

Tailoring Functionality and Durability of Polymeric Products by Modifying Processing Conditions

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We investigate new possibilities for modifying functionality of polymeric products by changing their material structure during processing and consequently their time-dependent properties, which define the durability of final products. In the first part of the paper we report on significant differences in material structure as observed at atomistic scale due to differences in processing conditions. A short overview of recent studies on multi-scale phenomena in material structure formation is included. Several experimental approaches are proposed for studying the effect of processing conditions on material structure formation and hence, the macroscopic properties of the final polymeric product.

The second part of the paper deals with two questions to be answered, (i) does current industrial polymer processing equipment (in our case extruder) allows processing under such conditions that initiate nonlinearities in the material structure formation processes, and (ii) to what extent can material structure be modified, and consequently the mechanical and other properties of the final polymeric product, by changing the thermo-mechanical boundary conditions (i.e., processing conditions).

We demonstrate that it is possible to modify the functionality of the final polymeric products by modifying the inherent material structure with properly selected processing conditions. We observed that the processing conditions within the range of temperatures and pressures that are typical for industrial extrusion of polymers can be changed so that we can significantly influence the structure formation and consequently the time-dependent mechanical properties of the material in solid state and, as a result, the functionality of the final product. Durability of polymeric products made from such material can be improved by several orders of magnitude! Utilizing this approach opens new possibilities for modifying the functionality of polymeric products and hence better competitiveness in the world market.

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0 INTRODUCTION

The quality of polymeric products is defined by their functionality and durability (i.e., long-term stability), which in turn depend on the structure of material in the product. The material structure, which is formed during melt solidification in the polymer processing stage and defines the time-dependent properties of the final product in solid state (i.e., its mechanical and other physical properties), is determined by the initial kinetics (i.e., the molecular structure of material, molecular distribution and molecular topology), and also by thermo-mechanical boundary conditions to which a polymeric material is exposed during a technological process. Optimal selection of the processing conditions ensures appropriate functional properties of the material and its durability.

At this point, a question arises whether it is possible, by changing technological parameters

of polymer processing in the industrial environment, to modify the structure of the material and consequently its time-dependent mechanical properties to such an extent that the functionality and durability of final products made of these materials could be improved. Knowing and understanding the effect of the technological parameters (temperature, pressure, humidity, mechanical loading) on the material structure formation which defines the behavior of the final product in solid state (i.e., its mechanical and other physical properties) offers new possibilities for the development of polymer products with improved functionality and durability.

We first discuss significant differences in material structure as observed at atomistic scale due to differences in processing conditions. A short overview of recent studies on multi-scale phenomena in material structure formation is included. Several experimental approaches are

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proposed for studying the effect of processing conditions on material structure formation and hence, the macroscopic properties of the final polymeric product.

0.1 Multiscale Phenomena in Material Structure Formation

Macroscopic properties of polymeric materials in solid state depend on their inherent structures. Thus, by modifying the structure of materials one may alter their macroscopic properties. The structure formation of polymers evolves over several steps, each beginning with different size and complexity of their building blocks as schematically shown in Fig. 1. This is a highly non-linear process, during which the non-linear multi-scale interactions between the boundary conditions and the inherent molecular rearrangements take place at different time-space scales, forming higher order structures at atomistic scale up to macroscopic dimensions. When materials with appropriately modified initial kinetics [1] and [2] are exposed to certain thermo-mechanical boundary conditions, they can exhibit exceptionally nonlinear (chaotic) behavior [3]. This means that even small changes in boundary conditions may lead to a completely different material structure in the solid state. It becomes evident that changes in boundary conditions at macro-scale can cause changes in material structure at atomistic scale [4] and [5].

As presented in recent study [4] of the proton motion in ‘bulk’ and in highly drawn ‘fiber’ polyamide 6 (PA-6) by proton nuclear magnetic resonance (NMR), products manufactured at two different processing conditions exhibit significantly different structure at atomistic level. A striking difference in the molecular dynamics between the slowly cooled ‘bulk’ sample and the rapidly cooled ‘fiber’ sample, prepared by spinning and exposed to extreme mechanical straining, was observed as seen in Figs. 2 and 3. These two samples exhibit significantly different thermal properties as well (see Fig. 4).

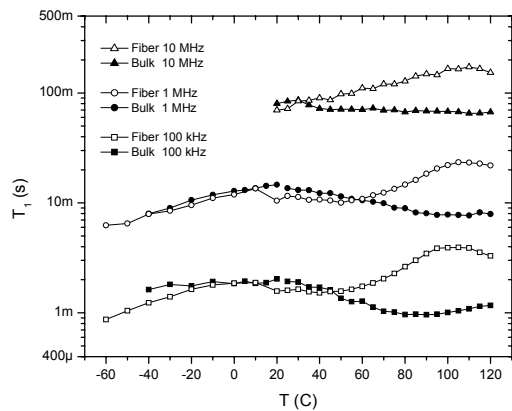


Fig. 2. Temperature dependence of the spin-lattice relaxation time, T_1 , of ‘bulk’ and ‘fiber’ PA-6 [4]

