

RECYCLING OF THE STYRENE FRACTION FROM POST-CONSUMER WASTE

RECIKLIRANJE STIRENSKE FRAKCIJE V GOSPODINJSKIH ODPADKIH

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This investigation studied the recovery of styrene materials with mechanical recycling of different natural domestic waste. The aim of this work was to evaluate the possibility of obtaining a material capable of competing, in some respects, with the virgin material. The two main problems of the recycling and recovery process were also addressed. These include the presence of impurities from other plastic materials, such as polyvinyl chloride (PVC) or polypropylene (PP), and the degradation of the recovered materials due to previous processing or the activities of external agents such as sunlight. In both cases, it was found that the recovered material exhibits a decrease in its mechanical properties and it is also difficult to recover. The use of the instrumental-analysis techniques, such as differential scanning calorimetry (DSC), is essential for predicting the quality of the material recovered from the residue.

Keywords: recycling, styrene materials, polystyrene, impurities, waste

V članku so avtorji študirali ponovno uporabo stirenskih materialov z mehanskim recikliranjem različnih naravnih domačih odpadkov. Cilj tega dela je bil ovrednotiti možnosti pridobivanja materiala, ki bi bil enakovreden čistemu stirenu za nekatere vrste uporabe. Pri tem so analizirali dva glavna problema, ki nastopata med recikliranjem in pri ponovni uporabi. To so predvsem nečistoče zaradi prisotnosti drugih plastičnih materialov, kot sta na primer: polivinilklorid (PVC) in propilen (PP). Drug problem pa je degradacija odpadnih materialov zaradi predhodnih procesov ali delovanja zunanjih vplivov, kot je sončna svetloba. V vseh primerih so poleg poslabšanja mehanskih lastnosti naleteli tudi na težave pri procesu ponovne uporabe. Avtorji ugotavljajo, da je pri tem ključna uporaba modernih instrumentalnih metod analize, med drugim diferencialna vrstična kalorimetrija (DSC), za napoved kakovosti recikliranega materiala iz odpadkov.

Ključne besede: recikliranje, stirenski materiali, polistiren, nečistoče, odpadki

1 INTRODUCTION

At present, researchers are examining the appropriateness of the use of plastic materials due to the impact of plastic waste on the environment. The accumulated-plastic-waste generation between 1950–2015 was estimated to be 381000 million tons.¹ In this period, the industrial production of plastics grew very fast so that it is estimated that only about 20 % of the generated plastic waste was recycled or incinerated. Although this index of recycling is expected to improve, the generation of plastic waste and the problems linked to it will increase. Due to their own characteristics and the variety of plastic materials found in the municipal solid waste (MSW), the polymeric materials found there are the most difficult to treat and recover. The plastic waste represents 14 % of the MSW even though it occupies about 40 % in volume due to its low density. According to H. Ritchie, M. Roser, with 302 million tons of plastic waste estimated

for 2015, the packaging industry is its largest generator, as can be seen from the data in **Table 1**.²

Table 1: Waste generation by the industrial sector estimated for 2015

Industry	Waste generation (%)
Packaging	46.7 %
Textile	12.6 %
Consumer goods	12.3 %
Automotive and transport items	5.6 %
Building and construction	4.3 %
Electrics and electronics	4.3 %
Industrial machinery	0.3 %
Others	13.9 %

Developing countries are more problematic in this respect than developed countries. Although developed countries are the largest waste generators, they are also more efficient at addressing these problems.^{3,4} On the contrary, developing countries have less control over the waste generated.⁵ This can be confirmed with the data indicating mismanaged plastic waste, shown in **Figure 1**.² Regardless of the region, pollution is a problem

