantly impact tensile strength, flexural strength, and storage modulus, a clear trend of decline emerges after a certain point, usually between 4th and 5th reprocessing, where appears to be a critical threshold, beyond which a more noticeable changes of material behaviour occur which is attributed to enhanced molecular mobility, chain scission, and potential microstructural changes induced by the recycling process.

Moving forward, further research and innovation are needed to address the challenges of contamination and degradation in mechanical recycling processes since potential of mechanical recycling of uncontaminated material's is clear. Hopefully, these results will encourage more mechanical recycling of pre-consumer waste.

Acknowledgments: *We would like to thank Stramex PET d.o.o. for providing materials for the study.*

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BIO-SUSHY PFAS FREE SOLUTION WITH FOCUS ON THERMOPLASTIC BASED POWDERS FOR FOOD PACKAGING APPLICATIONS

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Abstract: *BIO-SUSHY project aims to develop 3 PFAS-free coating materials partially or fully bio-based to be validated in 3 case studies textile, food and glass packaging. In parallel with material development covering sol-gel and thermoplastic powder coatings integration of safety and sustainability into the coating formulations using multidisciplinary approach of computational tools, predictive models and data-driven simulations is covered from an early R&D phase. The highlights from the latest results on bio-based biodegradable thermoplastic formulations using spray coating on paper substrates will be briefly presented.*

Acknowledgements: *Bio-Sushy project was Funded by the European Union GA number: 101091464. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Health and Digital Executive Agency (HaDEA). Neither the European Union nor the granting authority can be held responsible for them.*

Sn-CATALYSIS AS AN EFFICIENT DEPOLYMERIZATION STEP OF POLY(LACTIDE) TO LACTIDE

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Abstract: *Increasing the high-performance quality of recycled material, accelerating the renewable raw material and renewable energy, production technologies, renewable material addressing the non-toxic chemical with the generation of minimised waste; and secondly, improving the green way of producing plastic material are the main Economy Strategy plan. In this context, plastics made from renewable resources have advantages over fossil-based plastics and provide benefits to the circular economy. Therefore, the chemical recycling of renewable resources such as poly(lactide) (PLA) could be a beneficial approach to ensure the high quality of the produced material (monomer) and to add benefits to a circular economy. In this context, PLA-based plastics have been investigated. Due to its bio-based and renewable nature, PLA has been expanded in many applications such as packaging, biopharmaceutics, drug delivery carriers, 3D printing devices. In this context, many different types of chemical recycling based on depolymerisation have been developed, where the conversion of the end-of-life polymer into useful molecular weight compounds is crucial. The lactide obtained by chemical recycling is subjected to ring-opening polymerisation accompanied by catalysis to obtain high molecular weight PLA.*

In addition, the catalytic depolymerisation of PLA to lactide was investigated. In the literature, many salts have been used as catalysts for the depolymerisation of PLA. In our study, the depolymerisation step of PLA was investigated by varying the depolymerisation conditions such as concentration of tin salts as catalysts, time of depolymerisation and the potential of $Sn(OAc)_2$ as a catalyst in the depolymerisation of PLA has been demonstrated so far. The results of Sn-catalysed depolymerisation of PLA to obtain lactide, characterised by DSC, ATR-

FTIR and TGA methods, showed the presence of yields at 220°C (6 mbar) within 4 hours.

Keywords: poly(lactide) (PLA), chemical recycling, catalysis, $Sn(OCt)_2$

1 INTRODUCTION

The vision of Europe outlined in the European Circular Economy Strategy and the European Green Deal fully respects the concept of reuse, recycling and durability (European Commission, 2018b). Environmental concerns are increasing, and environmental legislation is becoming more stringent. Therefore, there is a trend towards research biodegradable polymer materials that could become alternatives to non-degradable fossil-based polymers. On the one hand, to increase the high-performance quality of recycled materials to address the generation of minimised amount of waste; and on the other hand, to improve the environmentally friendly way in which plastic materials are produced (European Commission, 2018a)(Hatti-Kaul, Nilsson, Zhang, Rehnberg, & Lundmark, 2020).

Plastics made from renewable resources have advantages over fossil-based plastics and offer benefits for the circular economy. A number of biodegradable polymers are already on the market (Chinaglia, Tosin, & Degli-innocenti, 2018; Mostafa & Tayeb, 2018; Shruti & Kutralam-Muniasamy, 2019). The most widely used material is polylactic acid (PLA) (Araújo, Oliveira, Oliveira, Botelho, & Machado, 2014). PLA, an aliphatic thermoplastic polyester derived from renewable resources such as corn starch, potatoes and sugarcane, is recognised as a bio-based and renewable polymer that is an alternative to petrochemical-based polymers (Ramot, Haim-Zada, Domb, & Nyska, 2016). The thermoplastic polyester has already been used in various applications, bioengineering (drug delivery, tissue engineering, 3D printed devices) and biochemistry, as well as for food packaging (Bang & Kim, 2012; Othman, 2014; Zhong, Godwin, Jin, & Xiao, 2020). The most effective way to synthesise PLA is the well-known ring-opening polymerisation of lactide, which is formed from lactic acid, a product of the fermentation of agricultural compounds, as shown in Figure 1.

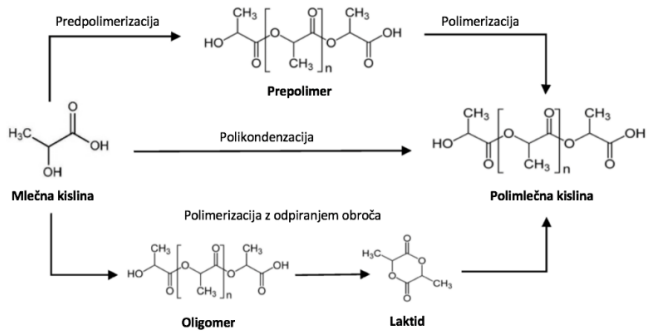


Figure 7. Synthesis of PLA; ring opening polymerization of lactide formed by lactic acid.

From an environmental point of view, the most important role of PLA is proper disposal, followed by recycling. Broadly speaking, there are two types of recycling, mechanical and chemical (Manufacturers, 2020; Mercante et al., 2018). Chemical recycling of renewable resources such as PLA could be a beneficial approach to ensure the high quality of the produced material (monomer) and contribute to a circular economy. The main challenge is proper disposal of the waste, followed by recycling to produce new materials. Many recycling techniques have been explored with varying degrees of success, as different recycling techniques release gases into the air that cause pollution. One of the most successful recycling techniques is chemical recycling through depolymerisation, where the recovered plastic is returned to its raw state and the polymer can then be resynthesised.

Chemical recycling of PLA involves a range of advanced recycling technologies that convert plastic waste into raw materials for the chemical industry, such as monomers, oligomers and hydrocarbons. These raw materials can be used to produce plastics without any degradation in quality and without any restrictions on the type of use. Several chemical recycling technologies are currently being developed and investigated, including depolymerisation, gasification and hydrocracking. Depolymerisation of PLA can take the form of pyrolysis, which yields a lactide product, and hydrolysis and alcoholysis, which yield lactic acid or other chemicals as products (Figure 2) (Abe, Takahashi, Kim, Mochizuki, & Doi, 2004).

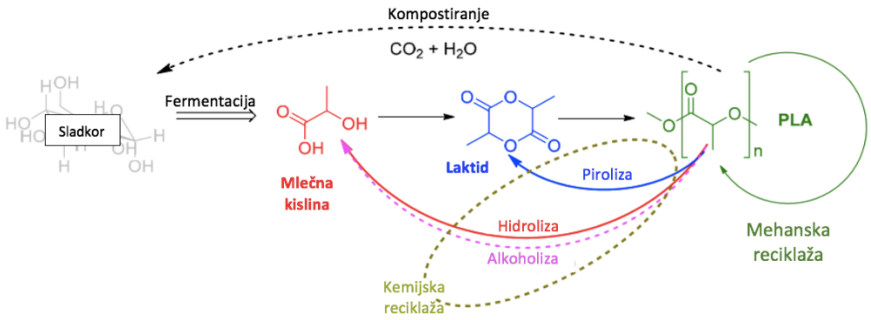
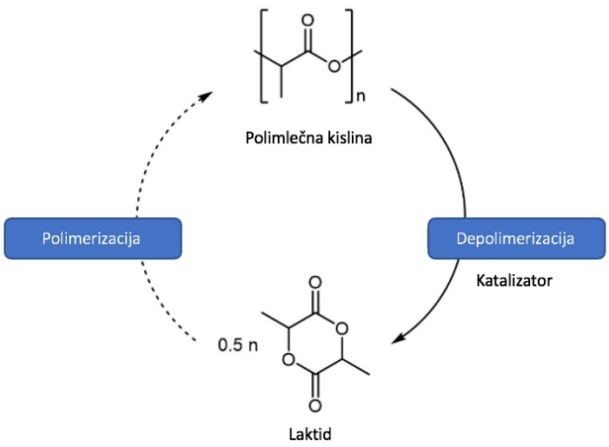


Figure 8. Recycling of PLA(McKeown & Jones, 2020).

The synthesis of valuable chemicals that would otherwise be lost as CO_2 (in incineration or composting) and the ability to synthesise new PLA with desired mechanical properties are the main advantages of chemical recycling over composting and mechanical recycling. Studies have shown that the production of lactic acid *D-lysine* by chemical depolymerisation is more energy efficient than the production of virgin material by the expensive fermentation route. An additional advantage of chemical recycling methods is that the process can be resistant to contamination by other plastics, reducing the need for costly segregation (Piemonte, Sabatini, & Gironi, 2013).

One of the chemical recycling methods is therefore the depolymerisation of PLA into a lactide product, which could be reused as a raw material for the production of PLA. The scheme of polymerisation and depolymerisation is shown in Figure 3, from which it can be seen that depolymerisation requires a suitable catalyst. The most commonly used catalysts that can be used for the depolymerisation of PLA to obtain lactide are zinc and tin based, such as $Zn(OAc)_2$ and $Sn(Oct)_2$.



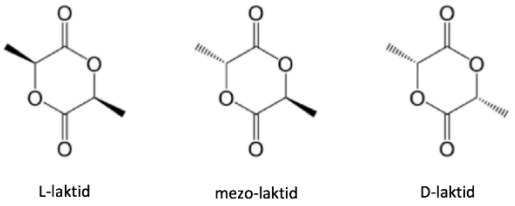


Figure 9. Polymerization and depolimerization step of PLA.

Lactide is a cyclic lactone ester with the molecular formula $C_6H_8O_4$. It is formed by the esterification of two or more molecules of lactic acid or another suitable hydroxycarboxylic acid. As mentioned above, lactic acid exists in a number of stereoisomeric structures, and so does lactide. L-lactide, D-lactide and mesolactide are known (Figure 3). All forms of lactide are transparent or off-white. The molecular weight of lactide is 144.13 g/mol and the melting point is between 95°C and 97°C.

Tin (II) 2-ethylhexanoate or tin octoate ($Sn(Oct)_2$), ($C_{16}H_30O_4Sn$) is a compound formed by the reaction of stannous oxide and 2-ethylhexanoic acid. It is a colourless liquid at room temperature, but often appears yellow due to impurities resulting from oxidation. Tin octoate has a molecular weight of 405.12 g/mol and a density of 1.251 g/cm^3. It is most commonly used as a catalyst for the polymerisation of various monomers, but in several studies, it has been used with zinc octoate as a depolymerisation catalyst in chemical recycling processes.

Prior to the synthesis of recycled lactide from PLA, which will be reported in a later chapter, we present here the preliminary study on the chemical recycling step of PLA using tin-based catalysts, $Sn(Oct)_2$. This is a novel investigation with respect to PLA and catalysts and involves the sum of the following complementary techniques: Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR) and Thermal Gravimetric Analysis (TGA). The data are analysed and evaluated.

2 MATERIAL AND METHODS

The depolimerization reaction conditions of PLA were studied using two commercially available test samples designated as PLA 3002D (PLA1) and PLA P400 (PLA2) (Table 1). The depolimerisation reaction of PLA as the main component was studied by varying the mass of PLA added and the concentration of catalysts $Sn(Oct)_2$ (Table 1).

Table 1. Depolimerization reaction condition of PLA.

Sample abrreviation	***PLA***	***Mass of PLA (g)***	***Concent.of catalysts (mol. %)***
PLA2-1	*PLA2*	*20*	*0,2*
PLA1-1	*PLA1*	*20*	*0,2*
PLA2-2	*PLA2*	*20*	*0,4*
PLA1-2	*PLA1*	*20*	*0,4*
PLA2-3	*PLA2*	*20*	*1*
PLA1-3	*PLA1*	*20*	*1*

Samples of PLA and catalyst $Sn(Oct)_2$ were first added to the flask. Glassware for the reaction was set up and the reaction mixture was heated under vacuum with stirring. For each sample, the flask containing the PLA was weighed, an appropriate volume of catalyst was added, and the flask was fitted with a magnetic stirrer and placed in a sand bath. During the process, the PLA melted and liquefied. The condenser was used to cool and crystallise the lactide.

