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ANALYSIS OF PHYSICAL PHENOMENA AND CHANGES IN THERMAL AND STRUCTURAL PROPERTIES OF POLYMER MATERIALS AFTER AGEING IN NATURAL CONDITIONS

INTRODUCTION

Natural (atmospheric) ageing is defined as a series of changes occuring in a material as a consequence of influencing of external factors. Usually this proces is initiated by sunlight (photodegradation). Its rate, on the other hand, is enhanced in particular by heat (thermodegradation) [1], as well as downfalls (hydrolytic degradation), air pollution, wind and internal stresses (mechanodegradation) [2]. Ageing under natural conditions is a process which causes slow destruction of polymeric materials [3], whereby the type and intensity of the entire changes depend incl. on the structure of the polymer or the type and intensity of the effect of factors causing changes in polymeric materials [4-5]. An extremely important role in the susceptibility to degradation is played by various types of modifying additives or polymer blends, especially of natural origin, which show lower resistance to environmental factors [6]. A complete understanding of the influence of atmospheric factors on changes in physical and mechanical properties of polymeric materials along with their correlation is important in terms of predicting the durability of materials. Past studies have shown that degradation of polymeric materials occurs much faster in hot, humid areas during exposure [7-9].

MATERIALS AND METHODS

The aim of this study was to determine the effect of atmospheric factors under the conditions of the European zone on the changes in the properties of selected polymeric plastics exposed for a period of 10 years.

The following thermoplastic materials were used for comparison: poly(amide) with 25% glass fibre content (PA6+25GF) and poly(styrene) (PS). The specimens were made on a KraussMaffei KM65-160 C4 injection moulding machine with a mould closing force of 650 kN. The obtained mouldings were exposed to atmospheric conditions in special holders set at an angle of 45°. The aged and non-aged samples were comparatively analysed by dynamic mechanical analysis (DMTA) and thermogravimetric analysis (TGA).

The recording of the mass changes of the tested samples with increasing temperature was carried out by thermogravimetric analysis (TGA) on a Netzsch STA 449 F5 Jupiter device. Analysis under dynamic conditions allows obtaining curves related to mass loss as a function of temperature. To improve the readability of the TGA curve, differential thermogravimetric analysis (DTG) is performed, where DTG curve is the first derivative of the thermogravimetric curve with respect to temperature or time.

Dynamic mechanical properties were tested using a Netzsch DMA 242 device. The specimens, in the form of beams measuring 56x10x4 mm, were subjected to three-point free bending of the specimen in a dedicated holder. The obtained results, prepared with Proteus Analysis software, were presented in the form of graphs of changes of storage modulus E' and the angle of mechanical loss tgδ as a function of temperature changes.

Tabele 1. Thermogravimetric analysis results for original and aged under natural conditions samples

Material	Mass change [%]	Residual mass [%]	DTG Peak [°C]
PA6 + 25GF original	72.91	24.45	452.6
PA6 + 25GF 10 years	71.43	27.90	440.2
PS original	99.47	0.12	428.4
PS 10 years	89.44	10.14	411.9

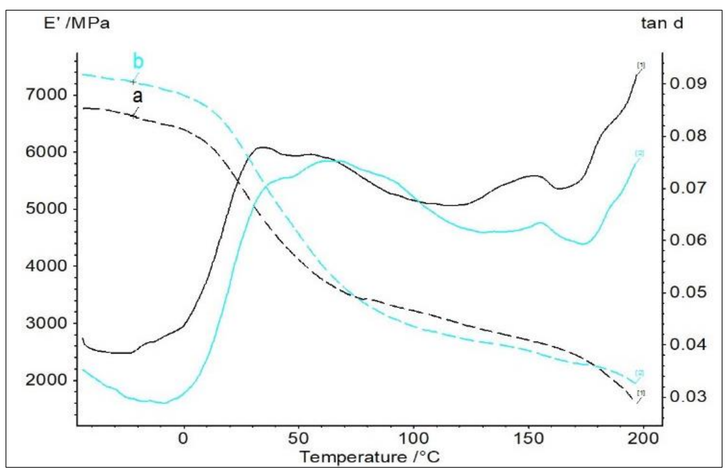

Fig. 1. The course of changes of storage modulus E' and angle of mechanical loss tgδ as a function of temperature changes for original (a) and aged PA (b)