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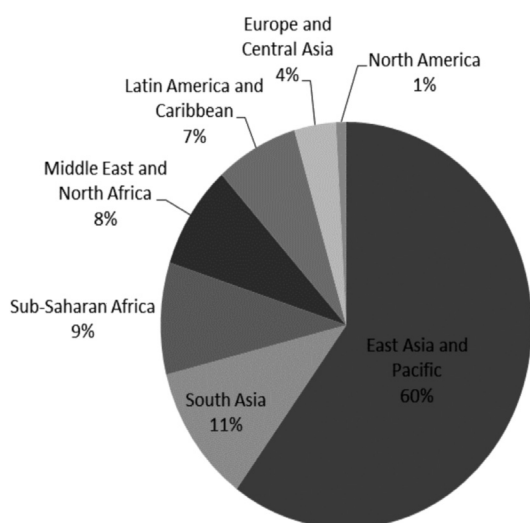


Figure 1: Mismanaged plastic waste by region for 2015

that transcends borders and nations as seen in the case of the microplastic pollution of the sea.⁶

Therefore, the problem of plastic waste can be addressed with the recycling of materials,⁷ incineration of waste⁸ and use of biodegradable materials.⁹ Among these possibilities, in this work, we addressed the improvement of the recycling technology. Within different types of plastics, the recovery of polystyrene materials constitutes an important line of research as they are the most consumed polymeric materials after polyolefins and PVC, covering approximately 7.5 % of the total consumption. In the group of polystyrene materials, it is possible to find both common-use materials, such as polystyrene (PS), styrene-butadiene (SB), and technical plastics, such as styrene-acrylonitrile (SAN), acrylonitrile styrene acrylate (ASA), acrylonitrile butadiene styrene (ABS).

Moreover, the recovery of household polystyrene waste was analysed in some studies. Polystyrene is a material present in packaging as well as in many everyday objects such as toys, hangers, office supplies and others. Among plastic materials, polystyrene represents about 6 % of the waste generated, exceeded only by polyolefins and polyethylene terephthalate (PET), as can be seen in Table 2.¹ It ranks seventh in the list.

Table 2: Generation of waste by type of plastic material as estimated in 2015

Plastic material	Percentage
Low-density polyethylene, LDPE	20.0 %
Polypropylene, PP	19.3 %
Polypropylene fibre reinforced polymer, PP-fibre	14.7 %
High-density polyethylene, HDPE	14.0 %
Polyethylene terephthalate, PET	11.2 %
Polystyrene, PS	6.0 %
Polyurethane, PU	5.6 %
Polyvinyl chloride, PVC	5.3 %
Others	3.9 %

Regarding the possibilities of plastic-waste recovery and revalorization, PS presents several problems.¹⁰ Due to the variety of its uses, it is difficult to visually separate PS from a waste stream. In this respect, it is very different from PE and PET whose packaging residues are easy to identify. Moreover, during a water-residue separation, when floating, its separation is difficult due to the density (1.05 g/cm^3).¹¹

When the separation of waste residues is easy, excellent-quality recycled materials are obtained, for example, in the case of the waste from polystyrene foams.^{12,13} Nevertheless, when some impurities are found, the separation process becomes difficult. The existence of aromatic rings causes PS to have a low compatibility even with the polymers derived from styrene, such as acrylonitrile-butadiene styrene (ABS), where the use of compatibilizers for their mixtures is recommended.¹³

To assess this behaviour, the aim of this work was to study the influences of 5 % of impurities on the mechanical properties of recycled polystyrene. As impurities, we selected the materials that can be found in packaging (PS, PET and PVC),¹⁴ materials from electronic waste (polyoxymethylene (POM), ABS and polycarbonate (PC))¹⁵ and biodegradable materials mainly found in the packaging industry (poly(lactic acid) (PLA), thermoplastic starch (TPS) and Poly(3-hydroxybutyrate) (PHB)).¹⁶

2 EXPERIMENTAL PART

2.1 Materials

Recycled polystyrene (PS) from food packaging and recycled polypropylene (PP) with reference PP1B were obtained from scrap. Neat low-density polyethylene (LDPE) Resistex 1614 FG and neat high-density polyethylene (HDPE) Alcudia 4910 were provided as pellets. Recycled polycarbonate (PC), recycled acrylonitrile butadiene styrene (ABS) and polyoxymethylene (POM) came from electrical- and electronic-equipment waste (WEEE). These materials were kindly supplied by Acteco S.L. (Ibi, Spain).