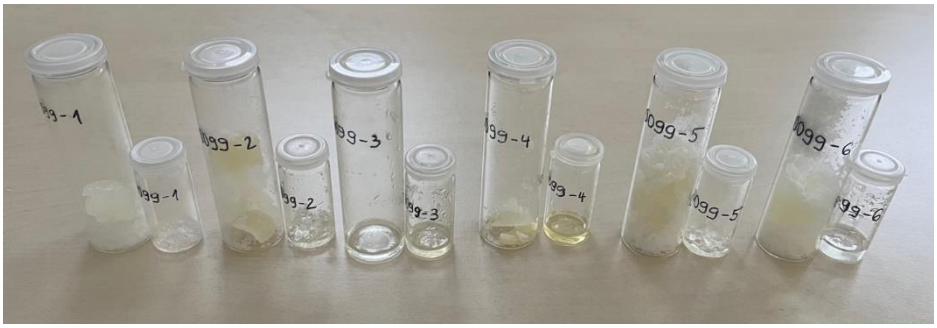


Figure 10. Product of PLA depolimerization.

The presence of the depolimerisation product, assumed to be L-lactide, was characterised by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (ATR-FTIR) and thermal gravimetric analysis (TGA).

DSC was used to evaluate the neat PLA reference material and the presence of L-lactide. Firstly, neat, depolymerised PLA was measured in the temperature range 25-200 °C in a high purity nitrogen atmosphere using a Mettler Toledo DSC 2 calibrated with indium for temperature and enthalpy and sapphire for heat capacity. Measurements were performed on samples of ~10-20 mg mass sealed in aluminium pans. A first heating scan up to 200 °C was performed to erase the thermal history and then the next main thermal protocols were applied as follows: standard cooling and heating at 10 K/min. Secondly, the L-lactide products of the prepared samples were tested in a nitrogen (N_2) atmosphere at a nitrogen flow rate of 20 mL/min and a temperature range of 25°C to 100°C, with a heating rate of 5°C/min. As we were only interested in the melting point

of the lactide, the samples were heated and cooled only once. ATR-FTIR spectra were monitored on a Perker Elmer, Spectrum 65. The spectra were recorded in the wavenumber range from 600 to 4000 cm^{-1} at room temperature (RT). Each spectrum was determined as an average of 32 scans at a resolution of 4 cm^{-1} for measuring background. All spectra presented here were baseline corrected and smoothed upon the measurement.

The thermodynamic properties of the neat PLA and the lactide products of the prepared samples were determined by TGA analysis on a Mettler Toledo TGA/DSC 3+ using 40 µL crucible. All samples were tested under heating in a nitrogen (N_2) atmosphere at a flow rate of 20 mL/min and a temperature range of 25°C to 550°C at a heating rate of 10°C/min. When the temperature reached 550°C, the samples were heated for a further 10 minutes in an oxygen (O_2) atmosphere at a flow rate of 20 mL/min.

3. RESULTS

The depolimerisation products were obtained from different PLA virgin material (Table 2). By comparing the weight of products with different depolimerisation time, the formation of lactide is assumed to be the main product.

Comparing the performance of samples PLA2-1, PLA1-1, PLA2-3 and PLA1-3, it can be seen that the amount of catalyst affected both the amount of lactide extracted and the rate of lactide formation itself. The type of PLA material itself did not have a major influence on the depolymerisation, as a comparable amount of lactide was obtained in the same depolymerisation time in both cases (18.69 g for sample PLA2-3 and 17.61 g for sample PLA1-3).

Table 2. Depolimerization product.

Sample	***Lactide weight [g]***	***mass [wt.%]***	***Depolimerization time [h]***
PLA2-1	*7,43*	*37*	*2,5*
PLA1-1	*11,62*	*58*	*4*
PLA2-2	*1,79*	*9*	*3*
PLA1-2	*2,57*	*13*	*3*
PLA2-3	*18,69*	*93,5*	*2,5*
PLA1-3	*17,61*	*88*	*2,5*

In Figure5, the spectra by ATR-FTIR are shown for all samples, including the PLA 3002D (PLA1) and PLA P400 (PLA2). The results of characteristics vibration band are in accordance with previous works on neat PLA. The absorption peaks between 2900-3000 cm^{-1} correspond to symmetric and asymmetric C-H bond stretching of the CH_3 group. The absorption peak between 1745-1750 cm^{-1} is

related to vibrations of the C=O bond due to the presence of the ester group. The peak between 1450-1455 cm^{-1} is characteristic of asymmetric vibrations of the CH_3 group bending. The absorption peak between 1357-1359 cm^{-1} corresponds to the bending vibration of the C-O-H group. The peak at 1267 cm^{-1} is related to the C=O double bond bending vibration and the peaks between 1181-1182 cm^{-1} correspond to the C-O-C stretching vibration of the ester groups (Črešnar, Aulova, et al., 2021; Črešnar, Klonos, et al., 2021).

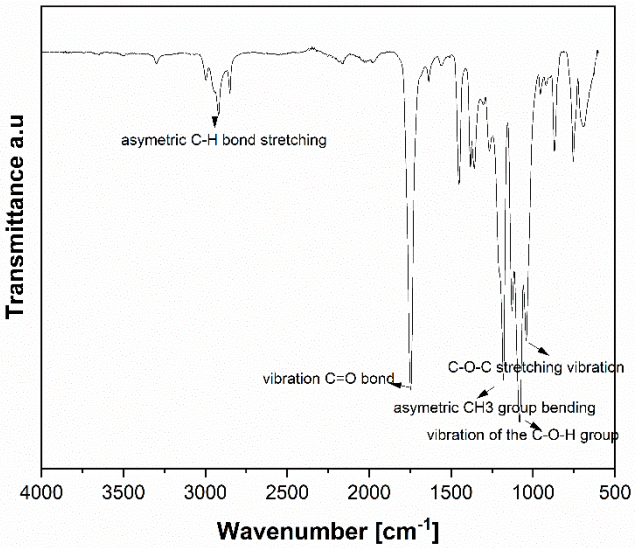


Figure 11. Characteristic vibration of neat PLA needed for depolimerization reaction in the wavenumber from 500 to 4000 cm^{-1}.

The ATR-FTIR spectra of the PLA depolimerization product samples are compared in Figure 6. The ATR-FTIR spectra of the lactide samples (Figure 6) showed the similar characteristic peaks between 2900-3000 cm^{-1} corresponding to symmetric and asymmetric vibrations of the C-H bond of the CH_3 group. Peaks observed in the range of 1750-1753 cm^{-1} where pronounced by the vibration of the C=O double bond occurs in the cyclic dilactone. The absorption peak between 1440-1460 cm^{-1} and the absorption peak at 1380 cm^{-1} correspond to symmetric and asymmetric bending vibrations of the C-H bond of the CH_3 group. The peak at 1265-1266 cm^{-1} corresponds to asymmetric vibrations of the C-O-C bond in the lactone ring and the peak at 1094-1095 cm^{-1} corresponds to symmetric vibrations of the C-O-C bond in the lactone ring (Nikolic et al., 2010).

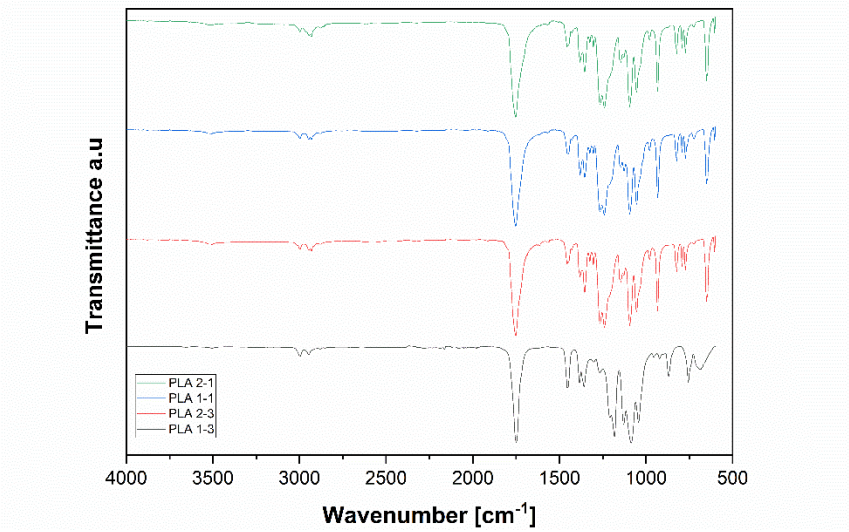


Figure 12. ATR-FTIR spectra of lactide samples in the wavelenght from 500 to 4000 cm^{-1}

The melting points of the PLA materials and all depolimerization products were determined by differential scanning calorimetry analysis. Figures 7 and 8 below show the thermograms of the neat PLA and the lactide product samples (PLA2-1, PLA1-1, PLA2-3 and PLA1-3).

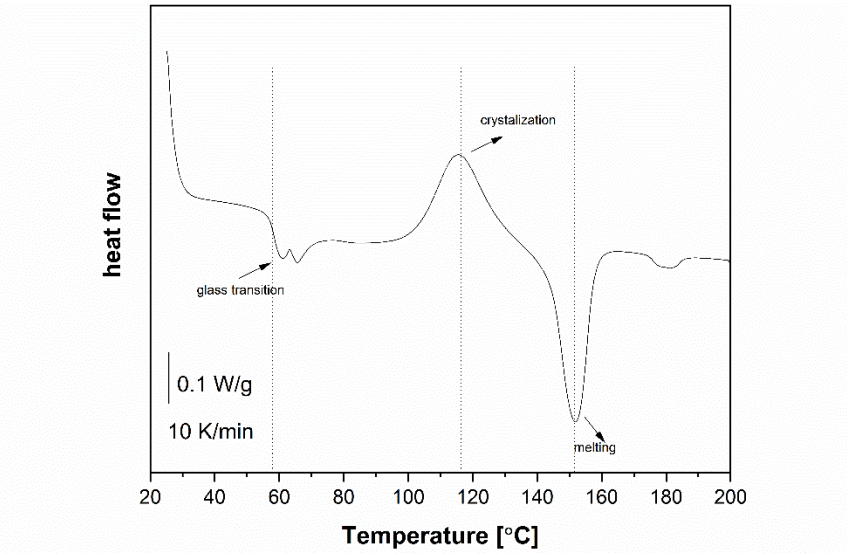


Figure 13. Differential scanning calorimetry (DSC) thermogram of neat PLA.

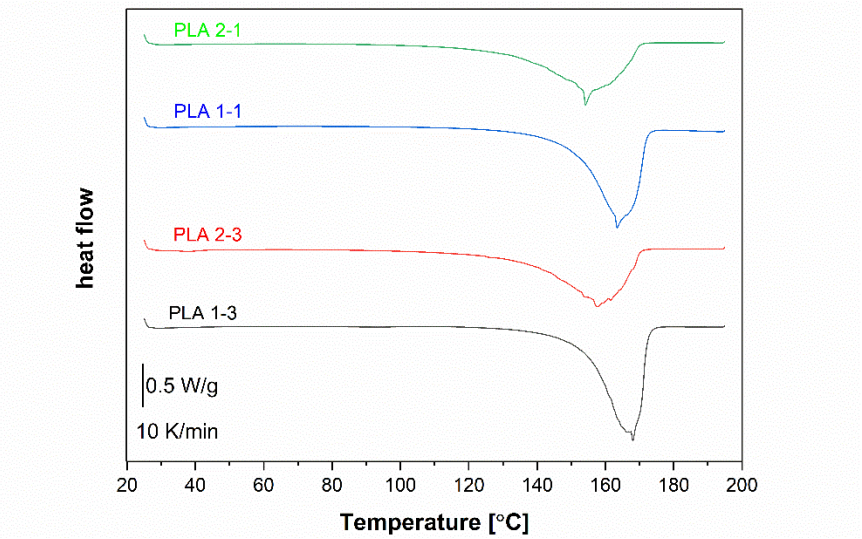


Figure 14. Differential scanning calorimetry (DSC) thermograms lactide.

It can be seen that the melting points obtained for neat PLA and lactide are reasonable, as neat PLA has a melting point between 150 and 200°C (Tarani et al., 2021) and lactide around 95°C. A *Tm* of 166.6°C and a Tg of 58.8°C were measured for PLA1, while a *Tm* of 150.9°C and a Tg of 58.4°C were measured for PLA2. In the case of PLA2, crystallisation can also be observed, measured at 119.5°C. Both samples were measured in segment 6 during the second heating. The lactide of sample 1 has a Tm of 95.9°C, the lactide of sample 2 at 91.1°C and the lactide of sample 5 at 93.6°C. A slight deviation is observed for sample 6, where the melting point drops below 90°C to 89.2°C. These curves have also been measured in the heating segment, that is in segment 2.

3 CONCLUSIONS

In summary, an easy-to-adopt chemical recycling method of two commercial PLAs has been established. The depolymerisation of PLA by pyrolysis, where the product of the lactide monomer was obtained by chemical reaction. More specifically, the method was focused on the tin-catalysed ($Sn(Oct)_2$), at 260°C and at a pressure of 6 mbar, depolymerisation of PLA to obtain lactide as depolymerisation product, which is an industrially relevant precursor for neat PLA.

The results also demonstrated the influence of catalysts on the depolymerisation time. It was shown that L-lactide depolymerised faster as the number of catalysts increased. The successful depolimerisation step of neat PLA was revealed by the

characteristic vibration band assigned to L-lactide and the temperature of the melting point Tm of L-lactide, which was found to be around 95°C including all depolimerisation product types.

