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Heating Temperature and Changes in the Physical and Structural Properties of Polymeric Materials

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The organic nature of the polymers can lead to instability of the material and even decomposition under different conditions. The article presents the results of the analysis of physical phenomena associated with thermal degradation of polymers. The samples produced by the injection moulding process were heated at 90°C for 5000 h. The research with the use of dynamic mechanical analysis were carried out on reference samples that were subjected to the thermal degradation process. The variability of physico–mechanical characteristics of the tested samples was determined in the range of the storage modulus and the tangent of the mechanical loss angle as a function of temperature. By means of thermogravimetric analysis, the loss of sample mass as a function of time during the annealing process was determined.

topics: polymeric materials, thermal ageing, termomechanical properties

1. Introduction

Mixing or blending materials is used to develop materials with new or improved properties. In these processes, it is extremely important to achieve a balance between strength and temperature resistance, and the ease of manufacturing such materials. Polycarbonate is characterised by high modulus, strength and impact resistance, as well as difficult processability. In turn, acrylonitrile–butadiene–styrene is a popular construction material due to its good mechanical and processing properties [1, 2]. The polycarbonate (PC) blend with acrylonitrile–butadiene–styrene terpolymer (ABS) is one of the most popular construction material, considered a good alternative to PC or ABS [3]. These blends are widely used in the production of car exterior and interior parts, as well as office automation equipment [4].

The organic nature of polymeric materials can lead to material instability or even decomposition under different conditions. Factors such as heat and high temperature can cause degradation of polymeric materials [5]. Therefore, it is important to conduct experimental studies to assess the resistance to elevated temperature of elements made of polymeric materials used in various industrial sectors [6, 7]. The composition of the polymer blend may influence the degradation behaviour and may differ from the degradation pathways of the individual components due to possible interactions between different types of material and degradation products. This may can lead to the stabilisation of the degradation process or acceleration of its rate compared to individual polymeric materials [8]. Observing thermal ageing of plastics at room temperature is very time-consuming, therefore, in order to shorten this time, accelerated thermal degradation tests are used [9]. Temperature and ageing time have a huge impact on the process of thermal degradation [7, 10, 11]. Long-term thermal ageing process often leads to decrease in mechanical properties [12, 13]. Damages from thermal ageing initially occur in the top layers of materials [14]. In the semi-crystalline materials subjected to the ageing process, the formation of new crystalline forms can be noticed as a result of breaking long chains, and thus increasing their degree of crystallinity. Under the influence of high temperature, the process of additional cross-linking of the material takes place [15, 16].

In this study, we attempted to investigate the effect of thermal ageing on changes in physico–mechanical properties with the use of thermal analysis of dynamic mechanical properties (DMTA) and thermal stability of an amorphous polymeric material.

2. Materials and methods

For the comparative tests, a PC/ABS blend from CHIMEI under the brand name WONDERLOY PC-365 with a 3% addition of GRAFE colour concentrate was used. The test samples were produced with the use of a KraussMaffei KM65-160 C4 injection moulding machine with a clamping force

of the mould of 650 kN. The obtained mouldings were placed in a pre-heated SANYO MOV-212S furnace. The ageing period began when the samples were placed in the furnace and lasted for 5000 h at a constant temperature of 90°C. The temperature at which the ageing process was carried out was determined on the basis of experimental tests with the use of thermogravimetry, so that the weight loss of the tested materials was as low as possible. The samples with mass of 20 mg were annealed in the STA 449 F5 Jupiter device from Netzsch at the temperatures of 90, 110 and 130°C in an atmosphere of air and argon. Thermogravimetric analysis (TGA) was also used to evaluate the thermal stability of the reference and ageing materials [17]. Samples with mass of 15 to 20 mg were heated at a rate of 10°C/min to a temperature of 750°C. Argon flow was used to avoid thermo-oxidative degradation.

In order to evaluate the changes that occur in the material as a result of degradation, the aged and non-aged mouldings were subjected to a comparative analysis of the dynamic mechanical properties. Samples, in the form of beams with dimensions of $56 \times 10 \times 4$ mm^3, were subjected to three-point free bending on the DMA 242 device from Netzsch [18]. The sinusoidal interaction of a variable force with a frequency of 1 and 10 Hz and a constant amplitude was introduced. The samples were heated in the temperature range of −150 to 120°C. The obtained results in the form of graphs of the changes of the storage modulus E' and the loss angle $\tan(\delta)$ were developed in the Proteus Analysis program.

3. Results

Figure 1 shows the results of initial annealing of samples for 100 h at different temperatures. These studies were necessary to determine the temperature of the thermal ageing process. It was important to heat the injection-moulded parts from PC/ABS blend to such a temperature that the loss of their mass was as low as possible. At 90°C, the weight loss was less than 2%. At higher temperatures, i.e, 110 and 130°C, the weight loss fluctuated within the range 4–4.5%. Additionally, in the case of the highest temperature, compared to the others, it can be observed that in the final phase of the annealing process, the dynamics of weight loss is higher.