Polyethylene-terephthalate (PET) type Bripet 1000 for bottle manufacturing, with an intrinsic-viscosity index of 0.80 dL/g , was obtained from Novatpet (Huesca, Spain). Recycled polyvinyl chloride (PVC) from credit-card waste was supplied by Crearplast, S.L. (Ibi, Spain). This PVC has a k-value of 62 (the kwert value is the viscosity measurement correlated with the molecular weight obtained in line with ISO 1628-2).

With regard to the biodegradable materials, poly(lactic acid) (PLA), commercial grade 6201D IngeoTM Biopolymer, was kindly supplied by Nature-Works LLC (Minnetonka, USA). This grade contains 2 % of D-lactic acid. Thermoplastic starch (TPS), commercial grade Mater-Bi® NF 866, was kindly supplied from Novamont SPA (Novara, Italy). Poly(3-hydroxybutyrate) (PHB), commercial grade P226 with an

average molecular weight of 426 KDa, was supplied by Biomer (Krailling, Germany). These materials were used in the form of pellets.

The main technical characteristics of the materials are presented in **Table 3**.

Table 3: Main properties of the used materials

Material	Melt-flow index (MFI) (g/10 min)	Density (g/cm ³)
PS	9 (200 °C/5 kg)	1.05
PP	20 (230 °C/2.16 kg)	0.905
LDPE	1.4 (190 °C/2.16 kg)	0.916
HDPE	0.90 (190 °C/2.16 kg)	0.949
PC	6.1 (230 °C/5 kg)	1.2
ABS	20.5 (230 °C/5 kg)	1.05
POM	9 (190 °C/2.16 kg)	1.41
PLA	22.5 (210 °C/5 kg)	1.24
TPS	3.5 (150 °C/5 kg)	1.27
PHB	10 (180 °C/5 kg)	1.25

2.2 Sample preparation

All blends were formulated, containing 95 % of PS and 5 % of another material considered as an impurity. The blending process of PS with biodegradable polymers was carried out using a screw extruder from Dupra S.L. (Castalla, Spain). The extrusion conditions included a rotor speed of 30 min⁻¹ and temperature of 180–200 °C. After that, samples for mechanical characterization were prepared with injection moulding on a Babyplast 6/6 from Cronoplanst S.L. (Abrera, Spain). The injection samples were normalized specimens for the tensile test with dimensions following ISO-527.

2.3 Sample characterization

The mechanical characterization was carried out using tensile and hardness tests. Tensile properties were assessed using a universal machine ELIB 30 from S.A.E Ibertest (Madrid, Spain) under the ISO-527 standard conditions. All the tests were carried out at room temperature at a speed of 10 mm/min, with a load cell of 5 KN. Five test pieces of each samples were characterized.

The Charpy impact resistance was measured using a Metrotec SA machine (San Sebastian, Spain), under the ISO-179 standard, with a 6-J pendulum. Five specimens were tested.

Fourier transformed infrared spectroscopy (FTIR) measurements were carried out using a Perkin-Elmer Spectrum BX infrared spectrometer from Perkin-Elmer Spain S.L. (Madrid, Spain) in a range of 4000–650 cm⁻¹, with a resolution of 4 cm⁻¹ and 32 scans.

Differential scanning calorimetry (DSC) was conducted with a Mettler Toledo DSC 821 equipment from Mettler Toledo (Schwerzenbach, Switzerland) using samples of 4–6 mg. The heating and cooling programs were performed at 20 °C/min in a nitrogen atmosphere (60 mL/min), with the first heating from 25 °C to

200 °C, then a cooling cycle from 200 °C to 50 °C and the second heating from 50 °C to 200 °C.