Acknowledgments: *We would like to thank Maruša Dolinšek from Faculty of Polymer Technology for all laboratory support work and Lara Gosak for characterization of material.*

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DEPOLYMERISATION OF POST-CONSUMER PET BOTTLES WITH AMINOLYSIS IN THE PRESENCE OF ORGANOCATALYST

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Original scientific paper
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Abstract: *Polyethylene terephthalate (PET) is a saturated polyester synthesized by the esterification of a dibasic acid (terephthalic acid) and a diol (ethylene glycol) and is used for fibres, bottles, films, and other moulded products. PET is recycled by both physical and chemical routes. The physical route generally consists of remelting and forming new products with the help of suitable additives. PET can be chemically reprocessed by complete depolymerisation into oligomers, monomers, and other by-products. In this way, a wide range of terephthalamide monomers can be produced, which can serve as building blocks for high-performance materials with desired mechanical and thermal properties. In this study, different amines (ethylenediamine - EDA, 1,4-diaminobutane - DAB, 1,6-diaminohexane - DAH) were used to depolymerise post-consumer PET beverage bottles. The bottles were cut into pieces with an edge length of less than 2 cm. Aminolysis of PET was carried out in the presence of organocatalyst (1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)) and with an excess of amine (ethylenediamine, 1,4-diaminobutane, 1,6-diaminohexane; 1.5 and 3 eq.). After completion of the reaction the product was isolated, washed with organic solvents and dried. The products bearing amino functional groups were characterised by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC).*

Keywords: PET bottles, aminolysis, depolymerisation, chemical recycling

1 INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most widely used thermoplastics in various applications, such as packaging, textiles, and engineering. However, the increasing production and consumption of PET also pose significant environmental challenges, especially regarding the disposal and recycling of PET waste. Mechanical recycling, the predominant method of recycling PET, has several limitations, such as deterioration of material properties, contamination by other polymers or additives, and accumulation of waste in landfills.(Brivio & Tollini, 2022; Schyns & Shaver, 2021) Chemical recycling, which depolymerises PET into its monomers or other valuable chemicals, offers an alternative and potentially more sustainable way of recovering pure material and reducing environmental impact.(Shojaei et al., 2020) However, chemical recycling also faces technical and economic barriers such as high energy consumption, low efficiency, and lack of market competitiveness.

One of the promising methods of chemical recycling is aminolysis, which is the reaction of PET with amines to produce terephthalamides.(Ghosal & Nayak, 2022; Gupta & Bhandari, 2019; Zhou et al., 2017) Terephthalamides are useful compounds that can be used as additives, modifiers, and building blocks for high performance materials, such as polyamides, polyimides, and polyurethanes. Terephthalamides have enhanced mechanical and thermal properties due to hydrogen bonding and rigidity of structure. Currently, most terephthalamides are prepared from dimethyl terephthalate (DMT) or terephthaloyl chloride (TC), which are the monomers of PET. However, using waste PET as a source of terephthalamides can potentially alleviate existing environmental concerns and positively impact the management of limited petroleum sources.

Aminolysis of PET is thermodynamically more favorable than alcoholysis, which is another common method of depolymerisation. However, aminolysis still requires catalysts or microwave irradiation to achieve efficient depolymerisation. In this paper, we report a novel organocatalytic aminolysis of PET using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a potent and versatile catalyst. We demonstrate that TBD can effectively depolymerie PET under mild conditions and produce various terephthalamides with different amines.

2 MATERIAL AND METHODS

2. 1 Materials

Post-consumer PET bottles and PET recyclates were used as as the PET source. The bottles were washed, dried, and shredded by hand to a size of about 4-6 cm^2.

PET recyclate and PET flakes were dried at 80°C under vacuum overnight prior to use.

2. 2 PET depolymerisation via aminolysis

The depolymerisation of PET (Figure 1) was performed using ethylenediamine EDA, DAB and DAH with excess of amine (4 and 8 mol eq.). TBD was used as catalyst.

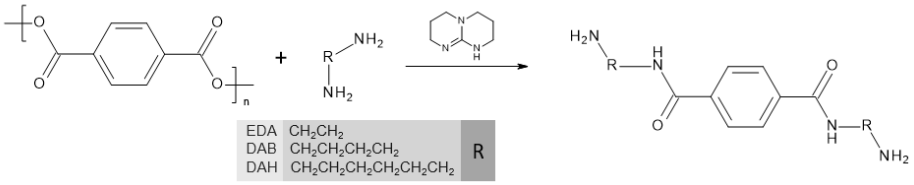

Figure 1. Scheme for PET depolymerisation via aminolysis.

PET flakes were placed into a 50 ml flask with excess amounts of ethylenediamine (4 or 8 mol eq.) and TBD (0.05 mol eq.). The flask was then heated under nitrogen atmosphere at 110°C for 90 min. The solution was then poured into 50 ml of hot toluene and filtered. The residue was dissolved in methanol and the filtrate was evaporated. The residue was washed with isopropanol and dried in a vacuum oven at 80°C, yielding a white powdery product.

The aminolysis, which was carried out with 4 mol eq. of amine, did not proceed with any of the amines used. Even when the reaction time was extended to 180 min, the reaction did not proceed. The conversions of the aminolysis with 8 mol eq. of amine are shown in Figure 2. As can be seen from the Figure 2, the conversion obtained depends on the amine chosen, being lowest for EDA (61.1 %) and slightly higher for DAB (82.1 %). In the case of DAH, the conversion was over 100 %, which is due to the presence of the unreacted amine.

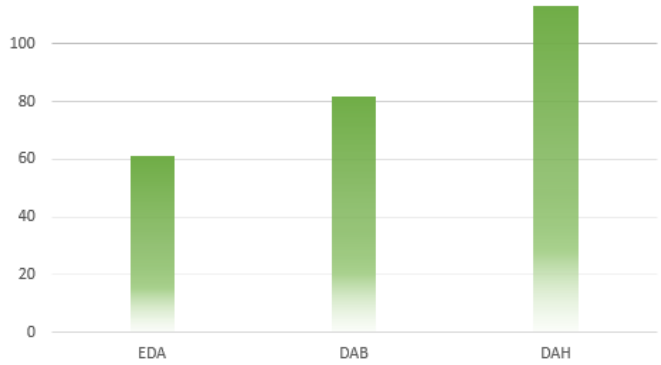

Figure 2. Conversions (%) of PET as a function of used amine (EDA, DAB, DAH). Aminolysis was conducted with 8 mol eq. of amine.

2. 3 Fourier transform infrared spectroscopy (FTIR)

In this study, terephthalamides obtained from organocatalytic aminolysis of PET were characterised by FTIR. The FTIR spectra of the samples were recorded using a PerkinElmer Spectrum 65 spectrometer equipped with a universal attenuated total reflectance (ATR) accessory. Spectra were recorded in the range 4000 – 600 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans per sample. The spectra were analysed using Spectrum software from PerkinElmer. The spectra (Figure 3) of the terephthalamides were compared with those of the starting materials PET flakes and the corresponding amines to confirm the formation of the amide bonds (1620 cm^{-1}) and the disappearance of the ester bonds (1714 cm^{-1}). The absorption band at 1714 cm^{-1} was assigned to the –C=O stretching of –COO–, the peak at 1095 cm^{-1} to the C–O trans vibration and the peak at 723 cm^{-1} to the out-of-plane C-H bending vibration of benzene. Compared to the spectrum of the PET flakes, the spectrum of the aminolyzed PET products contained new absorption peaks at 1540 cm^{-1} (in-plane -NH2 scissoring), 655 cm^{-1} (-NH_2 out-of-plane wagging), 1620 cm^{-1} (C=O stretch). In addition, the amine (-NH_2) peaks are observed at 3440–3350 cm^{-1}.

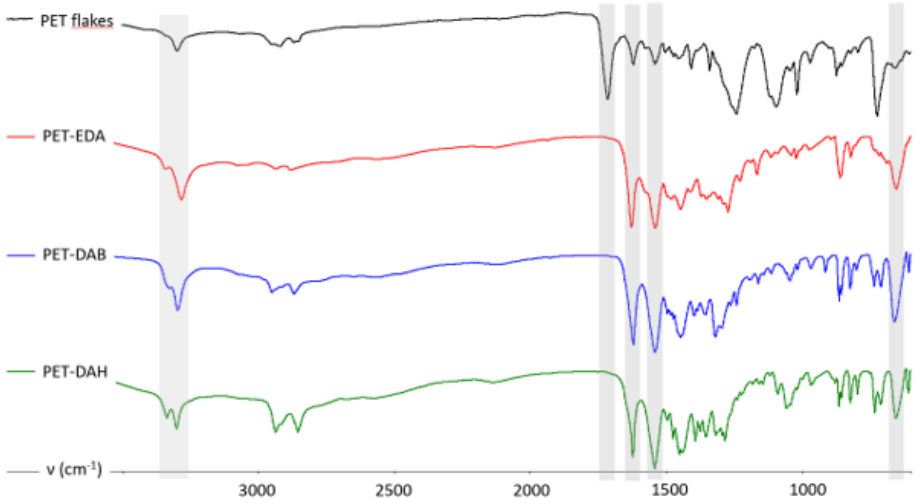

Figure 3. Fourier transform infrared spectroscopy (FTIR) spectra of samples.

2. 4 Differential scanning calorimetry (DSC)

In our study DSC (Mettler Toledo, TGA/DSC 3+) was used to determine the melting point of the aminolysis product and the Tg, melting and crystallization of PET. Cold crystalization temperatur for PET flakes was determined to be 149.9°C and melting point 246.2°C (the heating rate was 20°C/min and the N_2 flow was 20 mL/min). The melting points of the aminolysis products were in the range of 170 – 179°C, indicating terephthalamides.

3 CONCLUSIONS

We have demonstrated effective organocatalysis to promote aminolytic depolymerisation of PET flakes using TBD as a catalyst. Ethylenediamine, 1,4-diaminobutane and 1,6-diaminohexane were used as amines and terephthalamides were formed, which have great potential as building blocks due to their physical properties.

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WATER DISPERSABILITY OF PAPERS– BALANCING MATERIAL STRENGTH AND DISPERSIBILITY

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Abstract: *Water- dispersability of papers is useful in various applications as it disintegrates into its fibers after usage, and also is a fully biodegradable material. In this work, we have first introduced a test for the disintegration performance of different paper grades. Based on that disintegration and comprehensive statistical analysis we have performed a quantitative analysis on the technological and physical mechanisms responsible for a good paper dispersibility in water. Regarding technological parameters for paper production, we identified lignin content, degree of refining and addition of starch as relevant factors reducing paper dispersibility. Addition of a debonding agent, a surfactant, was not found to be effective here. In order to clarify the physical mechanisms governing paper disintegration behavior we analyzed paper properties related to mechanical strength and water uptake. We found a strong correlation between wet- and dry tensile strength of paper, both of which were highly affecting the dispersibility. Water uptake in the network, or water uptake into the fibers (WRV), or fiber wetting (contact angle) were not, or only very moderately, related to paper dispersibility. The only water absorption related paper property correlated to the disintegration results was liquid penetration speed measured with ultrasonic testing. We are concluding that the same mechanisms that are creating dry strength – high density and strong fiber-fiber bonding – are also responsible for a bad disintegration behavior. Principal component analysis revealed that paper strength and water penetration speed are not governed by different latent variables but instead are all strongly associated with the first principal component. This suggests that the same mechanisms are responsible for reduction of water penetration speed and wet/dry strength. A future solution*

of the problem might thus be to decouple network strength and water penetration, e.g. by identifying suitable additives that impart bonding strength to the network without reducing the access of water to break the fiber-fiber bonds.

FOOD PACKAGING PAPERS BASED ON BIOPOLYMERS POLYELECTROLYTE COMPLEXES

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Abstract: *In the context of plastic consumption reduction and environmental concerns on the production of more sustainable and circular packaging, the cellulosic based materials (paper and board) are considered most promising candidates largely due to the cost-effectives and their high rate of recyclability and biodegradability. Comparing with other materials, paper and boards are more resilient over a wider temperature range, are lighter and far more easily printed and to convert into containers with specified strength and stiffness. However, as food packaging material, paper has poor barrier properties for water and humidity due to the hydrophilic nature of cellulose fibers that are main component. The most currently applied technologies to improve the paper barrier properties to be adequate for food packaging applications consist of coatings with synthetic polymers and lamination with plastic or aluminium foils. Concerning on sustainability and circularity, these technologies have negative impact, having low recyclability and biodegradability rate. From these reasons there are opportunities and challenges for cellulose based packaging materials to design the appropriate barrier and active antimicrobial properties to reach the market performances expectations without impairing their recyclability and biodegradability. The biopolymers are attracting increased attention because they not only replace the synthetic polymers in different applications but also can provide new combinations of properties and can act as matrix for embed the active components to impart functional properties when are used in food packaging applications (i.e. antimicrobial or antioxidant features). In this context, the paper presents the results on utilization of xylan hemicelluloses and their acetylated derivatives as single biopolymer or as polyelectrolyte complexes by ionic interactions with other biopolymers such as chitosan polysaccharide. The*

polyelectrolyte complexes were used as coatings in single and multilayers for paper surface treatments (about 5 g/m2) in order to improve their barrier properties to water, water vapours, oxygen, oil and grease. The obtained results showed that for the papers coated with 50:50-acetylated xylan/chitosan formula, the level of water contact angle was about 92.8°, the water vapours transmission rate (WVTR) was about 30 g/m2.day and grease resistance was at KIT 8. These are comparable with reported results for flourochemicals treated papers. In addition, the papers coated with acetylated xylan and chitosan exhibited the high inhibition capacity against gram-positive bacteria Bacillus subtillis and fungi as Penicillium sp. and Aspergillus sp. The positive results obtained in this paper provide guidelines for obtaining of new food packaging materials produced from renewable resources which can be recycled or degraded without leaving contaminants or toxic residues into the environment. *Acknowledgement: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS—UEFISCDI, project number PN-III-P4-PCE-2021-0714, within PNCDI III.*

HEMP AND RICE STRAW VALORIZATION FOR THE DEVELOPMENT OF SUSTAINABLE ANTIOXIDANT-CELLULOSIC BASED CRYOGELS AND AEROGELS

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Abstract: *One of the strategies to ensure food safety is to extend the shelf life of food, therefore minimizing food losses and wastage. The main challenge in food production is to maintain food safety and improve nutritional and sensory quality in an affordable way. Shelf life depends on many factors, including the quality of raw materials, product formulation, type of preparation, packaging and storage conditions (Hosseini et al. 2020). Active food packaging has been proposed as a potential solution to achieve this goal. Among other desired functionalities, many active packaging concepts involve the release of antioxidants substances onto the food surface, as a way of improving the stability of oxidation-sensitive food products (Gomez-Estaca et al., 2014). The negative effects of oxidation on the nutritional and organoleptic properties of foods include: i) reduction in nutritional value due to destruction of essential fatty acids, proteins and lipid-soluble vitamins (A, D, E and K); ii) reduction in caloric value; iii) formation of rancidity (off-flavors); and iv) color changes due to darkening of fats and oils or degradation of pigments (Han et al., 2018).*

Mainly due to environmental concerns, novel active packaging concepts are being developed using biodegradable food packaging materials combined with natural preservatives. Therefore, the use of biopolymers, such as cellulose, has been proposed as a packaging constituent. Cellulose and its derivatives are attracting considerable attention due to their biocompatibility and environmental sustainability. Cellulose is a low-cost material with suitable mechanical properties and an excess demand in the global market. There is a large amount of agricultural waste and many processes need to be initiated to

make use of this waste. For example, some of the methods used in the fabrication of cellulose-based food packaging include solution casting, layer-by-layer assembly, extrusions, coatings, polymeric hydrogels, spraying, nano-emulsions, liposomes and adsorption (Liu et al., 2021).