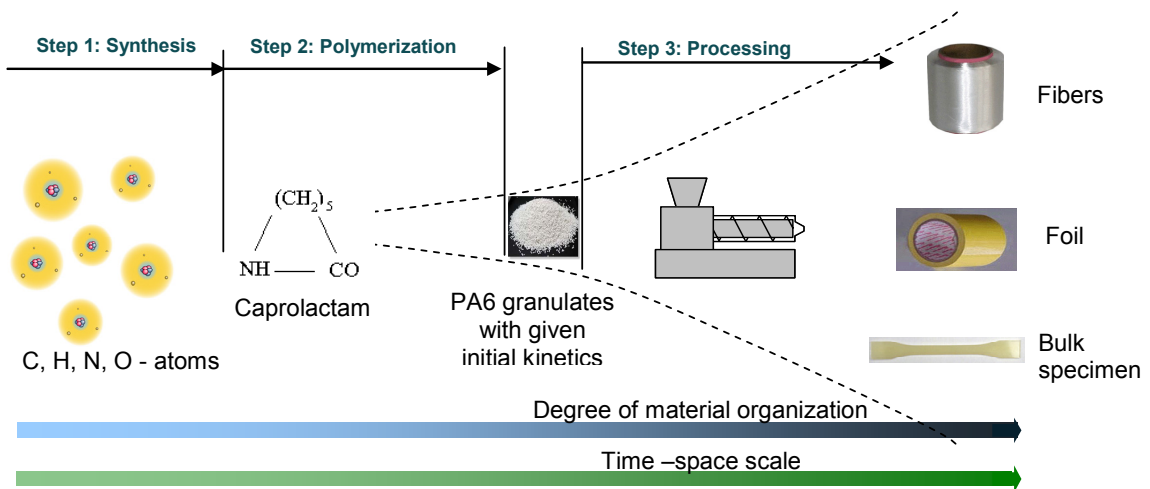


Fig. 1. Different phases of polymer structure formation [1]

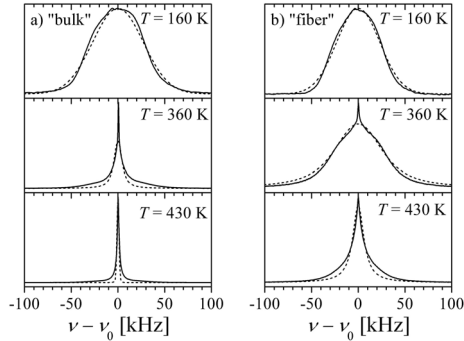


Fig. 3. Measured (solid line) and calculated (dashed line) proton NMR spectra of (a) 'bulk' and (b) 'fiber' PA-6 [4]

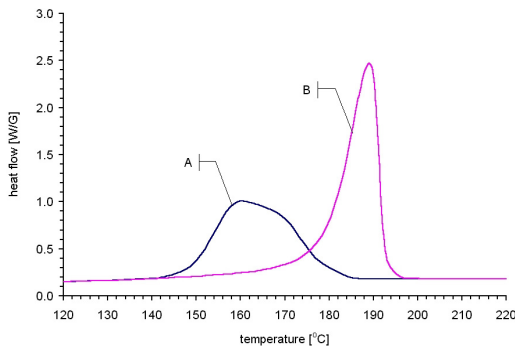


Fig. 4. DSC measurements of (A) 'bulk' and (B) 'fiber' PA-6. The glass transition and the pre-melting phenomena are shifted to higher temperatures. The onset of melting of 'fiber' samples is shifted for about 50 °C to higher temperatures [4]

Another example of complex multi-scale processes in the transition from the molten to the solid state is the spinning of polyamide fibers, where the variation of thermo-mechanical boundary conditions take place at about the same time-scale as the structural rearrangements of the molecules. As observed in a recent study [5] of PA-6 fiber structure by electron paramagnetic resonance (EPR), the differences in fiber production process enhance significantly different structures at atomistic level as shown in Figs. 5 and 6. Similarly the modifications in fiber production process enhance significant changes in the shrinking behavior of polyamide 66 (PA-66) fibers [6] (see Fig. 7).

Above presented experimental results correspond to the numerical simulations performed [7] to [10] and the analysis of polyamide structure formation during

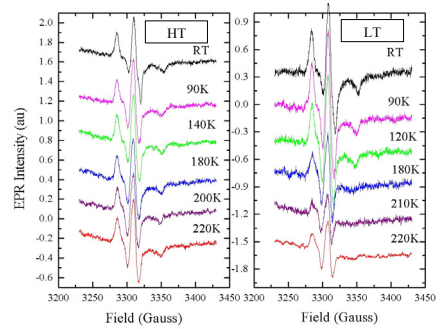


Fig. 5. Temperature dependences of the electron paramagnetic resonance (EPR) spectra of the 'high tension (HT)' and 'low tension (LT)' nylon 6 fibers [5]

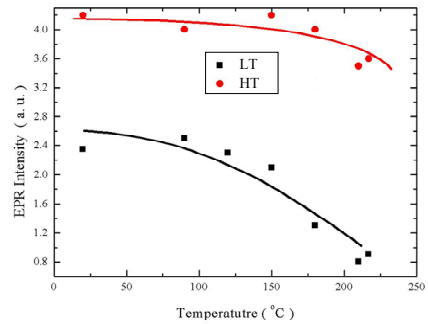


Fig. 6. Temperature dependences of the intensity of the EPR spectra of the 'high tension (HT)' and 'low tension (LT)' nylon 6 fibers [5]

