CHANGES OF RHEOLOGICAL PARAMETERS OF POLYPROPYLENE AND POLYETHYLENE AFTER EXPOSURE IN ALIPHATIC n-HEXANE

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Resume

Rheological properties of thermoplastic polymer materials before and after exposure to a chemical solution were evaluated using the frequency sweep test, which monitors changes in viscoelastic properties of polymers with respect to their molecular structure and their behavior in thermoplastic processing. As experimental material thermoplastic polyethylene and polypropylene samples were used and subjected to influence of n-hexane solution for period of 3 and 6 months. Measurements were performed using oscillating rheometer Physica Rheometer MCR301 and carried out at the temperatures of 160 °C and 80 °C. Degradation process resulted in changes of complex dynamic viscosity, storage and loss modulus, changes in molar mass and its distribution which sufficiently prove the rheological changes.

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1. Introduction

Polymer materials are nowadays the most important segment of production and consumption by volume among the all technical material. Ever since the emergence of plastics and more frequent application in all aspects of industry, this material has the necessary respect and a unique place on the world market for used materials. Growing applications of plastics for technically demanding parts ever put greater demands on the level of knowledge about the behavior of these materials [1].

Polymer materials represent an important area in which they are becoming predominant against other materials and has increases considerably and rapidly. Their relatively low cost, ease of installation, transportation, and long-term durability against environmental degradation (harmful environmental attack such as corrosion, rust and higher thermal stresses) make plastics an attractive alternative to metals. Among the most common polymers utilized in such applications are polyethylene (PE) and polypropylene (PP) [2, 3].

Rheology is the science of deformation and flow of materials [4]. It reveals information about the flow behavior of liquids but also the deformation behavior of solids, which is considered as typical behavior of polymers. In very short processing time, polymer may behave as a solid, while in long processing time material may behave as a fluid. This dual nature (fluid-solid) is referred to as *viscoelastic* behavior [5, 6]. Changes induced by the environment with degradation effect can be evaluated by rheological measurements which monitor changes in viscoelastic properties of the tested polymers. The fundamental of rheological characteristics is viscosity defined as internal resistance of material against shear stress or extensional stress [3,4]. It is necessary to realize the dual character of majority of polymer materials from viscoelastic point of view. The action of external force on the ideal viscous

material results in its deformation i.e. irreversible locomotion (movement) of macromolecules and after removal of the external force material retains its "new" shape. The action of external force on the ideal elastic material results in its deformation but after the removal of the external force, the material returns to its original shape. Polymers are generally characterized by the viscoelastic nature, which means that external forces cause partly permanent (viscosity element of polymer) and partly reversible (elastic element of polymer) deformation [7, 8].

Viscosity has a high importance for polymer processing, the change of viscosity is determined by changes of particular factors (temperature, pressure, molecular weight and its distribution, structure of the polymer, presence of additives in the polymer), which are characteristic for the polymer and may vary according to the effect of degradation processes [8]. Rheological investigations are very useful for developing technical polymers. Simple rheological measurements can be used in the quality control checks of raw materials and final products. Molecular structure and therefore the behavior of polymers during processing can be determined within a few minutes using rheological tests before the processing begins [4].

The aim of this study is the comparison of selected rheological properties of thermoplastic polymer materials before and after exposure in different environments with a degradation effect.

2. Experimental material and conditions of preparation

The polymers used in this study are commercially available and provided in the form of pellets by the plastics company Licharz. High density, low pressure PE 500 with the trade name PE HMW, and polypropylene PP was used as an experimental material.

PE 500 has littleor no branching and can therefore be called a linear hydrocarbon material.

The molecules are highly packed which makes it rigid. The Average Molar Mass ranges between 200,000 g/mol and 500,000 g/mol. Significant temperature is melting temperature, T_m = 130 °C/137 °C [5]. PP is translucent, partially-crystalline. The material properties are quite similar to properties of polyethylene PE 500 with some appreciable differences. It has a lower density, higher melting temperature T_m > 160 °C, typically T_m = 175 °C, higher rigidity and hardness and good fatigue resistance.