In this respect, hemp (Cannabis sativa) is an easy-to-grow plant that, by its very nature, does not require fertilisers or herbicides. It also contains 40-77% cellulose, depending on the growing conditions (Stevulova et al. 2014). Consequently, hemp can be used as a source of cellulose and other value-added compounds useful in the food packaging industry. One application in the meat industry is the production of absorbent pads that aim to reduce the exuded fluids from the product and, therefore, reduce the free water available for microorganisms (Castrica et al. 2020). In the present study, with the aim of developing antioxidant absorbent pads, hemp cellulose was used as a raw material for the production of aerogels and cryogels produced by supercritical drying and freeze-drying, respectively, which were then impregnated with an antioxidant extract from rice straw. As it is known that supercritical CO_2 produces aerogels with hairy beads, men while freeze-drying shoed a sheet-like morphology. Thus, the structure can influence the mechanical properties of the material and the water sorption capacity. The antioxidant extract was obtained as a by-product during the extraction of cellulose from rice straw through alkaline hydrolysis. The antioxidant capacity evaluated as the percentage of β-carotene bleaching inhibition showed high antioxidant activity (50.42%) in contrast to butylated hydroxytoluene (BHT) used as a reference antioxidant (77.96%).

To evaluate the development of hemp cellulose-based absorbent pads, the obtained aerogels and cryogels were further characterized to understand the effect of the drying method. First, both materials maintained their integrity when immersed in water, indicating that the hydrophobization of the cellulose during oxidation and homogenization was successful. In addition, the water sorption test showed that the cryogels and aerogels were able to absorb approximately 1.9 times their initial weight, indicating that both are good candidates for use as absorbent pads. However, aerogels presented significant shrinkage, when exposed to 100% RH, whereas cryogels remain almost the original size. On the other hand, TGA analysis showed that aerogels exhibited a shift in degradation peaks to higher temperatures. This demonstrates that aerogels have higher thermal stability than cryogels. Similarly, during compression tests aerogels did showed higher values than cryogels in the same compressive deformation

percentage, indicating that they are materials with higher resistance. The obtained materials differed in their density, compressibility, and water sorption. In addition, both materials were impregnated with the antioxidant extract, and the antioxidant capacity of the materials was evaluated. Thus, as a result of valorization strategies of hemp logs and rice straw residues, not only a food packaging material was developed but also a potential antioxidant delivery system.

Keywords: cryogels, aerogels, antioxidant, hemp, valorization

Acknowledgement: *The authors acknowledge funding from the Spanish Ministry of Science and Innovation under the research grants PID2020-112766RB-C21 and PID2020-112766RB-C22, and the Santiago Grisolia grant of Laura Cabrera-Villamizar (GRISOLIA/2021/050)*

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INK PRODUCTION WITH NATURAL SINOP CLAY PIGMENT AND EXAMINATION PRINTABILITY PROPERTIES OF ECO-FRİENDLY INK

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Original scientific paper
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Abstract: *Sinop clay is found in large quantities in the province of Sinop in the Black Sea region of Turkey and takes its name from this city. Sinop clay is abundant in this region. Due to its easy use and low cost, Sinop clay can be suitable for use in new and different industrial applications. Sinop clay, which was used in many fields before, was also used as an alternative pigment for lithography printing inks. In the study, lithography ink was prepared by using 20% and 25% pigment from the pigment prepared using Sinop clay. The prepared ink was printed on coated paper with the IGT C1 test printer.* ΔE *values were calculated by measuring the CIEL*a*b* values of the printed papers and comparing them with the Pantone catalogue. At the same time, the print gloss and rub resistance tests of the printed papers were carried out. The results were very close to the Pantone® 7527 C.* ΔE *difference between the two colors is 2.31. This shows that the difference is so close that it cannot be seen with the naked eye.*

Keywords: printing ink, pigment, pantone

1 INTRODUCTION

In recent years, with the seriousness of environmental problems, environmentalism has ceased to be a matter of choice and has become a basic condition that must be applied for the survival of humanity (Abd El-Gawad et al.,

2022). With the development of the economy, environmental protection and health have aroused great concern all over the world (Liu et al., 2018). As a result, more environmentally friendly, natural, and sustainable products have been turned.

All printing inks consist of four main components: colorants, binders, solvents, and additives. The properties of components change due to the printing process and the printing substrates that come into contact with the ink (Özcan, 2007; Sabin et al., 1997). Lithography printing processes require paste inks. Conventional printing inks used in these applications are usually created with the following formulation. A hydrocarbon and/or alkyd resin; a hydrocarbon solvent; a pigment; and optional additives. For example, a typical lithography ink composition is defined as 15-25% hydrocarbon or alkyd resinas a vechile, 50-70% mineral oil solvent and 15-20% pigment as colorant (Erhan et al., 1995).

The interest in pigments is increasing day by day both in scientific and practical applications. It is one of the main components of coating and ink manufacturers, which represents a very important sector in the industry due to its wide application areas (Abd El-Gawad et al., 2022.; Ozcan & Tutak, 2021). Pigment is the substance that gives an object its color. The perception of each pigment in different colors is entirely due to the chemical structure of that pigment and the bonds that make it up (Aydemir et al., 2018). In order to obtain sufficient color power on the substrate, lithography inks must be homogeneous and more pigmented compared to other inks (Hayta et al., 2022).

Natural pigments can be obtained directly from plants and microorganisms or can be found directly in nature. Natural pigment is not only harmless to the body, but also some pigments are beneficial to health due to trace elements. Environmentally friendly products have become the indispensable theme of today's technologies. However, the printing industry, which uses natural resources, will provide sustainable developments for printing for the future. Natural pigments will protect nature by eliminating the damage to the environment. It will increase the use of environmentally friendly inks in the market, especially by being used in food and packaging printing (Liu et al., 2014)

Sinop clay is found in large quantities in the province of Sinop in the Black Sea region of Turkey and takes its name from this city. Sinop clay is abundant in this region. Due to its easy use and low cost, Sinop clay can be suitable for use in new and different industrial applications. Sinop clay, which was used in many fields before, was also used as an alternative pigment for lithography printing inks.

Figure 1. Sinop Clay and its pigment state.

The aim of the study is to create a pigment from Sinop clay, which is a cheap and easily accessible natural pigment. Making Lithography ink from this created pigment. Printing with the produced ink, examining the prints in terms of printability, and producing ink in order to more easily reach the Pantone color obtained as a result of the mixture of many colors.

2 MATERIAL AND METHODS

2. 1 Preparation of ink

The soil taken from the Sinop region of Turkey is ground into pigment. The prepared pigments were mixed into the varnish formulation given in Table 1 at the rates in Table 2. and turned into lithography ink. Ink 1 contains 20% and Ink 2 contains 25% pigment.

Table 1. Ingrediends of varnish.

Ingredient	***Varnish***	***Quantity***
Oil	*Linseed oil*	*50 g*
Resin	*Phenolic resin*	*35 g*
°C/Time	*300°C/20 min*	

Table 2. Ingrediends of inks.

Inks	***Quantity***
Ink 1	*Varnish (78.5%) + Sinop pigment (20%) + Linseed oil (1.5%)*
Ink 2	*Varnish (73%) + Sinop pigment (25%) + Linseed oil (2%)*

2. 2 Printing and measuring of prepared Inks

Before test prints, glossy coated papers (Table 3) were conditioned in the print room at 23 ± 1°C and 50% ± 3% relative humidity for 24 hours. Test prints were carried out according to the ISO 2864-1:2017 is suitable for four-colour printing

on printability tester. Test prints were made with IGT C1 test print device under 400 N pressure. Each sample was printed on at least 5 different papers.

Table 3. Optical properties of papers used in printing.

Properties	***Paper***
Grammage	*170 g/m2*
Thickness	*151 µm*
Gloss (75°)	*61.3*
*L**	*95.03*
*a**	*0.98*
*b**	*-3.57*

Measurements of the printed samples were made with X-Rite eXact Spectrophotometer (X-Rite, Germany). The measurement conditions of the spectrophotometer were determined as polarization filter with 0/45º geometry with 2º observer angle with D50 illuminant in the range of 400-700 nm. Color measurements were made with CIE *L*a*b** color system according to ISO 12647-2:2013 standard. The measured color differences were calculated with Formula (1) according to the CIE ΔE_{00} ISO 11664-6:2014 standard. Gloss measurements of the prints were made using a micro-TRI-gloss (60° geometry) gloss meter (BYK Gardner, Germany) according to ISO 2813.

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \qquad (1)$$

2. 3 Rub resistance test

TMI Rub resistance tester was used to measure the abrasion on the papers on which the inks were printed. Measurements were made according to ASTM D5264-98 (2019) test standard, using metal test block weighing 920 gr weight, as 30 oscillations.

3 RESULTS

Optical properties, printability, *L*a*b** values and ΔE_{00} values of Sinop pigmented inks printed on coated paper were measured and analyzed. The measurement results are given in Tables 4 and 5. The surface images of the test prints are given in Figure 2.

*Table 4. Referance Pantone® color L*a*b*values.*

Reference Inks	***L****	***a****	***b****
Pantone 7527 C	*85.58*	*0.4*	*10.97*
Pantone 400 C	*78.06*	*1.03*	*7*

Pantone Warm Gray 1C	*85.16*	*1.47*	*2.11*

*Table 5. Measurement results of the inks L*a*b* values.*

				Pantone® 7527 C	*Pantone® 400 C*	*Pantone® Warm Gray 1C*
Inks	***L****	***a****	***b****	ΔE_{00}	ΔE_{00}	ΔE_{00}
Ink 1	*85.59*	*1.4*	*8.88*	*2.31*	*7.76*	*6.78*
Ink 2	*80.52*	*1.58*	*10.33*	*5.23*	*4.17*	*9.43*

When we look at the ΔE values obtained, it has been determined that the Ink1 values are quite close to the Pantone® 7527 C values. ΔE_{00} value was calculated as 2.31. This means that the human eye cannot diferentiate between the two colors. In addition, ΔE_{00} value was below 5 when Ink 2 and Pantone® 400 C were compared. It is within acceptable values.

Figure 2. Surface images of test prints.

When the surface images of the test prints are examined, it is seen that the pigment ratio creates a color difference.

Figure 3. Comparison of Ink 1 and Pantone® 7527 C surface images.

It is also seen in the image that the surface images of Ink 1 and Pantone® 7527 C are almost indistinguishable when compared.

Table 6. Gloss values of the inks.

Inks	***Gloss 60°***
Ink 1	*34.12*
Ink 2	*27.33*
Pantone 7527 C	*45.43*
Pantone 400 C	*49.4*
Pantone Warm Gray 1C	*53.85*

When the gloss values were compared, it was determined that the closest values were ink 1 and Pantone® 7527 C.

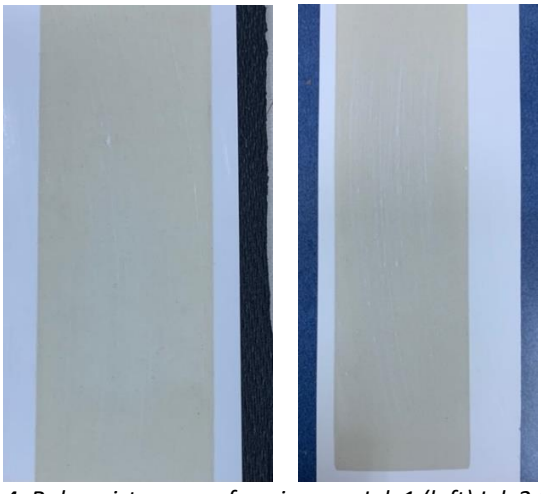

Figure 4. Rub resistance surface images Ink 1 (left) Ink 2 (right).