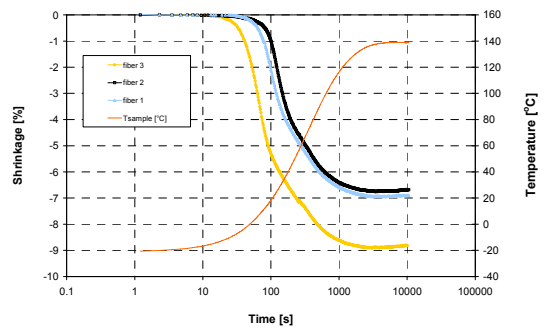


Fig. 7. Shrinkage of PA-66 fibers subjected to three different manufacturing conditions [6] solidification with the aid of positron annihilation [11] and [12]. By applying proper thermo-mechanical boundary conditions (technology) we can therefore modify the material structure, which is the result of nonlinear interactions of the polymer chain reorganization processes at different time-space scales from nano- to macro-scale, thus modifying physical properties of the

material by several orders of magnitude. Similar results are reported by some other research groups in the world [3], [13] to [21].

The recent studies on multi-scale phenomena in material structure formation as presented above show that by changing the material structure we may significantly influence the physical properties and durability (i.e., long-term stability) of final products, which opens new potential for tailoring the functionality of products. Changes in the material structure can be caused by modifying the initial kinetics of the material (i.e., by changing its molecular weight distribution, by adding nanoparticles into polymeric matrix, etc.), and more important, by changing the thermo-mechanical boundary conditions (i.e., technology) to which material has been exposed during processing.

The investigation of the latter, i.e., the effect of processing conditions on the material structure formation, and hence the durability and the functionality of the final product, is discussed in the second part of this paper.

1 THE PRESENT RESEARCH

We investigate whether it is possible, by changing technological parameters of polymer processing in the industrial environment, to modify the structure of the material and consequently its time-dependent mechanical properties to such an extent that the functionality and durability of the final products made of these materials could be improved.

Let us first consider the following questions: (i) which thermo-mechanical boundary conditions cause changes in material structure at which scale, and (ii) which changes in material structure cause which changes of physical properties of the material.

In order to answer these questions, first, a good understanding of the effect of temperature and pressure on the material structure formation is required, and second, we need sophisticated experimental devices for polymer processing and material characterization.

At the *processing level*, such an equipment is a laboratory extruder PolyLab OS (Thermo HAAKE Electron Corporation), see Figure 8, which enables an accurate control of the processing conditions (pressure, temperature, screw speed, torque) along the extruder cylinder

during polymer processing, but at the same time this equipment simulates (mimics) the real industrial processing conditions, appropriate for up-scaling. By using this device, the processing conditions within the range of temperatures and pressures that are typical for industrial extrusion of polymers, can be changed so that we can significantly influence the structure formation and consequently the time-dependent mechanical properties of the material and, as a result, the functionality of the final product, as discussed in the present paper. This opens new possibilities for modifying the functionality of polymer products, thus increasing their competitiveness in the global markets.

At the *material characterization level*, the analysis of changes in the material structure and the resulting physical properties of the final product, caused by variations in thermo-mechanical boundary conditions, requires at least three groups of measuring systems, i.e.:

- (a) equipment for analyzing the material structure at different observation levels, from atomistic to macro scale; for this purpose several experimental techniques are widely used, i.e., PALS, NMR, EPR, WAXS, SAXS, AFM, TEM, SEM, optical microscopy, thermal methods, etc.;
- (b) equipment for analyzing the time-dependent behavior of the material in solid state [22]; such an instrument, i.e., CEM apparatus for relaxation measurement [23] and [24], was recently ranked among ASTM recommendations (guidelines) for polymer testing. Proposed guidelines will be published in »Springer Handbook of Experimental Solid Mechanics« [25];
- (c) experimental approach for monitoring the solidification process; several research groups actively work on this subject [16] to [21] and [26] to [30].

This research deals with two questions to be answered, (i) does current industrial polymer processing equipment (in our case extruder) allows processing under such conditions that initiate nonlinearities in the material structure formation processes, and (ii) to what extent can material structure be modified, and consequently the mechanical and other properties of the final polymeric product, by changing the thermo-mechanical boundary conditions (i.e., processing conditions).

2 EXPERIMENTAL APPROACH

For the purpose of the present research we extruded low density polyethylene (LDPE) specimens under different (extreme) processing conditions using a laboratory extruder PolyLab OS (Thermo HAAKE Electron Corporation), see Figure 8, which simulates the real industrial processing conditions, but at the same time this equipment provides a better control of the conditions (pressure, temperature, screw speed, torque) along the extruder cylinder during polymer processing. The changes in the structure of extruded LDPE samples were analysed with different experimental methods with respect to the time-space scale of the structure observation. Optical microscopy was used to analyse the morphological properties, the thermal properties were determined by DSC measurements, and the shear creep measurements were performed to study the time-dependent mechanical behavior of LDPE samples. The proposed approach enabled us to examine the type and the magnitude of the structural changes in polymer product and consequently its mechanical and other properties, which can be achieved by changing processing conditions) in the industrial environment.