These thermoplastic materials have very good chemical plus electrical resistance, relatively low density 0.91 – 0.96 g/cm^3, low absorption, good resistance at high negative temperature, good workability and some other properties like coefficient of friction, abrasion resistance and impact toughness [6].

Chemical environment with degradation effect was performed for exposure of tested material. Polymer samples of plate shape with dimension of 10 x 55 x 3 mm were exposed to aliphatic hydrocarbon n-hexane, immersed in a separated container for 3 and 6 months at laboratory temperature.

3. Measuring technology and interpretation of used method

The measurements were performed using oscillating rheometer Physica Rheometer MCR301 with the Convection Temperature Device CTD450, a unique chamber that offers gradient free measurements and a direct measure of the sample temperature. The sample temperature equals the sensor temperature at any time. The chosen method was the frequency sweep test (FS), which characterize the viscoelastic properties of polymers with respect to their molecular structure and their behavior in thermoplastic processing [4].

Thermoplastic polymer sample was placed inside the chamber between two parallel plates with diameter of 25 mm. Approximately

5 minutes later polymeric material was completely molten. Special care has to be taken with respect to air bubbles. Finally the gap of 1 mm between the plates was established. Measurements were carried out at the temperature of 160 °C and 180 °C, according to the nature of the material and following conditions: an amplitude of $\gamma = 5$ %, an angular frequency ranging from 500 to 0.05 1/s.

The principle of material evaluation is based on evaluation of measured parameters which are shown in the diagram (Fig. 1). The process of degradation is followed by changes of molecular mass (as networking or macromolecular chains breaking) which should be reflected in the measured parameters.

The analysis of the cross-over point (COP) between the storage modulus G' (measure for the elastic properties) and the loss modulus G" (measure of viscous properties) in the frequency sweep, as seen in Fig. 1, makes it possible to obtain the qualitative picture of the average molar mass and molar mass distribution. Furthermore, we are able to monitor the position of the intersection of the curves characterizing the state of both modulus and indicate the transition from viscous deformation behavior to the more elastic behavior. COP is qualitative characteristics of the material [9]. The polymer degradation can result in changes of the values of measured characteristics. Position of the COP in horizontal direction provides information about the average molar mass and position of the COP in the vertical direction signals the difference in the molar mass distribution.

4. Results and discussion

Changes of rheological properties of PP and PE 500 after exposure in n-hexane were evaluated by Frequency Sweep test (FS). The differences in complex viscosity and modulus defining viscous and elastics characteristics of polymer samples are shown in Fig. 2 ÷ Fig. 6. These measurements were carried out only in exposed surface layers that were replaced from the exposed sample in depth of 0 to 300 μm and 300 to 600 μm.

Measurements of rheological characteristics of PP and PE 500 exposed in n- hexane for a period of 3 months (Fig. 2 and Fig. 3) and 6 months (Fig. 4 and Fig. 5) show the changes of complex viscosity η*, as well as G' and G"
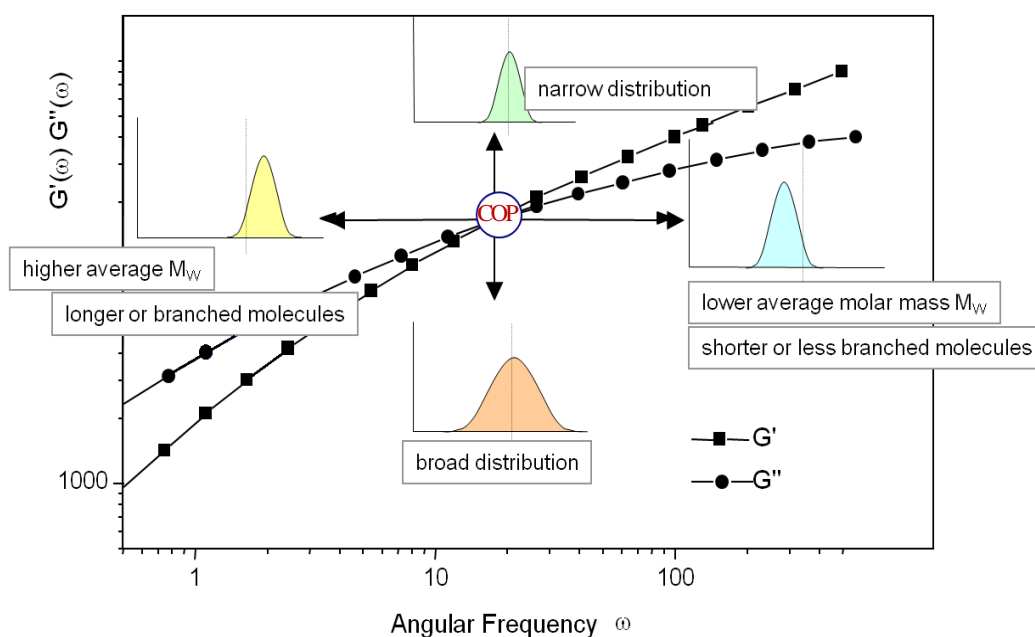