Ink rub resistance refers to the degree of ink film that is scratched or peeled off by rubbing. The main factors affecting the rubbing resistance of the ink are the basic properties of the paper, the composition of the ink and the printing conditions. (Wenhua et al., 2012) When looking at the images, it has been determined that the ink rub resistance is better in Ink 1 than Ink 2. As the pigment ratio increased, the rubbing resistance decreased.

4 CONCLUSIONS

It is known that environmentally friendly products have come to the fore in recent years. The use of natural and nature-identical raw materials will also protect the future of the world. In this context, lithography ink was produced with the pigment obtained from Sinop clay, which is natural and easily obtained from the Sinop region, which is both inexpensive and very easy to process.

The CIE *L*a*b** values of the obtained ink were measured and compared with the Pantone® catalogue. As a result of the comparison, Pantone® 7527 C color and Ink 1 were extremely similar. The calculated ΔE_{00} value is 2.31. This showed that the ink would successfully create the same color.

When the gloss values were compared, it was determined that especially ink 1 was close to the gloss values of Pantone 7527 C ink.

When the rub resistance was examined, it was determined that the increase in the pigment ratio in the ink decreased the rub resistance value of the ink.

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DIGITAL PRINTING IN THE PACKAGING INDUSTRY

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Professional paper
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Abstract: *Digital printing is one of the youngest printing techniques. It can be divided into several types, but the most popular are ink jet and electrophotography. Those printing techniques can be used for different products and enable cost-effective short print runs, customization, options, and quick turnaround times, making it a preferred choice for businesses and individuals seeking efficient and on-demand printing solutions.*

Printed products can be divided into publication, commercial printing, and packaging. The packaging group contains labels, cartons, corrugated, flexible, rigid plastics, and metal printing.

The packaging industry plays a vital role in today's global economy. It encompasses various activities in designing, manufacturing, and distributing packaging materials and solutions. Its primary objective is to protect products, ensure safe transportation, and enhance their presentation to consumers.

The packaging industry is a dynamic and essential sector that constantly adapts to meet the evolving demands of businesses and consumers. Its innovations and advancements contribute significantly to the efficient and effective delivery of goods while addressing environmental concerns and enhancing customer experiences.

More packaging printing businesses are now turning to digital printing. It allows for customization, short print runs, and rapid turnaround times, enabling brands to create personalized and targeted packaging designs. With digital printing, companies can achieve vibrant colors, intricate designs, and variable data printing, allowing product differentiation, brand consistency, and enhanced shelf appeal. Additionally, digital printing reduces waste and eliminates the need for

printing plates, making it a more sustainable and cost-effective option for low volume packaging production.
This paper presents the market's current state and predictions for digital printing in the packaging industry.

Keywords: biodegradability, compostability, lignocellulosic material, packaging

1 INTRODUCTION

Printing processes encompass two primary categories: conventional and digital. Conventional printing methods, despite their stark differences, share a common element known as the "printing plate." This printing plate serves as the intermediary for transferring ink onto printing substrates. Within the realm of conventional printing, four prominent techniques emerge: Letterpress, Gravure, Planographic, and Screen Printing (Kipphan, 2001).

Digital printing techniques, on the other hand, dispense with the need for a permanent master. They can be categorized into several groups based on the underlying physical or chemical principles that govern them (Kipphan, 2001). These categories include Electrophotography, Inkjet, Ionography, Magnetography, Thermography, Photography, X-graphy, and others.

Among digital printing methods, Electrophotography and Inkjet stand out as the most widely used techniques for producing a wide array of printed products.

Electrophotography, in particular, involves a series of five essential steps. (Novaković and Kašiković, 2013; Kipphan, 2001; Kašiković, Novaković and Jurič, 2016; Majnarić, 2015):

1. Imaging,
2. Inking,
3. Toner transfer (printing),
4. Toner fixing,
5. Cleaning (conditioning).

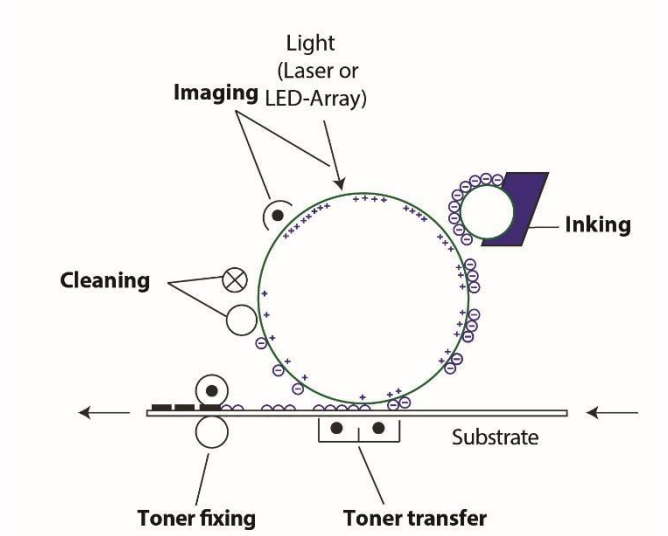

Figure 1. Electrophotography.

The inkjet printing process represents a computer-to-print technology wherein ink is dispensed through nozzles. This method eliminates the necessity for a printing master, enabling direct imaging onto the substrate (Kipphan, 2001). This efficiency makes it the swiftest way to imprint information onto a substrate. Within the realm of inkjet printing, two principal groups are prominent: Continuous Inkjet (CIJ) and Drop on Demand Inkjet (Figure 2).

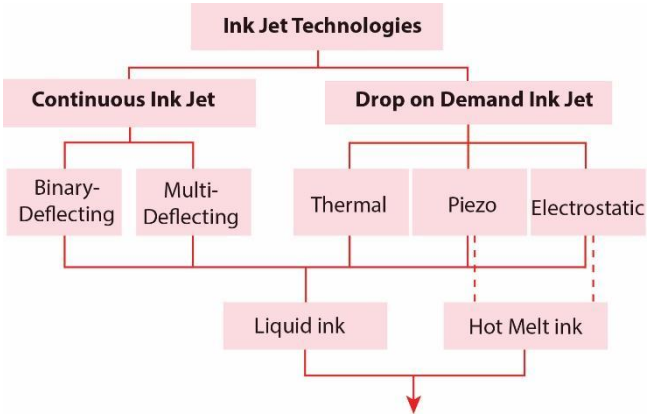

Figure 2. Inkjet technologies.

The primary distinction between these processes lies in how they handle ink droplets. In drop-on-demand inkjet processes, ink droplets are generated only when necessary for the printed information. Conversely, continuous inkjet systems produce a continuous flow of tiny ink droplets, with only a portion

directed onto the substrate based on the image signal. Unprinted droplets are collected and returned for reuse (Soleimani-Gorgani, 2015).

Printed products can be categorized into three primary groups: publications, commercial printing, and packaging (Kasikovic, et al., 2016b). The publication group encompasses newspapers, magazines, books, directories, and catalogues. Commercial printing includes photo products, advertising materials, business forms, identification documents, promotional items, security documents, transactional documents, and general commercial print products. The packaging group consists of labels, cartons, corrugated materials, flexible packaging, rigid plastics, and metal printing.

Notably, the packaging group has been experiencing consistent growth (Kašikovic, et al., 2016a). In contrast, publication volumes and value have seen significant declines, largely due to alternative digital media versions that compete with traditional print products, such as e-books, online publications, electronic media, and social media. Commercial printing witnessed a decline until 2015, with volume remaining stable until 2020 and a slight increase in value (Smith, 2017).

The packaging industry plays a critical role in the global economy by engaging in various activities related to designing, manufacturing, and distributing packaging materials and solutions. Its primary objectives are to protect products, ensure safe transportation, and enhance product presentation to consumers.

The packaging industry is a dynamic and indispensable sector that continually adapts to meet the evolving demands of businesses and consumers. Its innovations and advancements significantly contribute to the efficient and effective delivery of goods while addressing environmental concerns and enhancing customer experiences.

An increasing number of packaging printing businesses are transitioning to digital printing. This shift allows for customization, shorter print runs, and rapid turnaround times, empowering brands to create personalized and targeted packaging designs. Digital printing enables vibrant colors, intricate designs, and variable data printing, fostering product differentiation, brand consistency, and enhanced shelf appeal. Additionally, digital printing reduces waste and eliminates the need for printing plates, making it a more sustainable and cost-effective option for low volume packaging production.

This paper presents an overview of the current state of the market and provides predictions for the future of digital printing in the packaging industry.

2 PACKAGING AND LABELS MARKET

The worldwide print and printed packaging sectors constitute a substantial industry. In 2017, the total revenue from print operations reached nearly $780 billion, which is equivalent to an astounding 48.73 trillion A4 prints (Smith, 2017).

In terms of constant value, the global market has shown growth since 2012, going from $749 billion to $821 billion. However, the overall print volume has declined, dropping from the equivalent of 49.6 trillion A4 prints in 2012 to 48.49 trillion A4 prints in 2022. Looking ahead, there is anticipated growth in real value, but the total print volume continues to decrease. This trend is driven by ongoing changes in product mix, with an increasing emphasis on higher-value items, especially within the packaging sector (Smith, 2017).

From a macroeconomic perspective, the situation appears generally favorable. However, this masks the diverse prospects for various product categories, printing processes, and regional markets.

2. 1 Printed packaging market

In addition to non-printed packaging materials like glass, films, and plain boxes, printed packaging encompasses various forms, including corrugated packaging, cartons/sleeves, flexible packaging, rigid plastics, and metal containers. Printing on packaging serves a dual purpose by not only promoting the product to potential buyers but also offering essential information about its contents. On a global scale, the packaging industry is experiencing growth, driven by increasing populations, the shift from agriculture to industrialization, and the ongoing trend of urbanization. Packaging plays a pivotal role in enabling efficient supply chains, ensuring that a diverse array of products reaches markets worldwide *(Smith, 2017).*

Each of these packaging categories has numerous driving factors, enhancing choices and convenience while optimizing supply chain operations. The choice of printing methods varies across regions. In North America, flexography (Flexo) dominates corrugated and flexible packaging, whereas in Asia, gravure takes precedence. This is due to quality-conscious Japanese packaging converters who initially faced challenges in achieving the desired quality with flexo, especially for printing kanji text characters, before durable plates became available. The digital print sector is rapidly evolving, and inkjet technology is expected to make significant advancements until 2022, particularly in corrugated packaging, cartons, flexible packaging, and direct-to-shape printing *(Smith, 2017)*.

Over a ten-year period, printed packaging output is projected to grow by 34.4% in real terms, excluding the effects of inflation. In volume terms, this growth is estimated to reach 36.4%. By 2022, the total output will be slightly less than the equivalent of 10 trillion A4 prints. Packaging represented 44.8% of the total value of all printing activities in 2012, a figure represented rise to 55.9% in 2022. This underscores the increasing significance of packaging within the broader printing industry, although in terms of volume, it remains a smaller segment, accounting for 16.5% in 2012 and 23.6% in 2022.

2. 2 Labels market

Product labels serve the dual purpose of conveying essential information about a product's contents and enticing potential users to engage with the item. These labels also maintain their importance throughout the lifespan of the product, catering to end consumers, including households and workplaces. In certain contexts, such as pharmaceuticals in dispensaries or hospitals, the information on labels can be of critical significance (Smith, 2017).

Printed labels come in various forms, including wet-glued labels, pressure-sensitive labels, shrink and stretch sleeves, or in-mould labels. Additionally, there is a substantial sector dedicated to multi-part tracking labels utilized in logistics and supply chain management.

In the realm of litho printed paper labels and in-mould labels, narrow-web flexo presses dominate, especially in the pressure-sensitive (self-adhesive) category where labels are applied by machines at high speeds. Digital printing has made substantial inroads into the label market, particularly through electrophotography, with HP Indigo leading the market, followed closely by Xeikon, as well as numerous manufacturers of narrow-web inkjet presses. Xeikon, for instance, introduced its first inkjet machine in 2017 and subsequently acquired the EFI Jetrion business in October 2017, more than a decade after its parent company, Flint, had sold Jetrion to EFI (Smith, 2017).

In 2017, global revenues from printed labels amounted to slightly less than $37.0 billion. The market is projected to grow at an average Compound Annual Growth Rate (CAGR) of 4.1% through 2022 in terms of value. Simultaneously, the print volume is increased from 856 billion A4-sized sheets in 2012 to over 1.42 trillion A4 sheets in 2022, marking a growth of two-thirds within a decade (Smith, 2017).

2. 3 Digital printing in packaging and labels market

In table 1 and 2 are presented digital printing processes used in global packaging and label market *(Smith, 2017)*.

Table 1. Digital printing processes used in global packaging printing market, 2012–22.

$ million	***2012***	***2022***	***CAGR (%) 2017–22***
total	*307,475.50*	*413,552.10*	*3.1*
Electrophotography	*56.20*	*1,568.20*	*22.5*
Inkjet	*1,035.40*	*7,312.50*	*26.3*
Billion A4 prints	***2012***	***2022***	***CAGR (%) 2017–22***
total	*7,331,658*	*9,998,829*	*3.5*
Electrophotography	*309*	*11,721*	*21.9*
Inkjet	*4,417*	*96,876*	*39.4*

In Table 1, we observe the utilization of digital printing processes within the global packaging printing market output, spanning the years 2012 to 2022, presented in millions of dollars (adjusted for constant 2016 prices and exchange rates). The data illustrates a substantial increase in these processes during this period (Smith, 2017).