The results of this research show that it is possible to change the technological conditions in the range of temperatures and pressures, typical for polymer extrusion in industrial environment, in such extent that we significantly influence the structural formation and consequently the time-dependent mechanical properties of the material, and hence the functionality of the final product. We observe that by changing the processing conditions in the industrial environment the durability of polymer products improves for several orders of magnitude! That opens new possibilities in the field of modifying the functionality of polymer products and hence better competitiveness in the world market.

3 POLYMER PROCESSING

3.1. Material

Low Density Polyethylene (LDPE) OKITEN[®] 245 S by Dioki was chosen for three reasons: it is the most widespread material in polymer processing technology, it is easy to handle, and does not easily form structures.

Should the proposed analysis show that the processing conditions have a significant effect on the structural formation and consequently on the time-dependent mechanical behavior of the final LDPE product, this would mean that the processing technology will influence also other types of polymeric materials which form more complex structures.

3.2. Laboratory extruder

PolyLab OS laboratory extruder by Thermo HAAKE Electron Corporation (see Fig. 8) was used for the production of the LDPE specimens. It is a twin-screw co-rotational extruder with the extrusion part length to screw diameter ratio 40:1. The device allows adaptation of the length of extrusion part barrel to a ratio of 25:1. The machine, consisting of the *driving part* RheoDrive 4 and the *extrusion part* Rheomex PTW 16, operates with a through put rate of 5 kg/h in rpm range of 0–1100 min⁻¹. The maximum operating pressure is 100 bar, the maximum temperature 400°C (the lowest temperature is determined by room conditions), and the maximum torque 129.6 Nm.



Fig. 8. The PolyLab OS laboratory twin-screw co-rotational extruder (Thermo HAAKE Electron Corporation), consisting of A – RheoDrive 4 and B – Rheomex PTW 16

3.3 Thermo-mechanical Conditions for LDPE Extrusion

The range of processing parameters that can be changed during polymer extrusion process depends on the extruder capacity and polymer properties. The lower and the upper limit of the temperature tolerance range for LDPE, i.e., 130–270°C, was determined by DSC measurements. During the LDPE material extrusion process, we varied the number of the screw revolutions and the temperature along the extruder barrel. At a certain temperature which was the same on all ten heaters along the extruder barrel, we set the number of screw revolutions, and recorded the pressure value in the melt at the extruder outlet and the torque on both screws during the extrusion process. The tolerance range of the pressure and torque values was $\pm 10\%$. The next step was to change the number of revolutions and repeat the procedure at the same temperature. At each temperature, the operating range of revolutions was 10–250 min^{-1} . The operational range of thermo-mechanical boundary conditions under which LDPE can be

extruded on the PolyLab OS laboratory extruder is shown in Figs. 9 and 10. During the extrusion, the screw torque reached a critical operating level, and therefore it was taken into account as a key parameter for determining the extreme thermo-mechanical conditions of the LDPE specimen extrusion.

3.4. Specimen Preparation Conditions

Based on the analysis of the thermo-mechanical boundary conditions of LDPE extrusion (see Figs. 9 and 10), we selected four different combinations of processing conditions, illustrating extreme conditions of extrusion, i.e., lowest pressure – lowest temperature, highest pressure – lowest temperature, lowest pressure – highest temperature, highest pressure – highest temperature. The processing parameters defining these conditions are shown in Table 1. Under these conditions, we produced the specimens of extruded LDPE intended for subsequent analysis of their structure formation as the result of these modified processing conditions.

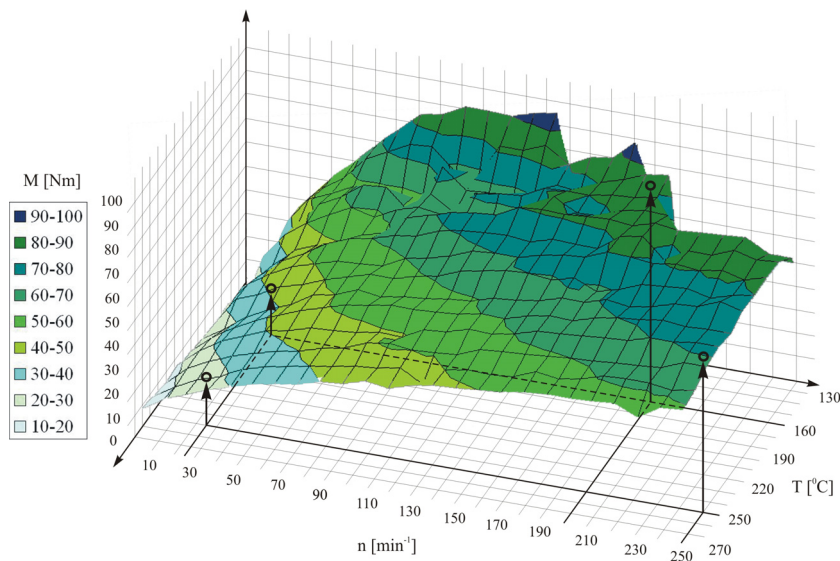


Fig. 9. The torque, M , measured on the screws during the extrusion process, depending on the set temperature, T , along the extruder barrel and the set number of screw revolutions, n , during LDPE extrusion. It was observed that the higher the temperature in the extruder barrel the more slowly the torque on screws increases with the increasing number of screw revolutions. The extreme torque values were reached at the lowest temperatures (close to 130°C) and the number of revolutions of about 150–200 min^{-1} . Arrows indicate 4 extreme conditions at which LDPE specimens were extruded