Fig. 1. Determination of selected rheological characteristics G', G" of material during FS test
(full colour version available online)

modulus in both surface layers but only in PP samples. PE 500 indicates no changes of measured material functions values in comparison with the original material. Rheological functions of PP material show a similar viscosity at higher angular frequencies but they differ a lot at lower one. At low angular frequencies the loss modulus G'' is running above the storage modulus G' [4]. From the shift of COP to higher angular frequencies its evident that average molar mass of PP is decreasing towards to depth of tested layer. In this state molecules are shorter or less branched. The molar mass distribution does not change as the vertical shift of COP is not very notable. At angular frequencies above the COP elastic properties are dominant over the viscous (fluid) properties. We can monitor that the area in the depth of $300 \div 600$ μm is affected more than the surface layer of $0 - 300$ μm, in which material properties are much more similar to properties of unexposed material. This is because of the diffusion process of n-hexane molecules which pass through polymeric chains and interfere the configuration of polymer material. As can be seen diffusion is much more intensive in the top layer where molecules of solution are still in motion; further to depth they are more bounded to polymeric chains.

Comparison of measured rheological functions of PP and PE 500 after 3 months and 6 months exposition in solution of n-hexane prove that process of degradation of polymeric material caused by diffusion process of molecules of chemical environment has similar effect in both periods of time. The curves of complex viscosity η*,G' and G'' modulus of PP samples (Fig. 6) have similar course and differ only in the layer of $300 - 600$ μm due to active diffusion process. Exposed samples of PE 500 retain the same characteristics as original material.

5. Conclusions

From the study, the following conclusions can be drawn:

- Changes in the structure of studied polymers due to degradation effect caused by exposition in n-hexane solution can be monitored by rheological measurements. This was reflected in the measured rheological parameters and variables like complex viscosity, molecular mass and its distribution, modulus characterizing elastic and plastic properties.

- The results prove that the exposure of PP and PE 500 in n-hexane only influenced the degradation of PP samples which varied
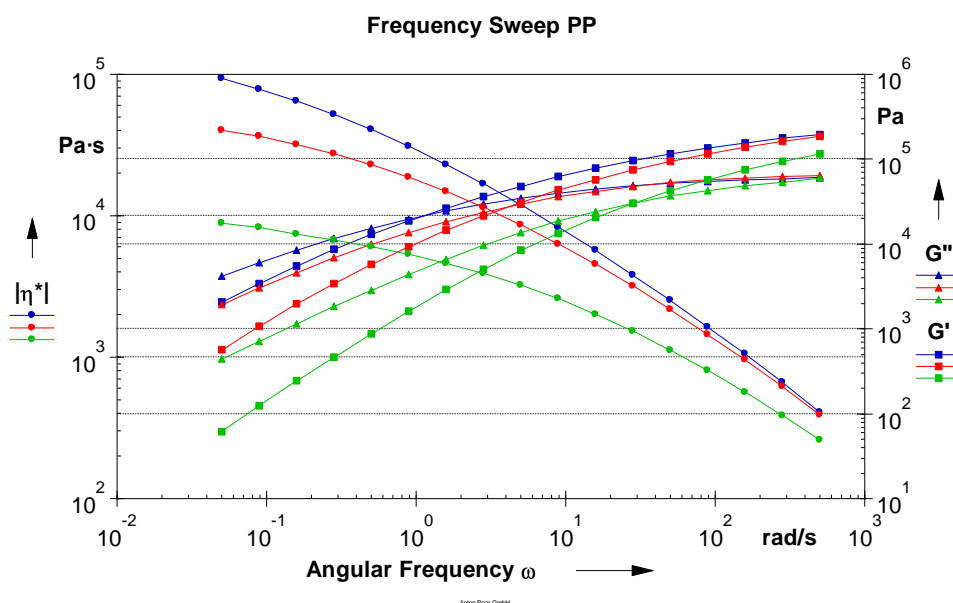
Frequency Sweep PP