Specifically, in the realm of electrophotography, the market value has surged from $56.2 million in 2012 to $1,568.2 million in 2022, accounting for less than 1% of the market's total value. Meanwhile, inkjet technology has experienced remarkable growth, escalating from $1,035.4 million in 2012 to $7,312.5 million in 2022, albeit still representing less than 2% of the market's overall value.

Throughout the 2012-2022 timeframe, print volumes have also demonstrated significant growth. Electrophotography contributed to this increase, albeit to a smaller extent, with print volumes rising from 309 billion A4-sized sheets to 11,721 billion A4-sized sheets, which constitutes just 0.11% of the total print volume. In contrast, inkjet technology has seen substantial growth, with print volumes surging from 4,417 billion A4-sized sheets in 2012 to an impressive 96,876 billion A4-sized sheets in 2022, albeit still representing less than 1% of the total print volume.

In Table 2, we examine the application of digital printing processes within the global label printing market output from 2012 to 2022. The figures are presented in millions of dollars, adjusted for constant 2016 prices and exchange rates. The data highlights a significant expansion of these digital printing methods during this time frame (Smith, 2017)..

Table 2. Digital printing processes used in global label printing market, 2012–22.

$ million	***2012***	***2022***	***CAGR (%) 2017–22***
total	*28,166.10*	*45,220.90*	*4.1*
Electrophotography	*4,705.60*	*7,596.20*	*2.8*
Inkjet	*1,054.80*	*6,705.80*	*13.3*
Billion A4 prints	***2012***	***2022***	***CAGR (%) 2017–22***
total	*855,632*	*1,425,072*	*5.5*

Electrophotography	*49,416*	*96,994*	*5.2*
Inkjet	*10,846*	*100,258*	*17.5*

Specifically, in the domain of electrophotography, the market value has surged from $4,705.62 million in 2012 to $7,596.2 million in 2022, constituting just under 17% of the market's total value. On the other hand, inkjet technology has witnessed remarkable growth, escalating from $1,054.8 million in 2012 to $6,705.8 million in 2022, although it still represents slightly less than 15% of the market's overall value.

Throughout the 2012-2022 period, print volumes have also shown substantial growth. Electrophotography has contributed to this increase, albeit to a lesser extent, with print volumes rising from 49,416 billion A4-sized sheets to 96,994 billion A4-sized sheets, making up approximately 6.8% of the total print volume. In contrast, inkjet technology has experienced significant growth, with print volumes surging from 10,846 billion A4-sized sheets in 2012 to an impressive 100,258 billion A4-sized sheets in 2022, representing more than 7% of the total print volume.

3 DIGITAL PRINTING FOR PACKAGING AND LABEL APPLICATIONS

The evolution of digital printing technology for packaging applications continues to drive progress, offering increased production flexibility and unleashing creativity in packaging design. This innovation benefits not only converters but also brand owners who engage in on-demand printing and labeling.

The digital printing packaging market is categorized into Packaging Type, Printing Technology, and End-User Industry. In terms of printing inks, the market is segmented into UV-based inks, solvent-based inks, and dye sublimation inks. Printing technology covers inkjet printing, electro photography, magnetography, and thermal printing. Packaging types include folding cartons, corrugated, labels, flexible packaging, and others. End-user industries encompass food & beverages, automotive, pharmaceuticals, and others. Geographically, the global digital printing packaging market analysis spans North America (including the U.S., Canada, and Mexico), Europe (comprising the UK, France, Germany, Italy, and the rest of Europe), Asia-Pacific (encompassing China, Japan, India, South Korea, and the rest of Asia-Pacific), and LAMEA (encompassing Latin America, the Middle East, and Africa). (https://www.alliedmarketresearch.com/digital-printing-packaging-market-A08308)

Assessing packaging types, labels commanded over two-thirds of the global digital printing packaging market in 2021 and are anticipated to retain their market dominance until 2031. During the same period, the flexible packaging segment is poised for significant growth in adopting digital printing. – (https://www.packagingdigest.com/digital-printing/whats-happening-digital-printing-packaging)

Food and beverages constitute two major categories for digitally printed packaging, exemplifying the seamless fit of digital printing, particularly for craft and artisanal consumables. For companies in the consumer goods sector, digital printing technology delivers high-quality packaging while unlocking the benefits of small production runs, personalized packaging, waste reduction, swift turnaround times, and the capacity for real-time modifications to packaging designs.

In the pharmaceuticals and cannabis industries, brand owners are increasingly turning to digital printing to address the need for localized packaging, legally mandated variable data, and agile, frequent design adjustments. Advancements in equipment expand the range of packaging materials and formats amenable to digital printing, spanning from aluminum beverage cans to food wrappers and metallized-film pouches. Furthermore, a broader array of digitally printed embellishments is now within reach, including raised finishes, spot coating, digital foiling, and metallic inks.

3. 1 Digital printing examples in packaging and label industry

European pharmaceutical reimporters are uncovering a multitude of advantages by taking label printing activities under their own roof. Notably, digital printing has emerged as a solution that effectively tackles numerous challenges for these enterprises, which specialize in repackaging medications for distribution across countries within the European Economic Area (https://www.packagingdigest.com/digital-printing/whats-happening-digital-printing-packaging).

The labels on pharmaceutical products must continuously adapt to cater to diverse factors, including local regulatory demands, multiple languages, and variable information such as expiry dates, lot numbers, and track-and-trace codes. Additionally, these labels frequently require the incorporation of printed anti-counterfeit features.

Furthermore, pharmaceutical reimporters encounter fluctuating print run sizes, with some runs comprising as few as 50 labels. Digital printing's ability to handle variable data and accommodate short print runs positions it as a highly prized in-

house technology for these companies (https://www.packagingdigest.com/digital-printing/whats-happening-digital-printing-packaging).

Figure 3. In-house printing streamlines drug labeling.

Colordruck Baiersbronn, a packaging producer and printer, harnessed the power of digital printing to craft 40 distinctive candy boxes for participants attending an annual gathering of esteemed confectioners in Switzerland (https://www.packagingdigest.com/digital-printing/whats-happening-digital-printing-packaging).

Within each of these meticulously crafted boxes lies a handcrafted praline, encased in a cube-shaped paper wrapper adorned with a unique image of a majestic mountain peak. To achieve this diversity of prints on the wrappers, the printer employed HP SmartStream Mosaic digital printing software, capable of generating countless variations of images.

Colordruck went a step further by creating vibrant, sizeable prints to grace the inside of the box lids. Each box featured a distinct image, ensuring a unique experience for each recipient. The exterior of the box top featured small, abstract alpine images, serving as a preview of the imagery found on the wrappers. These miniature representations were also created using digital printing techniques.

To add a personalized touch, the converter incorporated the recipient's name and event details through digital foiling on the top of the box.

Figure 4. Digital foiling personalizes chocolate boxes.

Sealed Air, now operating under the name SEE, is fully embracing digital technology with the introduction of its prismiq digital packaging brand. The prismiq digital printers cater to the requirements of both converters and brand owners who handle their own printing. These technologies place a particular emphasis on flexible packaging for food.

SEE utilizes its large-format prismiq 5540 digital printer to provide customers with digitally printed flexible packaging. This wide-format system excels in high-speed, full-color, photographic-quality printing and is compatible with metallic and invisible inks (https://www.packagingdigest.com/digital-printing/whats-happening-digital-printing-packaging).

The range of materials the 5540 printer can work with includes rollstock plastic films, shrink bags, mailers, and fiber-based packaging. Notably, it can print on both sides of packaging materials, accomplishing this automatically through the use of a turn bar in the press.

The prismiq product line also encompasses small-format digital printers that brand owners can integrate into their packaging lines, resulting in retail-ready packages. Some of these systems are significantly smaller, with a size that's just one-tenth of conventional presses.

Currently, SEE is conducting tests of the small printers with ecommerce and food-protein brand owners. Potential applications include personalized, on-demand packaging featuring unique images, messages, and codes. The company aims to make some of these smaller systems commercially available in early 2023.

Figure 5. Prismiq digital packaging brand.

The landscape of digital printing solutions for beverage companies, especially craft producers, is expanding as digital can printing becomes more accessible. This technology offers a range of advantages for small to midsize brand owners, including the ability to produce small print runs, quick changeovers, and cost-effective limited-edition and personalized packaging.

Furthermore, direct-to-can digital printing offers environmental benefits by eliminating the need for labels on cans. Craft brands adopting this approach make their packaging significantly more recyclable (https://www.packagingdigest.com/digital-printing/whats-happening-digital-printing-packaging).

Craft Canning + Printing, a subsidiary of Eastside Distilling based in Portland, Oregon, has recently installed a German-made Hinterkopf D240.2 digital can printer to cater to this segment of the beverage market. The D240.2 model boasts an impressive print resolution of up to 1,200 dots per inch, enabling the system to generate photorealistic images with seamless ink coverage. This printer excels at producing fine gradients, subtle shading, and crisp text and edges.

Notably, Craft Canning + Printing has set a minimum order requirement of 400 cans, available in either 12- or 16-ounce volumes. By offering digital can printing with such a low minimum order quantity, they have made it a viable option for small beer, wine, and cider companies, granting them access to professional-looking, sustainable packaging solutions.

Figure 6. Digital can printing.

4 CONCLUSION

The label and packaging industry is poised for a transformative evolution, with digital printing at the forefront of this paradigm shift. Through a comprehensive review of current trends and emerging technologies, it is evident that the future of digital printing in this industry holds immense promise and potential.

Customization and Personalization: Digital printing enables the production of labels and packaging with unprecedented levels of customization and personalization. As consumer preferences continue to diversify, brands will increasingly turn to digital printing to create unique and tailored packaging solutions that resonate with their target audiences.

Short-Run Flexibility: The agility offered by digital printing in accommodating short print runs and quick changeovers is paramount. This flexibility allows brands to respond swiftly to market demands, reduce waste, and optimize inventory management, ultimately leading to cost savings and improved sustainability.

Advanced Printing Technologies: Advancements in inkjet and electrophotography technologies are enhancing the quality and speed of digital printing. High-resolution, photorealistic graphics, intricate designs, and vibrant colors are becoming standard features, further blurring the line between digital and traditional printing methods.

Sustainability and Eco-Friendliness: The elimination of traditional label substrates, such as adhesive-backed paper, in favor of eco-friendly alternatives is a growing trend. Digital printing's reduced waste, minimal setup requirements,

and compatibility with recyclable materials position it as an eco-conscious choice in the label and packaging industry.

Smart Packaging Integration: Digital printing can seamlessly incorporate smart packaging elements like QR codes, NFC tags, and augmented reality features. This convergence of digital and physical realms enhances consumer engagement, product traceability, and brand-consumer interactions.

Industry 4.0 Integration: The integration of digital printing with Industry 4.0 technologies, such as IoT-enabled machinery and AI-driven production optimization, will further streamline production processes, minimize downtime, and maximize efficiency.

Market Expansion: Digital printing is breaking down barriers in terms of market access, making it a viable option for smaller businesses and niche markets. The reduced barriers to entry will democratize the label and packaging industry, fostering innovation and competition.

In conclusion, the future of digital printing in the label and packaging industry is one marked by innovation, sustainability, and adaptability. As technology continues to advance and consumer expectations evolve, digital printing will play a pivotal role in enabling brands to differentiate themselves in a crowded marketplace. Embracing digital printing not only offers operational efficiencies but also opens up new avenues for creativity and customer engagement. As a result, it is imperative for industry stakeholders to invest in digital printing technologies and stay at the forefront of this transformative journey. The label and packaging industry stands on the brink of a digital renaissance, and those who embrace it will shape the future landscape of this dynamic and evolving sector.

Acknowledgments: *This paper has been supported by the Ministry of Science, Technological Development and Innovation through project no. 451-03-47/2023-01/200156 "Innovative scientific and artistic research from the FTS (activity) domain".*

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APPLICATION OF INK WITH PUFF EFFECT FOR IMPROVEMENT OF ERGONOMIC PROPERTIES OF PACKAGING

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Original scientific paper
doi: 10.5281/zenodo.10008254
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Abstract: *Ergonomic packaging should provide the handling of a product efficiently, effectively, and intuitively, ensuring ease of access to the product and safe grip of the packaging, thus improving user experience. Consumers should be enabled to comfortably lift, hold, and open packaging. This can be achieved by an appropriate size, shape, and material of the packaging. The aim of this paper was to investigate the possibility of using screen-printing and ink with added puff base to enhance the ergonomic properties of the packaging. The added puff base gives the print a three-dimensional shape and surface properties associated with greater surface roughness, also it enhances tactile perception and provides a more secure grip. This preliminary study was conducted by objective and subjective evaluation methods. The experiment was conducted to characterize the effect of differences in tactile properties of the specimen's contact surface on the force achieved by manually pulling. The specimens were printed on three different substrates using a manual screen printing technique. In addition to the substrate, the amount of added puff substance in ink (0%, 10%, 20%, and 30%) was also varied. The total number of different printed samples was 12. Results indicate that the specimens with a rough surface result in better grip and higher manual pulling force.*

Keywords: packaging, ergonomics, puff base

1 INTRODUCTION

Tactile perception and interaction with objects play a key role in our daily lives. The sensitivity of the skin of the palm gives us a sense of touch, which provides us with feedback about the outside world and allows us to interact with the products we use (Striano and Bushnell, 2005). Touch is one of the most basic ways of communicating with the environment, which enables us to handle objects and evaluate their tactile properties (Darden and Schwartz, 2015).