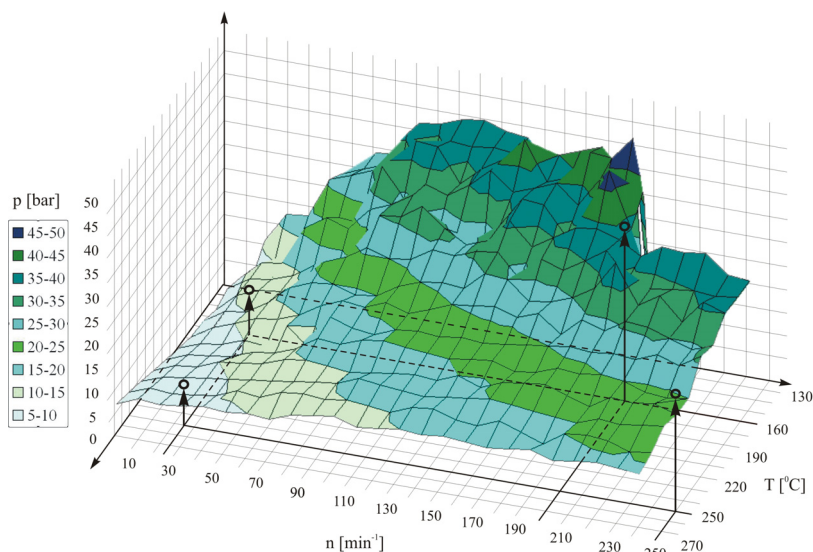


Fig. 10. The pressure, p , measured in the melt at the extruder outlet, depending on the set temperature, T , along the extruder barrel and the set number of screw revolutions, n , during LDPE extrusion. Similarly to the torque measurement, the maximum pressure appears at low temperatures in the cylinder, but this happens at a higher number of revolutions (over 200 min^{-1}). As opposed to torque, the increase of the pressure resulting from the increasing number of screw revolutions is less distinct at high temperatures, while at low temperatures the pressure increases more markedly than torque. Arrows indicate 4 extreme conditions at which LDPE specimens were extruded

The geometry (i.e., shape and dimensions) of LDPE specimens, i.e., cylinders of 6 mm in diameter, was defined by the requirements of the creep measuring device [31] to [36]. For this purpose, a unique extruder die fitting was made to which a tool in the form of a glass tube with an internal diameter 6 mm and a length of 200 mm was fastened (see Fig. 11). The extrusion process of the polymer melt which exited from the extruder through the die fitting and entered into the glass tube in the selected conditions lasted until the melt was evenly mixed and constant conditions were established in the extruder barrel. Then the glass tube with melt was removed and inserted into the insulation system (see Fig. 12), where the specimen slowly cooled down. This specimen extrusion procedure was performed under four different processing conditions (see Table 1).

The specimen production process consists of three consecutive segments, i.e., heating and melting of the granulate in the extruder barrel, melt extrusion into the glass tube where the process of cooling is already going on, followed by slow cooling in the insulation system. Fig. 13 schematically

illustrates the temperature profiles of specimen production at two temperatures of melt, i.e., 168°C or 263°C , measured at the outlet from the extruder. The melt temperature was higher than the set temperature (i.e., 160°C or 250°C , respectively) at all ten heaters along the extruder barrel as the consequence of the conversion of the mechanical energy generated by the rotation of screws to heat and consequently producing the rise of temperature in the barrel. The granulate in the extruder was first heated from the room temperature (approx. 25°C) to the temperature of 168°C or 263°C (depending on the set temperature), which was measured at the outlet of the melt from the extruder. During this time, the melt pressure generated by the rotation of screws and measured at the outlet from extruder, increased to 23 or 77 bar (at the number of screw revolutions of 25 and 200 min^{-1} , respectively) at the lower temperature, and to 20 or 37 bar (at the number of screw revolutions of 25 and 250 min^{-1} respectively) at the higher temperature (see Table 1).

Table 1. The set and the measured processing parameters of LDPE specimen extrusion. We selected the lowest and the highest temperature for extrusion, i.e., 160°C and 250°C, respectively. At these two set temperatures we influenced the pressure in the melt measured at the exit from the extruder by changing the number of screw revolutions. At the lowest temperature and the number of screw revolutions of 25 and 200 min⁻¹, we achieved the pressures of 23 and 77 bar, respectively. In the case of the highest temperature and the number of screw revolutions of 25 and 250 min⁻¹, we achieved pressures of 20 and 37 bar, respectively.