Fig. 2. Rheological parameters of PP exposed in n-hexane for 3 months;
original (blue), 0 - 300 μm (red), 300 – 600 μm (green)
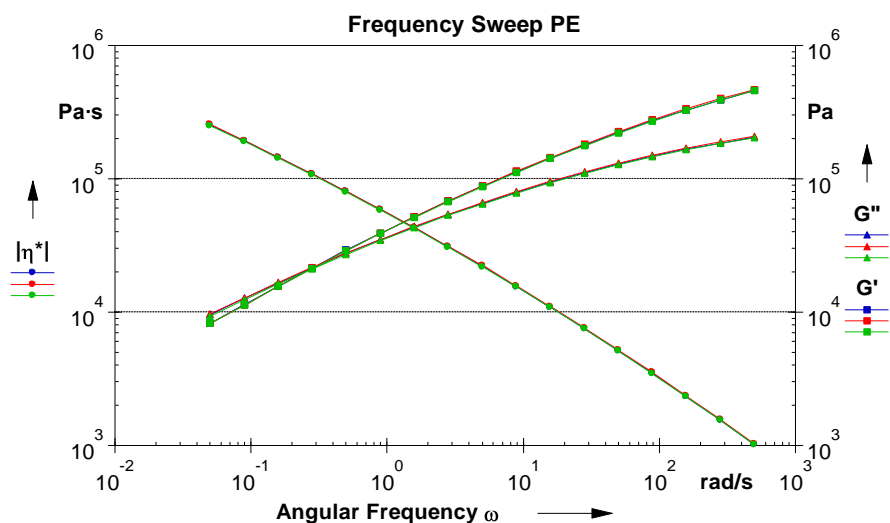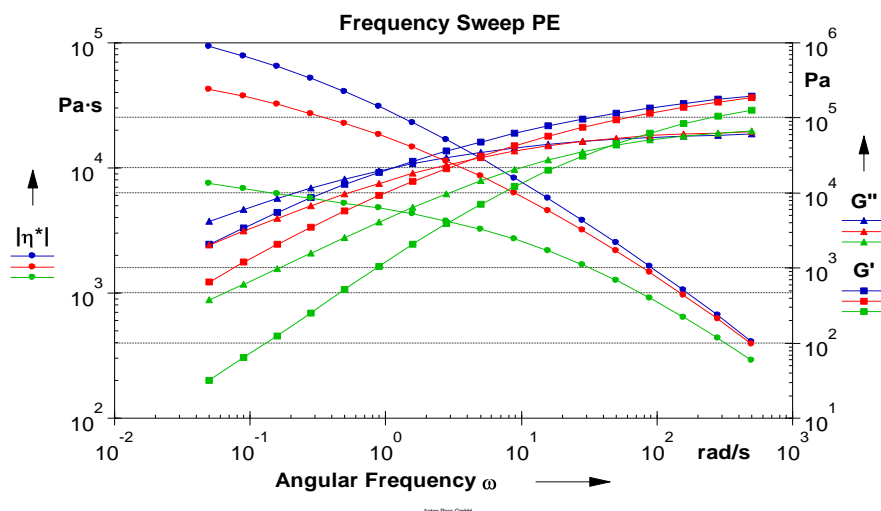
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Fig. 3. Rheological parameters of PE 500 exposed in n-hexane for 3 months;
original (blue), 0 - 300 µm (red), 300 – 600 µm (green)
(full colour version available online)