Haptic perception refers to the perception of tactile properties of materials and surfaces. Although consumers use a wide range of vocabulary to describe the haptic impression of materials and surfaces (Meyer, 2001; Kawazu et al, 2000), Hollins identified two robust dimensions of haptic perception - hardness: hard-soft and roughness: smooth/rough (Hollins, 1994). In this context, friction between human skin and object surfaces plays a key role. Friction allows us to safely handle objects (Veijgen, Masen and Van Der Heide, 2012; Veijgen, Van Der Heide and Masen, 2010; Derler and Gerhardt, 2012). Although research has been done dealing with tactile perception and friction between skin and materials, little is known about the perception of slipperiness and its effect on grip safety (Bergmann Tiest, 2010). Some research has focused on grip and sliding when lifting objects, analyzing the effect of object shape and surface materials on grip (Kinoshita et al, 1997; Jenmalm, Goodwin and Johansson, 1998). However, these studies did not deal with the improvement of materials and surfaces, nor did they take psychophysical factors into account. Studies on the measurement of friction between skin and materials show the complexity of the overlapping parameters. Further research is needed to better understand the perceived quality of achieving a firm grip (Derler et al, 2009; Bergmann Tiest, 2010).

Screen printing with added puff base in the ink is a technique that gives a three-dimensional effect and texture to prints (Figure 1).

Figure 1. Screen printing with puff effect (613originals, 2023).

It involves using a special printing ink or paste that contains an additive called a "puff base". When the print is exposed to heat during the drying process, the puff base expands, creating a raised or puffed appearance on the surface of the print. By incorporating a puff base, the print exhibits altered surface characteristics that can be visually and tactile perceived.

The subject of this paper is the investigation of the tactile characteristics of prints created using the manual screen printing technique with the addition of a puff base. One notable outcome achieved through the inclusion of the puff base in the printing ink is an increase in roughness. The study aims to explore the potential use of such prints in enhancing the ergonomic properties of products designed for manual use, such as packaging. In the context of manual product manipulation, roughness plays a significant role. Higher levels of roughness provide a more secure grip, facilitating the handling and manipulation of the product.

2 MATERIAL AND METHODS

The objective of the experimental part of the research is to test the hypothesis through laboratory work. The proposed hypothesis is that prints printed by manual screen printing technique with the addition of a puff base in ink could be used to improve the ergonomic characteristics of packaging. This paper examines the impact of incorporating a puff base in printing on both comfort and manual pulling forces. The research was carried out through an experiment followed by a survey. Given that printing with the addition of puff base in different percentages produces prints with different characteristics, e.g. roughness changes, the experiment investigated the maximum hand-pulling forces of an object coated with printed samples, with the assumption that the tactile properties of the printed sample will affect the feeling of comfort and manual pulling forces. Prints were printed on different paper materials and different amounts of added puff base (0%, 10%, 20%, or 30%). 14 participants completed the survey and experiment, 7 male and 7 female. All participants were between 25 and 35 years old. The ambient temperature of the room was 23+/- 2°, and the relative humidity was 50+/-2%. Seo et al (2008) were engaged in similar research, based on which the methodology of this research was defined.

2. 1 Test samples

The test samples were printed by the manual screen printing technique on a carousel machine manufactured by Centropapir, model no.S.6S4T.B. All prints were printed in black using water-based Teflex ink. Teflex manufacturer's puff base was added to the ink in three different percentages of 10%, 20%, and 30%.

The screen printing mesh count of 120 l/cm was used. After printing, the prints were dried at 133°. The prints were made on different paper substrates, including bulky paper (164-180 g/m^2), matte-coated kunstdruk paper (257-300 g/m^2), and paperboard (250 g/m^2). The print had a rectangular shape in size of 135 x 30 mm and 100% coverage. Given the variations mentioned, 12 different types of prints were obtained (Table 1). It is noteworthy to mention that additional tactile characteristic of these exact prints on textile materials were evaluated and discussed in a previous study (Bošnjaković et al, 2022).

Table 1. Categorization of printed samples.

Print type specimen name	***Substrate***	***The added amount of puff base in the ink***
1-0	*bulky paper (164-180 g/m^2)*	*0 %*
1-10	*bulky paper (164-180 g/m^2)*	*10 %*
1-20	*bulky paper (164-180 g/m^2)*	*20 %*
1-30	*bulky paper (164-180 g/m^2)*	*30 %*
2-0	*paperboard (250 g/m^2)*	*0 %*
2-10	*paperboard (250 g/m^2)*	*10 %*
2-20	*paperboard (250 g/m^2)*	*20 %*
2-30	*paperboard (250 g/m^2)*	*30 %*
3-0	*matte-coated kunstdruk paper (257-300 g/m^2)*	*0 %*
3-10	*matte-coated kunstdruk paper (257-300 g/m^2)*	*10 %*
3-20	*matte-coated kunstdruk paper (257-300 g/m^2)*	*20 %*
3-30	*matte-coated kunstdruk paper (257-300 g/m^2)*	*30%*

2. 2 Experimental apparatus, survey, and procedure

Participants entered the measurement room individually and received instructions. They were given the freedom to adjust their position in front of the experimental apparatus based on their dominant hand (Rowson and Yoxall, 2011; Peebles and Norris, 2003). The experimental setup (Figure 2) incorporated a Shimadzu Compact Tabletop Testing EZ-LX machine, equipped with a 2.5 kN measuring cell and a testing speed of 1 mm/min. The TrapeziumX software was utilized to record the maximum manual pulling force values during the tests in newtons (N). To accurately measure the manual pulling force exerted on the samples, instead of using conventional clamping tools the tool coated with printed samples was used. The height of the tool was customized to accommodate the individual's height, ensuring optimal comfort during the experiment. Specifically, the participants were instructed to use their fingertips, with their thumb being placed on one side of the coated tool while the other fingers secured the sample on the opposite side (both sides were coated with the same printed sample). Their task was to pull the coated tool with the maximum force possible in a downward direction. As soon as the participant

sensed the slip of the sample through their fingers, they immediately stopped pulling which concluded the measurement.

a)  b) 

Figure 2. a) Experimental apparatus b) Participant testing the samples.

Subsequently, participants were presented with a survey. The survey consisted of 12 sections, corresponding to the number of tested samples. Within each section, participants were asked to assign a grade to predefined characteristics on a scale ranging from 1 to 10. A rating of 1 represented the lowest grade, while a rating of 10 represented the highest. Participants were asked to evaluate the pleasantness to the touch and the ease of manual pulling. To give subjective estimates through tactile perception, participants gently ran their fingertips across the surface of each sample, drawing upon established methodologies (Wongsriruksa et al, 2012; Bergmann Tiest, 2010; Srinivasan, Whitehouse and LaMotte, 1990; Hollins et al, 2000; Chen and Ge, 2017). This survey not only made it easier to gather subjective ratings but also provided participants with a short break to rest their hands, muscles, and nerves. The same organized method was used for each sample until all different variations were tested.

3 RESULTS

Figure 3 shows the results of the conducted survey on tactile evaluations of printed samples. Everyone had the task of evaluating samples based on two criteria: pleasantness to the touch and ease of manual pulling, which reflects stability and grip security (1 - lowest grade, 10 - highest grade). Samples 3-10, 3-20, and 3-30, printed on matte-coated kunstdruk paper, received the highest estimates in terms of pleasantness to the touch. Additionally, it was observed that samples 1-10 and 2-10, when compared to other samples printed on the

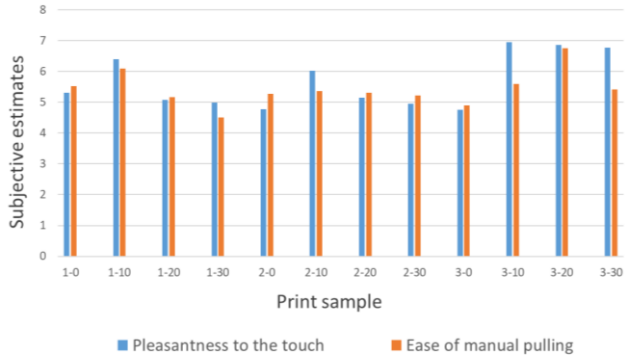

Figure 3. Graphic representation of the results of subjective estimates of printed samples by 14 participants.

same material, were rated more favorably due to their lower value of added puff base (10%) in terms of touch pleasantness. Additionally, it was observed that samples 1-10 and 2-10, when compared to other samples printed on the same material, were rated more favorably due to their lower value of added puff base (10%) in terms of touch pleasantness. Regarding the subjective estimates of ease of manual pulling, it is important to note that these ratings were generally lower compared to the ratings for pleasantness to the touch. The highest ratings were obtained for samples printed on matte-coated kunstdruk paper sample 3-20, followed by 1-10. It is noted that regarding both evaluated criteria, namely pleasantness to the touch and ease of manual pulling, the samples with a small amount (10%) of added puff base received better subjective estimates compared to the print samples without it. The normal distribution function was utilized to calculate the normal distribution based on the specified mean values of manual pulling forces and standard deviation (Figure 4). The mean values of manual pulling forces and standard deviations are given in Table 2.

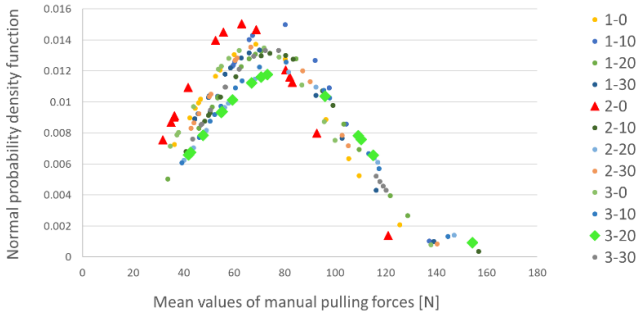

Figure 4. The normal distribution function for every printed sample.

Table 2. Mean values of manual pulling forces and standard deviations.

Specimen	*Mean values of manual pulling forces [N]*	*Standard deviation*	*N*
1-0	*69.17*	*29.08*	*14*
1-10	*76.32*	*26.51*	*14*
1-20	*75.27*	*29.69*	*14*
1-30	*71.32*	*29.82*	*14*
2-0	*62.86*	*26.32*	*14*
2-10	*75.70*	*30.30*	*14*
2-20	*78.18*	*33.26*	*14*
2-30	*71.99*	*28.98*	*14*
3-0	*67.99*	*29.31*	*14*
3-10	*77.54*	*31.61*	*14*
3-20	*78.37*	*33.50*	*14*
3-30	*75.25*	*29.82*	*14*

Figure 4 displays the two most significant curves: one representing the manual pulling forces of the sample observed with the highest forces achieved, along with the highest standard deviation (depicted by green rhombus signs- sample 3-20), and another curve representing the printed sample observed with the lowest forces achieved along with the lowest standard deviation (depicted by red triangle signs- sample 2-0). The absence of significant deviations from normality is reflected in the standard deviations. Notably, the curve for the 3-20 sample clearly shows a rightward shift of the normal distribution, indicating favorable characteristics for manual pulling forces.

A one-way repeated measures ANOVA was conducted to assess the effect of the printed sample on forces achieved by manual pulling. Mauchly's test of sphericity, which examines the assumption that the variances of the differences between all possible pairs of within-subject conditions are equal, was evaluated. Due to a violation of the sphericity assumption, the Greenhouse-Geisser correction was applied. The main effect of the printed sample was found to be statistically significant, $F(4.745, 61.691)=3.582$, $p<0.05$, indicating a significant difference in forces achieved by manually pulling across the levels of printed samples. Post-hoc pairwise comparisons using Bonferroni correction revealed significant differences between specific levels of printed samples. Specimen 2-0 demonstrated significantly lower forces achieved by manual pulling compared to 1-10, 1-20, 2-10, 2-20, 3-10, 3-20, and 3-30. This result indicates that maximum manual pulling forces were significantly higher for samples with added puff base compared to those without it.

4 CONCLUSIONS

Ergonomic packaging aims to provide efficient, effective, and intuitive handling of a product, ensuring a secure grip for improved user experience. In this research, the aim was to investigate the potential of utilizing screen-printing and ink with an added puff base to further enhance the secure grip properties of packaging. The puff base introduces new visual and tactile effects, transforming the print into a three-dimensional one with altered surface characteristics. Notably, the addition of a puff base enhances the roughness of the printed surface, which is crucial for secure grip and effective manipulation of packaging. The research methodology involved an experimental setup followed by a survey to evaluate the maximum forces of manual pulling of printed samples. The prints were applied to various paper materials, with varying percentages of puff base added (0%, 10%, 20%, and 30%). A total of 12 different printed samples were generated. It was found that samples with added puff base exhibited significantly higher subjective estimates regarding pleasantness to the touch and ease of pulling. In accordance with that, recorded pulling forces were also higher in the case of printed samples with added puff base in the ink compared to samples without it. This effect can be attributed to multiple factors. Firstly, the addition of a puff base increased the roughness of the print surface, providing a more tactile and textured grip, which in turn facilitated a firmer hold and increased friction during manual pulling. Secondly, the altered tactile properties, such as increased softness and texture and the three-dimensional effect contributed to an improved perception of grip, thereby leading to higher manual pulling forces. Also, psychological factors related to the visual perception of depth and texture created by the presence of the puff base may have influenced participants to perceive an enhanced grip and subsequently provide higher forces during manual pulling. These findings suggest the potential of incorporating a screen printing technique with added puff base in the ink to enhance grip characteristics and manual manipulation of packaging products.