3 RESULTS AND DISCUSSION

Regarding the mechanical behaviour reported in **Figure 2**, the influence of the impurities on the PS properties changes according to the material used. For example, when mixed with POM, the reduction of the tensile strength reaches 20 %. This means that the tensile strength of the blend with impurities is 80 % of the tensile strength of the pure PS. On the other hand, some materials, such as LDPE or HDPE, cause a 5-% decrease. Technical materials, like PET or PC, seem to have a larger influence on the properties of the recycled PS. This is due not only to the chemical incompatibility but also to the high temperatures required for processing technical plastics.

The Charpy impact energy allows us to easily verify the influence of different impurities on the properties of the recycled materials. In **Figure 2**, it is possible to observe that the decrease in the toughness (linked to the impact energy) is acceptable when using polyolefins (HDPE, LDPE). Nevertheless, when using technical plastics (PC, PET, POM), the decrease in the toughness becomes important. In the case of POM, its easy degradation behaviour becomes a disadvantage in a PS recovery process. With regard to the presence of a biodegradable material, PLA does not have a high influence, but TPS and PHB exert an important influence on PS. Therefore, in a PS-recycling process, it is important to control the grade of impurities of different materials. In addition, it is important to establish the tolerance limits depending on the final properties desired.

With regard to certain impurities, it is necessary to confirm their presence in the recycled PS. In this case,

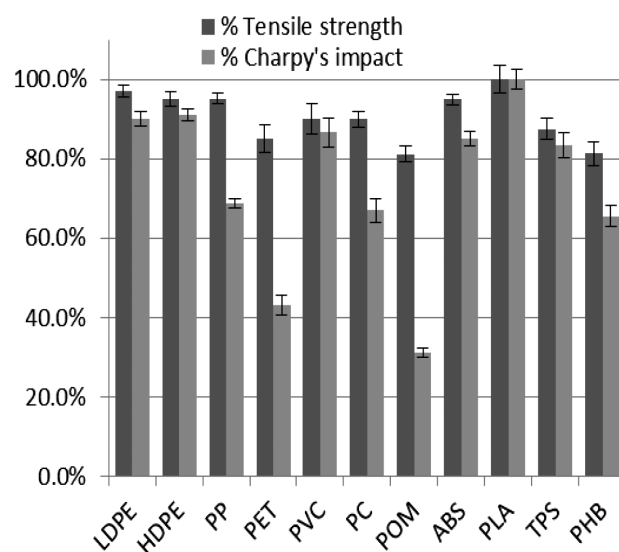


Figure 2: Effects of 5-% impurities on the mechanical properties of polystyrene

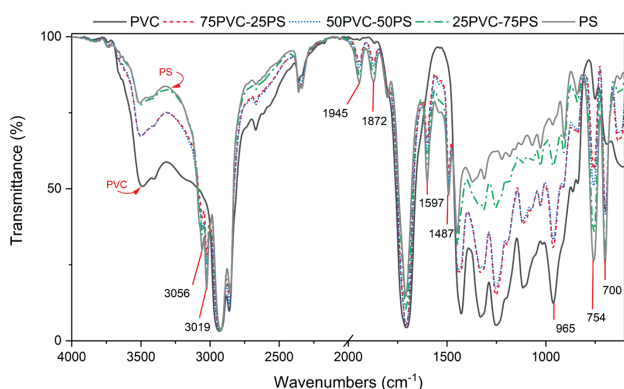


Figure 3: Comparative FTIR spectra of PVC, recycled PS without impurities and recycled PS with different percentages of PVC impurities

infrared spectroscopy is a very useful control tool. The FTIR spectra of PS are very characteristic, allowing us to identify the presence of impurities, as can be seen in **Figure 3**.

In the case of polyolefins, due to the difficulties of comparing the FTIR spectra of the contaminated samples, differential scanning calorimetry (DSC) is a more efficient technique for detecting the presence of impurities. In **Figure 4**, we can see DSC curves of the PS and PS with impurities. Due to the amorphous microstructure of PS, fusion enthalpies of the polyolefins are clearly detected. Moreover, depending on the temperature of the peak, it is possible to infer the type of polyolefin (PP, HDPE, LDPE) contaminating the recycled PS.