Fig. 4. Rheological parameters of PP exposed in n-hexane for 6 months;
original (blue), 0 - 300 µm (red), 300 – 600 µm (green)
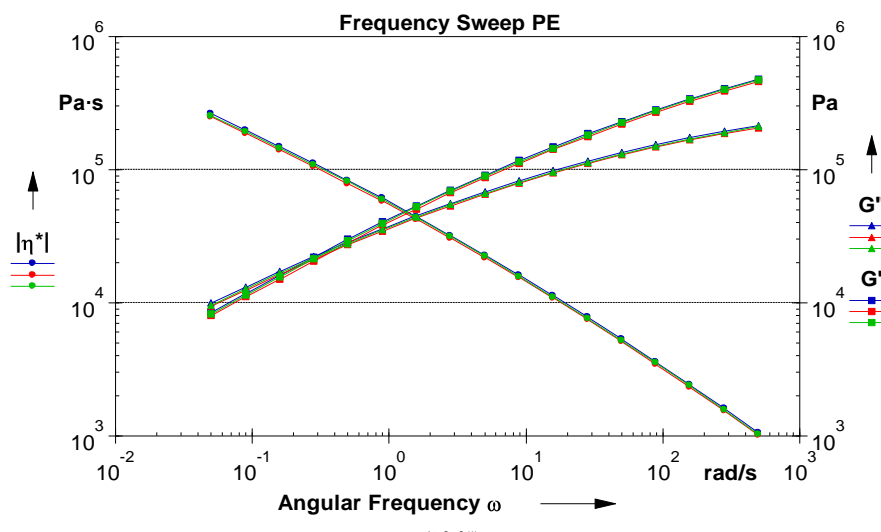*(full colour version available online)*

Fig. 5. Rheological parameters of PE 500 exposed in n-hexane for 6 months;
original (blue), 0 - 300 µm (red), 300 – 600 µm (green)
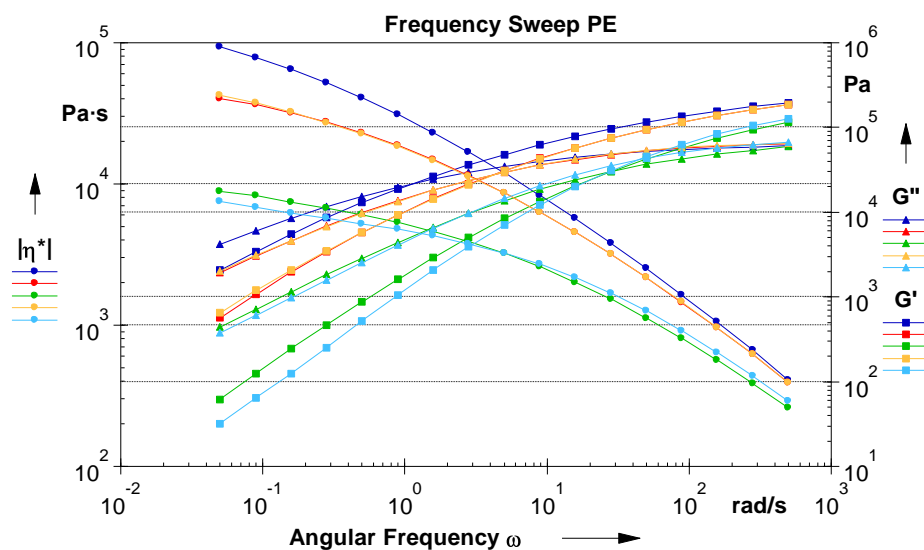*(full colour version available online)*

*Fig. 6. Rheological parameters of PP exposed in n-hexane for 3 and 6 months; original (blue),
after 3 months 0 - 300 µm (red), after 3 months 300 – 600 µm (green), after 3 months 0 – 300 µm
(yellow), after 3 months 300 – 600 µm (light blue)*

(full colour version available online)

in particular layers. The rheological characteristics of polyethylene material stay unchanged.

- Diffusion of molecules of n-hexane causes decrease of complex viscosity at low angular frequencies as well as decrease of complex and loss modulus. Shift of COP indicates changes as drop of average molar mass due to decomposition of bonds between the basic chains or decomposition of basic chain itself.

Acknowledgements

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