Acknowledgments: *This research (paper) has been supported by the Ministry of Science, Technological Development and Innovation through project no. 451-03-47/2023-01/200156 "Innovative scientific and artistic research from the FTS (activity) domain.*

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THE POSSIBILITY OF PRINTING ON BIOPOLYMER PACKAGING MATERIALS

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Original scientific paper
doi: 10.5281/zenodo.10008267
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Abstract: *In the realm of packaging, there has been a long-standing tradition of utilizing a significant amount of plastic materials. However, there is an increasing demand within the food packaging sector to shift away from petrochemical-based packaging materials and adopt more environmentally friendly biodegradable alternatives. Biodegradable packaging materials derived from natural sources have the potential to address the issue of disposing synthetic plastics. Using biodegradable polymers for packaging production, partial solution to the problem of accumulating solid waste comprised of conventional non-biodegradable polymers can be offered. Particularly, there is a notable interest in utilizing biopolymers derived from agricultural and industrial waste. The objective of this scientific research is to explore the feasibility of printing on biopolymer materials used in packaging, considering the need to display essential information on the packaged products. Specifically, chitosan and gelatin were selected as the materials for the samples. To conduct the research, a test chart containing a QR code was generated, and the UVLED printing technology (Apex 1610 machine), was employed. Following the printing process, the samples were subjected to both visual and objective analyses. The objective analysis involved assessing the legibility of the QR code, thereby determining the accuracy of the printed content, including the intricate thin lines within the code. The findings of the study indicate the need for further investigation in this field.*

Keywords: biopolymers, chitosan, gelatin, printing

1 INTRODUCTION

Biopolymers, also known as IV generation packaging, are self-destructive, biodegradable materials, obtained from renewable resources. As macromolecular substances, natural polymers or biopolymers can be found in nature as parts of plant or animal tissues (Lazić and Novaković, 2010).

It can be argued that biopolymers are among the most environmentally friendly packaging materials due to their complete ecological balance and compatibility with the environment (Lazić and Popović, 2015). The necessity to complete the natural cycle of matter, in which the end of one cycle ushers in the start of the following, gave rise to the concept of biodegradable polymers made from renewable sources, or biopolymers (Popović et al., 2018).

Biopolymers fall into three broad categories (Fabra et al., 2014; Šuput et al., 2021):

1. Biopolymers extracted from biomass such as agricultural, animal processing, forest or ocean waste, e.g. polysaccharides and proteins of vegetable or animal origin. They are usually classified according to the dominant building material. The main groups of chemical compounds, which serve as sources for biopolymers extracted from biomass, are polysaccharides, proteins and lipids.

2. Polymers artificially synthesized using biological or bio-produced monomer units via classical polymer synthesis routes, for example, polylactic acid or polylactide (PLA), bio-based polyethylene terephthalate (Bio-PET) and bio-polyolefins.

3. Polymers produced from wild or genetically modified microorganisms, for example, bacterial cellulose and polyhydroxyalkanoates (PNAs) such as polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), and poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV).

Rearranging the polymer chains in the film matrix and lowering the molecular weight are both steps in the preparation of biopolymer films. The polymer chains are first dissolved in a suitable solvent, and as a result, new hydrophilic and hydrogen bonds, as well as ionic or electrostatic attraction, are generated during the evaporation process. Due to the high concentration of reactive side chains in polysaccharide and protein solutions, the networking process is intense, resulting in the development of stiff and brittle films. Plasticizer molecules can be added to biopolymer films to improve their qualities by dispersing throughout the matrix structure of the film and giving the produced film an appearance of flexibility and extensibility (Popović et al., 2018).

Application of biopolymers is wide and includes coatings and films. Coatings application implies forming a biopolymer layer directly on the surface of food product by spraying, dipping or coating, whereas films are self-standing structures which are applied after being formed separately (Šuput et al., 2015).

Biopolymer films and coatings can be used to coat food, separate ingredients, form a barrier against oxygen, flavors, oils and moisture. Biopolymer films and coatings can protect food from light-induced chemical changes, oxidation of nutrients, moisture loss, and surface microbial growth. They can also improve the visual and tactile qualities of product surfaces (Popović et al., 2018). Apart from these important application examples, they can be used as carriers of functional active agents because they have the effect of a matrix for encapsulation that is reflected in the required minimum doses, limited volatility and controlled and gradual release of active components from the food surface (Bonilla et al., 2013).

In this way, their function is reflected in the protection of food products from oxidation and microbiological spoilage, which leads to an improvement in the quality and improvement of the safety of the packaged product. Besides, if edible films and coatings are produced from edible biopolymers and food-grade additives they can be consumed alongside food, providing additional nutrients, possibly enhancing sensory qualities and may include quality-enhancing antimicrobials (Šuput et al., 2015).

Packaging plays a pivotal role in product protection, but its extensive usage raises significant environmental concerns. The utilization of conventional materials like plastics in packaging contributes to pollution and waste accumulation. Consequently, a pressing need exists to transition towards sustainable materials such as biopolymers.

At present, a crucially unexplored domain within this field pertains to the potential of printing on biopolymers, which holds significant importance in enabling the utilization of these materials for packaging products requiring informative labelling. This investigation will shed light on the possibility of printing on biopolymers, chitosan, and gelatin, demonstrating their potential as eco-friendly alternatives for various applications. Successful printing on these biopolymers can unlock numerous opportunities.

2 MATERIAL AND METHODS

2. 1 Sample

Chitosan and gelatin were selected as the materials for the samples.

Chitosan film: Chitosan film-forming solution was prepared by dissolving chitosan powder in acetic acid (1 % volume concentration) to reach chitosan mass per volume ratio of 10 kg/m^3. The solution was left stirring overnight on a magnetic stirrer to dissolve chitosan. Film-forming solution was filtered and poured into Petri dishes (20 g per dish) and dried at room temperature.

Gelatin film: Aqueous gelatin solution 10% (w/w) was prepared and left for 30 minutes at room temperature to undergo gelation, and then dissolved in a water bath at 50°C for about 20 min. Afterwards, 0.1 g glycerol/g gelatin was added and stirred. Film forming solution was poured into Petri dishes (20 g per dish) and dried at room temperature.

2. 2 Printing

In order to conduct the experiment, a test chart was designed and depicted in Figure 1. This test chart comprises a QR code, lines, text, and solid fields of primary (CMYK) colours. The lines and text were utilized to visually assess the printability, while the QR code was employed to verify the readability of the encoded data, thereby assessing the print sharpness. Colour patches are only visually analysed.

Figure 1. Test chart used in experiment.

The chosen printing technique in this case was the UVLED printing technology, specifically Apex 1610 machine, was employed.

3 RESULTS AND DISCUSSION

Figure 2 illustrates the appearance of the printed samples. The visual evaluation indicates that ink bleeding occurred when printing on gelatin, while notably superior print quality was attained on the chitosan substrate. Both substrates allowed legibility of 4 pt text, while the smallest text (2 pt) was only barely visible. For optimal text printing, a sans-serif font size of 4 pt (using Roboto font) would be recommended as the lower limit.

The lines were precisely and sharply printed, even at a thinness of 0.176 mm, and remained clearly visible on both substrates.

Despite ink bleeding on the gelatin substrate, successful QR code reading was achieved with both substrates. The reading was performed under typical conditions that an average consumer would use, such as daylight illumination and a distance necessary for the camera to achieve optimal focus. The experiment involved two mobile phones, one running the IOS operating system and the other with Android.

Furthermore, it is noteworthy that colour printing is feasible on these substrates as they are transparent and do not interfere with the colour output.

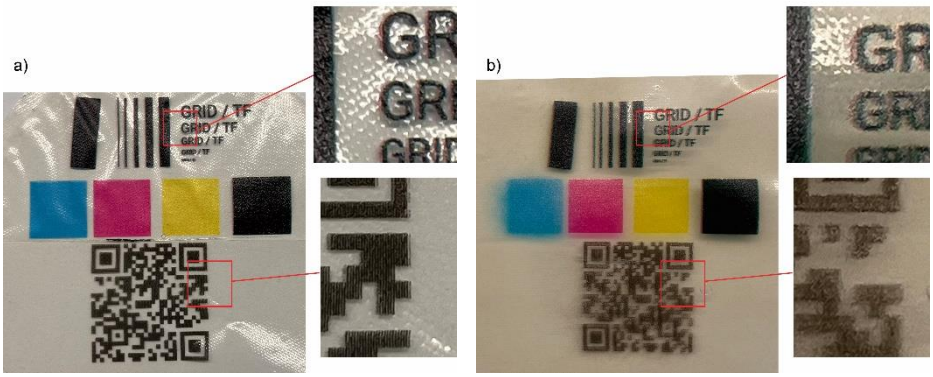

Figure 2. Printed and digitized samples.

4 CONCLUSION

This research will contribute to an improved understanding of the feasibility of printing on biopolymers as a sustainable packaging approach. Discovering solutions for printing on these materials can significantly mitigate the adverse

environmental impacts of packaging while providing essential information to consumers. Advancements in this field can promote sustainable practices in the industry and support the transition towards a more ecologically responsible future. Ultimately, the findings of this research can serve as a foundation for further innovations in packaging and material applications.

Acknowledgments: *This research (paper) has been supported by the Ministry of Education, Science and Technological Development through project no. 451-03-68/2022-14/ 200156 "Innovative scientific and artistic research from the FTS (activity) domain"*

This paper is a result of the program of the Ministry of Education, Science and Technological Development, Republic of Serbia, No. 451-03-47/2023-01/ 200134.

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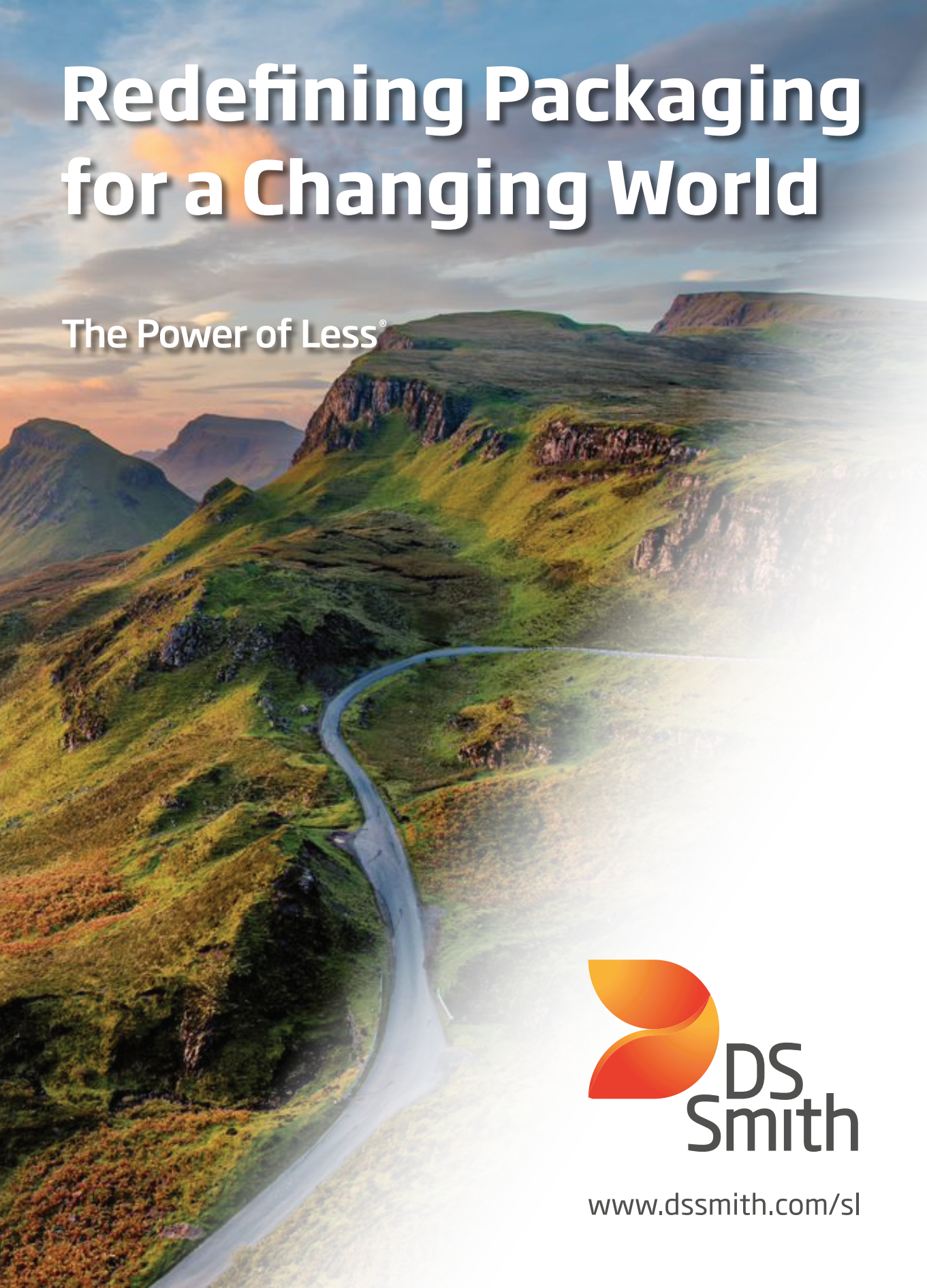
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