Specimen name	Processing parameters				
	Set quantities		Measured quantities		
	$T_{cylinder}^1$ (°C)	n^2 (min ⁻¹)	T_{melt}^3 (°C)	p_{melt}^4 (bar)	M^5 (Nm)
LDPE_168_23	160	25	168	23	30
LDPE_168_77	160	200	168	77	105
LDPE_263_20	250	25	263	20	28
LDPE_263_37	250	250	263	37	75

- ¹ The temperature set on the ten heaters along the extruder barrel
- ² The number of screw revolutions
- ³ The temperature of the melt measured at the outlet from the extruder barrel
- ⁴ Pressure measured at the outlet from the extruder barrel
- ⁵ Torque measured on the screws

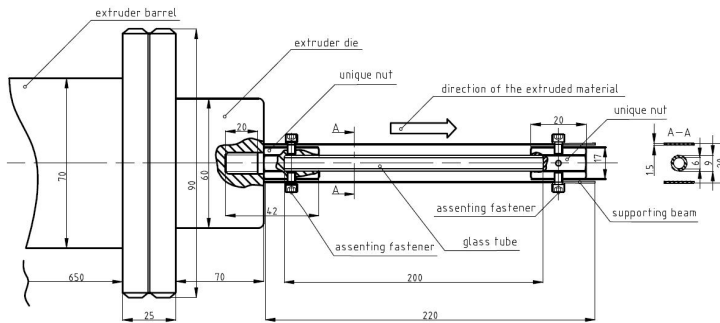


Fig. 11. Unique die fitting with the glass tube tool

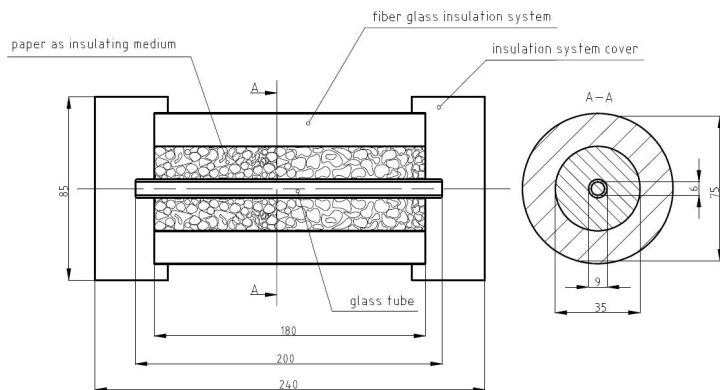


Fig. 12. Insulation system for slow cooling of glass tubes with extruded polymer

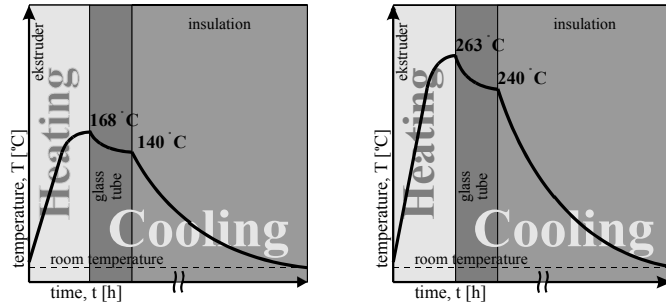


Fig. 13. Schematic diagram of the temperature profiles for producing extruded LDPE specimens at two different temperatures of melt, i.e., the lowest temperature, 168°C (left), and the highest temperature, 263°C (right)

The extrusion process pushed the melt at the outlet from extruder into the glass tube, which was open at the end (i.e., exposed to normal air pressure of 1 bar), whereby the pressure dropped to 1 bar, and the temperature fell to 140°C or 240°C, respectively (depending on the set temperature, see Fig. 13). After a period of approximately 10 minutes, required for the equilibrium state to be established in melt along the entire extruder barrel under the set processing conditions (i.e., temperature and the rotational speed of the screws), the extrusion process was stopped, the glass tube with the extruded LDPE removed and then inserted into the insulation system where the extrudate was cooling down to room temperature for approximately 90 minutes. The extruded LDPE specimen was then removed from the glass tube and prepared for the analysis of morphology, thermal properties and time-dependent mechanical behavior.

4 MATERIAL CHARACTERIZATION

4.1. Morphological Analysis – Optical Microscopy

The analysis of the *morphological properties* of the extruded LDPE specimens (see Fig. 14) showed that specimens extruded at a lower temperature (168°C) exhibit oriented structure in the form of concentric rings, while no orientation was observed in specimens extruded at a higher temperature (263°C). This indicates that a random structure forms at higher temperatures when the response times are short, while at lower temperatures when the material response times are long, molecules keep the configuration, which has been forced on them by the mechanical shear loading through the screw rotation and is reflected in the structural orientation of the solid product.