On the other hand, the contaminations of PS due to PVC are easily detectable. Its presence is quantifiable with thermogravimetry (TGA). This is due to the jump detected at about 200 °C caused by the hydrochloric acid. In addition, depending on the mass loss detected with TGA, it is possible to calculate the percentage of PVC in a sample. The jump in a neat PVC represents 64 % of the mass loss.¹⁷

In the cases of PS and PVC blends, both materials have some compatibility. Nevertheless, the presence of PVC decreases the toughness of the PS. There is an easy

way to predict the compatibility of the two polymeric materials, i.e., a comparison of the solubility parameters (δ). These parameters are reported in reference,¹⁸ but it can also be estimated through the method proposed by P. A. Small. Each group of organic compounds has a value linked to the molar attraction. The sum of the contributions of all the components, divided by the molecular mass and multiplied by the density gives a theoretical value of this parameter.¹⁹ Based on this method, the solubility values and the molar attraction of the molecular groups calculated for the PS-PVC blends are shown in **Table 4**.

Table 4: Solubility values calculated as Small's molar-attraction constants

Group	F^* (cal ^{1/2} c.c. ^{1/2})	Group	F^* (cal ^{1/2} c.c. ^{1/2})
-CH ₃	214	-C ₆ H ₅	735
-CH ₂ -	133	-O-	70
-CH<	28	-H	80–100
>C<	-93	-OH	83
>C=O	275	-Cl	270
Polymer	Structure	$\delta_{(cal)}$	(cal ^{1/2} c.c. ^{1/2})
Polystyrene	(C ₈ H ₈) _n		8.7
PVC	(C ₂ H ₃ Cl) _n		9.7
DEHP	(C ₆ H ₄ (COOC ₈ H ₁₇) ₂)		9.5

A PS residue that has PVC impurities will not only cause problems in the recycling process but also generate incompatibility phenomena leading to relatively low mechanical properties of the resulting material. Therefore, a direct recovery of these materials is not feasible. To solve this problem, a more efficient prior separation must be done, although the use of compatibilizers may also be a solution. The compatibilizers may be reactive products or products that contribute to the mixing of the components, such as the use of plasticizers, which can be natural.^{19,20} In this work, bis(2-ethylhexyl) benzene-1,2-dicarboxylate, known as di(2-ethylhexyl) phthalate (DEHP) was selected as the plasticizer. This product has a high compatibility with PVC²¹ and polar groups due to ester and a non-polar group due to olefinic chains. These