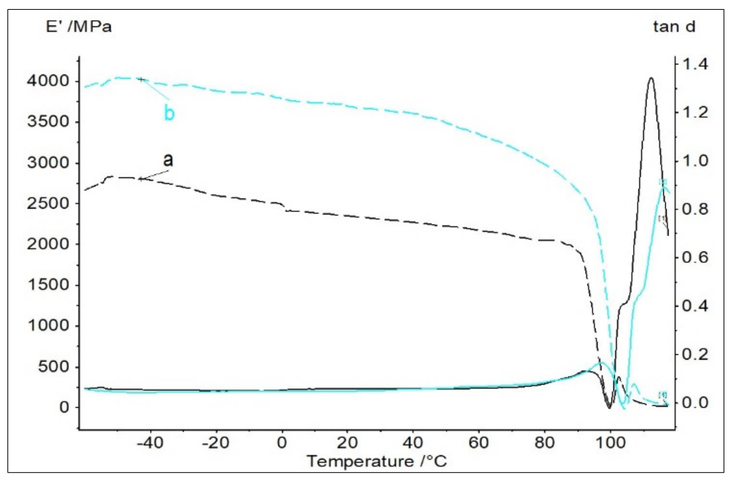

Fig. 2. The course of changes of storage modulus E' and angle of mechanical loss tgδ as a function of temperature changes for original (a) and aged PS (b)

RESULTS

Table 1 presents the summary results of the thermogravimetric analysis for the original and aged under natural conditions samples. The influence of atmospheric factors on changes in the mass of the tested specimens was determined. Due to the observation of changes of the tested surfaces, only the surface layer of the samples, where the influence of degradation factors and thus the observed changes were the largest, was selected for tests. For the primary samples made of pol(amide), the TGA and DTG curves remain constant until temperature of 252 °C is reached. Thereafter, a rapid weight loss of about 73% is observed. Analysis of the DTG curve shows that the highest rate of mass loss occurs at 452.6 °C. Ageing under natural conditions has shifted the temperature of the fastest mass loss as well as the rapid mass decrease towards lower values. The higher percentage of residual mass may indicate the loss of polymeric material on the surface of the aged samples. In turn, in the case of samples made of poly(styrene), the TGA and DTG curves remain constant up to a temperature of about 179 °C for original samples and about 120 °C for samples aged under natural conditions. The highest mass loss rate for the original samples occurs at 428.4 °C, while this value is 16.5 °C lower for the degraded samples. The higher residual mass of the aged samples may indicate the presence of organic compounds, formed under the influence of atmospheric conditions, which did not decompose under the influence of high temperature in the furnace chamber.

The effect of atmospheric conditions on the changes of dynamic mechanical properties for poly(amide) and poly(styrene) at vibration frequency of 1 Hz is shown in Figs. 1÷2. The dashed lines indicate the storage modulus and the solid lines - the values of the tangent of the mechanical loss angle.

The ageing of poly(amide) under natural conditions caused a decrease in the value of the storage modulus (Fig. 1) in comparison with the original material. For the non-aged material the value was 7400 MPa, while for the aged material it was 6800 MPa. A shift in the temperature at which the maximum occurs in the case of poly(amide) aged in natural conditions by several degrees can also be observed. In the temperature range 75 ÷ 180 °C, it can be observed that the values of storage modulus after ageing are larger than before, as well as a smaller difference between the positions of the two curves than at the beginning. Analysing the course of changes of the mechanical loss angle tgδ one can notice a similar range of temperatures in which the studied materials show the glass transition transformations. The aged samples are characterized by larger values of the angle in the course of the curve in comparison with the values obtained for the non-aged samples. Near the glass transition temperature, the viscoelastic properties change rapidly with changing temperature. The glass transition is more visible for the original material, not-subjected to natural ageing. Atmospheric conditions caused a decrease in stiffness, which may be related to the presence of more glass fibre on the surface compared to the reference sample.

Figure 2 shows the course of changes of the storage modulus E' and the mechanical loss angle tgδ as a function of temperature for unaged and aged poly(styrene) under natural conditions. It can be seen in the graph that the effect of weathering conditions caused a significant increase in the value of the storage modulus, which indicates an increase in the stiffness of the tested material. For the reference sample this value was 2830 MPa, while for the aged sample - it was 4040 MPa. In the case of the tangent of the mechanical loss angle, a shift in the temperature, at which the maximum occurs, can be observed.

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CONCLUSIONS

The analysis of the obtained results allows concluding that ageing under natural conditions influences the changes of properties of selected polymeric materials to varying degree, depending on their morphology.

Analysing the thermogravimetric curves, one can notice the differences in the values of residual masses as well as in the values of temperatures at the beginning and the end of weight loss and the values of temperatures at which the weight loss is the fastest.

The properties of aged polymeric materials depend largely on their supermolecular structure. Atmospheric factors had influenced the decrease in stiffness of the sample made of poly(amide) and its increase for the sample made of poly(styrene).