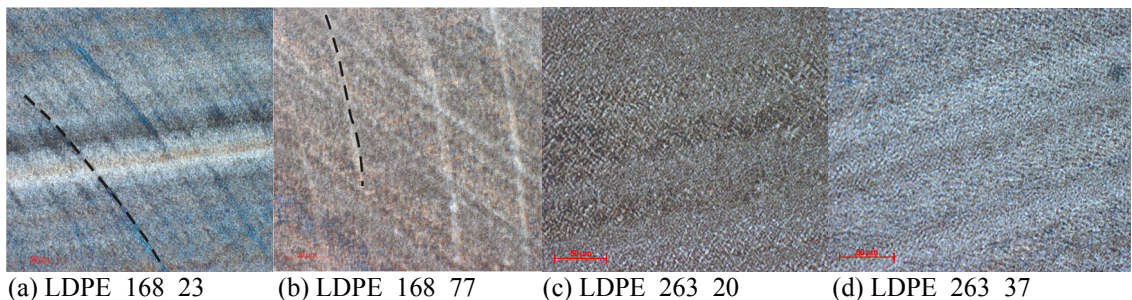


Fig. 14. Optical microscopy images of extruded LDPE specimens, produced at different processing conditions, (a) LDPE_168_23: $T = 168^{\circ}\text{C}$, $p = 23 \text{ bar}$, $M = 30 \text{ Nm}$, $n = 25 \text{ min}^{-1}$, (b) LDPE_168_77: $T = 168^{\circ}\text{C}$, $p = 77 \text{ bar}$, $M = 105 \text{ Nm}$, $n = 200 \text{ min}^{-1}$, (c) LDPE_263_20: $T = 263^{\circ}\text{C}$, $p = 20 \text{ bar}$, $M = 28 \text{ Nm}$, $n = 25 \text{ min}^{-1}$, (d) LDPE_263_37: $T = 263^{\circ}\text{C}$, $p = 37 \text{ bar}$, $M = 75 \text{ Nm}$, $n = 250 \text{ min}^{-1}$. The optical microscope Axioskop 2 MAT (Carl Zeiss) was used to analyze the morphological structure of 40 μm thick LDPE extrudates at 500x magnification using polarized light

The results are in conformity with the theory of the nonlinear processes in the material during structure formation as a consequence of three effects: temperature, pressure and shear. For detailed explanation see [31].

4.2. Thermal Analysis – Differential Scanning Calorimetry

The *thermal analysis* of the extruded LDPE specimens showed no difference in thermal properties (i.e., crystallization and melting temperatures) due to different processing conditions (see Table 2). It is highly probable that because of the nature of this experiment the method is not sufficiently sensitive to detect changes in the structure by measuring the thermal characteristics of the material.

4.3. Analysis of time-dependent mechanical properties – Shear creep testing

The *analysis of the time-dependent mechanical properties* of the extruded LDPE specimens was done based on the shear creep experiments, performed by using the shear creep torsionmeter, which was developed in CEM [31] to [36]. The results of shear creep compliance analysis determine (i) the temperature stability of products, (ii) their time stability which determines durability, and (iii) the frequency stability of products during dynamic loading.

4.3.1 Temperature stability

The temperature stability analysis tells us how much the shear creep compliance changes with a change in temperature. It becomes evident that the effect of temperature on shear creep compliance is least distinctive in the material with the most complex (oriented) structure (i.e., the specimen extruded at 168°C and 23 bar) as seen in Fig. 15. A change in temperature from 30 to 80°C initiates a noticeably smaller change in this material than in other materials. This shows that the material with the most oriented structure is also most temperature-stable.

4.3.2 Time stability

The comparison of the shear creep curves at the reference temperature of 39°C (see Fig. 16)

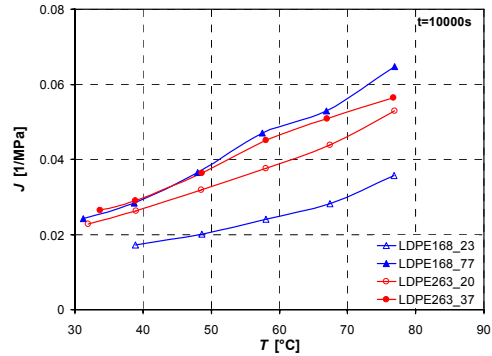


Fig. 15. Temperature dependence of shear creep isochrones at the longest time of 10.000 s, determining the experimental window of the measurement, obtained from the segments of shear creep measurement for four extruded LDPE specimens produced under different processing conditions

shows that by changing the processing parameters within the operating range of the laboratory extruder we can improve the time dependence by as much as ten to more than one million times.

The comparison of the time and temperature stability of the extruded specimens shows that the effect of the same polymer processing conditions on the temperature stability differs from the effect on the time stability of these products, which indicates an extremely nonlinear effect of the thermo-mechanical boundary conditions.

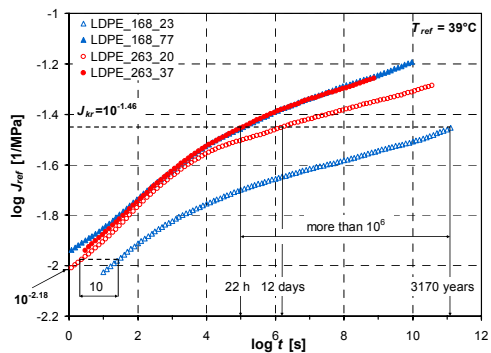


Fig. 16. The shear creep master curves at the reference temperature of 39°C, showing logarithmic time-dependence of the shear creep compliance for four extruded LDPE specimens produced under different processing conditions

If we are able to maintain the processing conditions (in our case extrusion) very accurately,

operation in the range of nonlinear processes within the material can be used to our advantage in order to improve the mechanical properties by several orders of magnitude.

4.3.3 Frequency stability

In line with the theory of linear viscoelasticity, we calculated the dynamic properties of the LDPE extrudates from experimentally determined shear creep curves by using software based on the Emri-Tschoegl algorithm [37] to [42] for the calculation of dynamic material functions from static ones across the mechanical spectrum. By comparing the dynamic material functions of the extruded LDPE specimens (see Figs. 17 and 18), we analyzed the behavior of materials under dynamic loading.