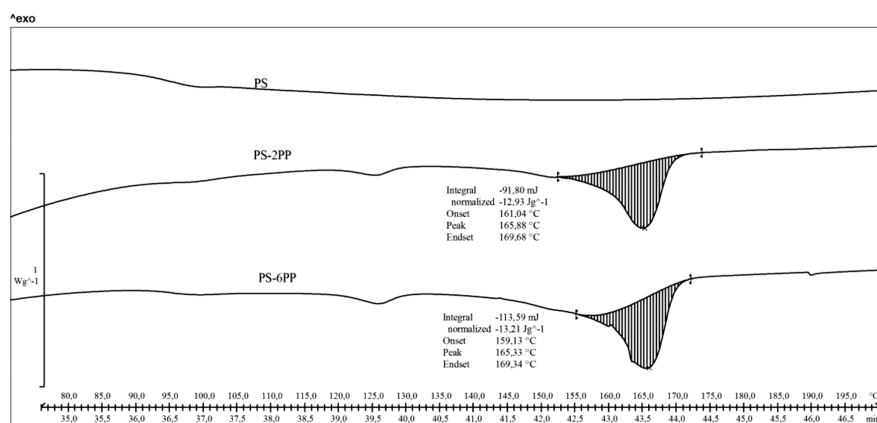


Figure 4: DSC curves of recycled PS without impurities and PS with 2- and 6-% PP

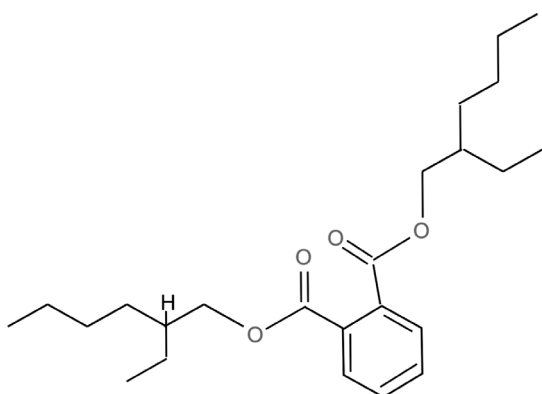


Figure 5: Molecular structure of di(2-ethylhexyl) phthalate, $C_{24}H_{38}O_4$ or $C_6H_4(COOC_8H_{17})_2$ ²²

characteristics make it an excellent compatibilizing agent, with a solubility parameter close to those of both polymers (PS and PVC). The molecular structure of DEHP can be seen in **Figure 5**. Thus, the incorporation of DEHP improves the recycling process, acting in two ways, as a lubricant and as a compatibilizer of the two materials.

Figure 6 shows the effect of DEHP on the Charpy impact resistance when PS is blended with different amounts of PVC as the impurity. Without the compatibilizer, the materials show a clear incompatibility, as can be seen in the evolution of the resilience values. This behaviour improves with the incorporation of 30 phr (parts per hundred) of DEHP per 70 phr of PVC.²³ However, DEHP should be restricted in its used since an excess would result in a loss of PVC properties due to migration processes.

For a PVC:DEHP ratio of 70:30, the results show an improvement in both the final properties and the compatibility of the mixture. Therefore, the incorporation of plasticizers improves both the recovery process and the compatibility of the mixture. For this reason, the recovering process can be interesting from an industrial point of view. The resulting material will have acceptable macroscopic and microscopic properties.

4 CONCLUSIONS

The recovery and recycling of styrene is very interesting since this material is responsible for 6 % of the post-consumer waste generated. However, its recovery is almost zero for some types of waste, such as packaging products. The main problem for the recovery of polystyrene (PS) is the presence of impurities in the plastic waste. Regarding the impurities, it should be noted that if they are polyolefins, PS is not greatly affected, accepting 5 % of impurities. This amount can be easily controlled with differential scanning calorimetry. On the contrary, impurities from technical materials, such as PET, PC or POM, make the PS recycling and recovery difficult, even in low percentages. Its detection can be easily done with infrared spec-

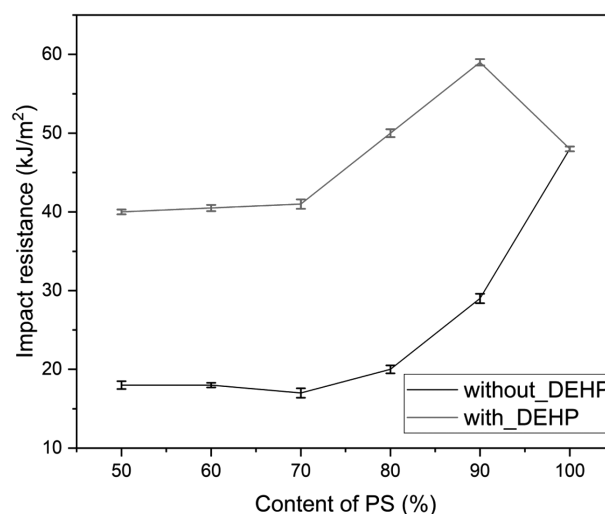


Figure 6: Impact-resistance-energy variation of the mixtures of PS blended with different amounts of PVC with and without DEHP

troscopy. If this kind of contamination is detected, a more efficient separation of the residues must be performed. With respect to the new biodegradable materials, whose use is increasing, the behaviour is variable. PS allows the presence of PLA, but it changes the mechanical properties when having other contaminants, such as PHB. Finally, although there is a chemical compatibility between PS and PVC, the presence of PVC directly affects the PS recycling process. The use of compatibilizers allows a technically and economically profitable recovery.

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