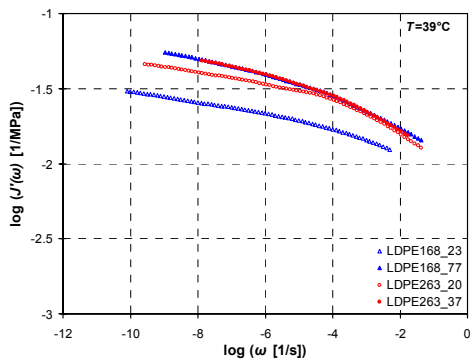


Fig. 17. Frequency dependence of the real part of dynamic shear creep compliance, J' , calculated from the master curves of shear creep at the reference temperature of 39°C for four extruded LDPE specimens produced under different processing conditions

The material with the highest degree of orientation, which was produced at the lowest temperature and the lowest pressure (168°C, 23 bar), has better frequency stability than others regarding the ability of the material to return to the initial state after the cessation of loading. On the other hand, this material has the least ability to dissipate energy (damping) compared to the materials produced at a higher temperature and a higher pressure, which is reflected in the smallest value of the imaginary part of dynamic shear creep compliance, J'' . At the same time, it is evident that with respect to the amount of energy

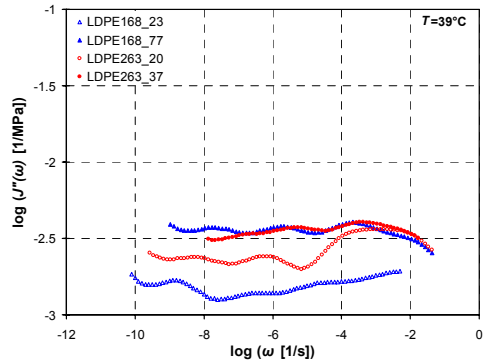


Fig. 18. Frequency dependence of the imaginary part of dynamic shear creep compliance, J'' , calculated from the master curves of shear creep at the reference temperature of 39°C for four extruded LDPE specimens produced under different processing conditions

lost, which is not returned by the material after unloading, the frequency stability, $J(\omega)$, is similar for all materials. We arrive to a similar conclusion by comparing the frequency dependence of the damping indicator, $\tan \delta$ (see Fig. 19), which expresses the damping characteristics of the material. We find that all four specimens of extruded LDPE are frequency-stable at lower frequencies, while at higher frequencies they become very sensitive to any changes in the excitation frequency.

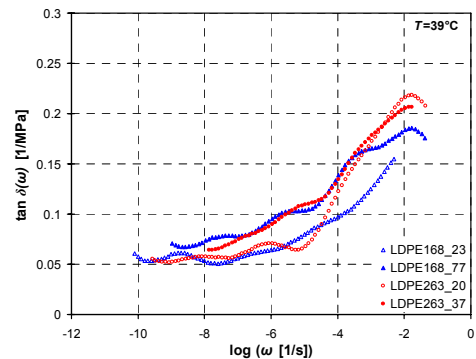


Fig. 19. Frequency dependence of the damping indicator, $\tan \delta$, calculated from the master curves of shear creep at the reference temperature of 39°C for four extruded LDPE specimens produced under different processing conditions

There is a critical frequency below which the material damping is practically independent of the

excitation frequency and above it the frequency dependent material damping changes by a factor of more than 2 (100%).

The relevant findings indicate that modification of the processing conditions within the range of temperatures and pressures typical for industrial polymer extrusion processes can improve the temperature stability of LDPE consumer products exposed primarily to static loads during their use by a factor of 2, the time-stability can be improved from 10 to more than 1,000,000 times (see Fig. 16), and the frequency stability above the critical frequency can differ for a factor of more than 2 (100%).

Improving the mechanical properties generally decreases production capacity which means that an optimum balance between the product quality and quantity produced should be found for each product within a price bracket. When producing simple products, technology optimization is of no special relevance since the quantity of product (and not the quality level) is a decisive factor in production. However, when manufacturing products whose durability and temperature stability are important requirements, the optimization of the technological process is of the key relevance.

5 CONCLUSIONS

The recent studies on multi-scale phenomena in material structure formation show that by changing the material structure we may significantly influence the physical properties and durability (i.e., long-term stability) of final products, which opens new potential for tailoring the functionality of products. Changes in the material structure can be caused by modifying the initial kinetics of the material (i.e., by changing its molecular weight distribution, by adding nanoparticles into polymeric matrix, etc.), and more important, by changing the thermo-mechanical boundary conditions (i.e., technology) to which material has been exposed during processing.

The investigation of the latter, i.e., the effect of processing conditions on the material structure formation, and hence the durability and the functionality of the final product, has found that by changing the processing conditions within the scope of the temperatures and pressures typical for polymer extrusion in industrial conditions it is possible to

significantly affect the material structure formation and consequently its time-dependent mechanical properties, which determine the functionality and durability of the final product. These findings open new possibilities in modifying the functionality of polymer products, and consequently contribute to their better competitiveness in the global market.

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