Figure 2 shows the characteristics of the thermal decomposition for samples from PC/ABS before and after thermal ageing for 5000 h (208 days). The influence of the annealing time and temperature on the thermal stability of the tested samples was determined. No heterogeneous structure of the investigated materials was observed, as evidenced by one-stage decomposition processes.

For the non-aged samples, the initial decomposition temperature was approximately 362°C with a weight loss of 85.5%. After thermal ageing for 5000 h, it was observed that the onset of the decomposition of the polymeric material was much

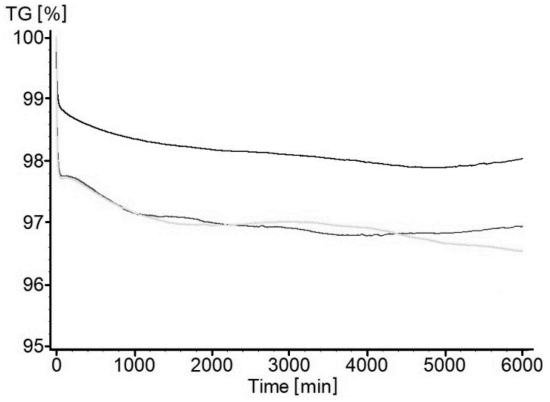

Fig. 1. Weight loss of the PC/ABS blend during annealing at the following temperature: (black line) 90°C, (gray line) 110°C, (light gray line) 130°C.

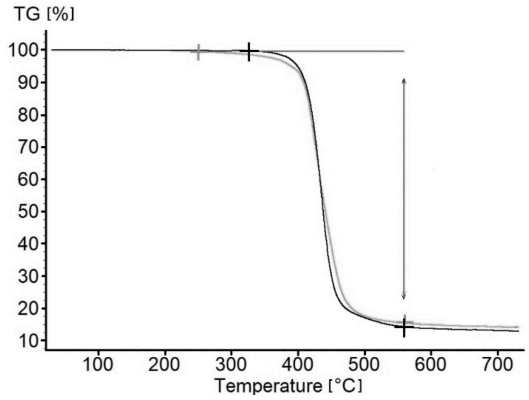

Fig. 2. TGA charts of PC/ABS samples before (black line) and after (gray line) thermal ageing for 5000 h.

earlier — at 251°C. The weight loss was 84.1%. With long-term ageing, breaks in the bonds in molecular chains are likely, which in the result reduces the temperature of the onset of degradation. The end of thermal degradation for the original and aged material occurs at the same temperature — about 559°C. The obtained results showed that the accelerated thermal ageing environment contributed to some extent to the deterioration of the thermal stability of the PC/ABS blend.

Figure 3 shows the course of changes in the storage modulus E' and the mechanical loss angle $\tan(\delta)$ as a function of temperature at the vibration frequency of 10 Hz for the unaged and aged PC/ABS blend at elevated temperature. The storage modulus is marked with solid lines and the values of the mechanical loss angle are marked with dashed lines. The frequency of 1 Hz was omitted in the presented results due to the identical nature of changes in dynamic mechanical properties in comparison to the higher frequency. It proves the low dependence of the viscoelastic behaviour of the tested material on the strain rate.

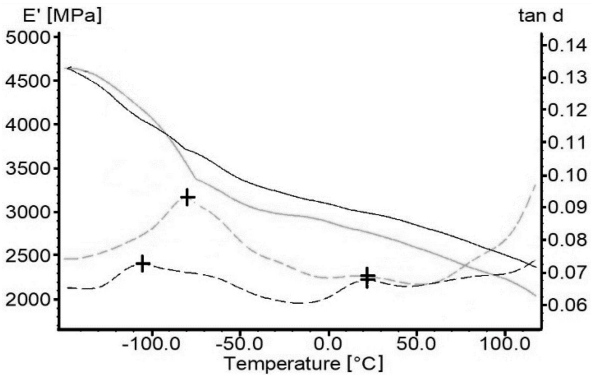

Fig. 3. The course of changes of the storage modulus E' and the angle of mechanical loss tan(δ as a function of temperature changes for primary (solid line) and aged (solid gray line) PC/ABS.

Comparison of the results of the storage modulus for aged and non-aged samples shows that the storage modulus in the temperature range from −90 to 120°C for the aged specimens has a higher value than for the unaged specimens in the same test conditions. Lowering the value of the storage modulus to a higher value for both samples may be justified by the greater mobility of the polymer chains at elevated temperature. In the temperature range from −150 to −90°C, the value of the storage modulus of the reference sample is slightly higher than that of the aged sample. With increasing temperature, the difference between the values of the storage modulus of the primary and after ageing samples increased.

When analysing the course of changes in the angle of the mechanical loss tan(δ), one can notice the occurrence of two, less distinct peaks at the temperatures of −105.5°C and 22°C. In the case of the aged sample, the main clear tan(δ) peak occurs at −80°C, while the secondary peak, less distinct compared to the original material is at 22°C. The glass transition is more visible for material aged at elevated temperature. As the temperature increases, the damping properties of PC/ABS blends increase. As a result of numerous changes taking place in the material under the influence of elevated temperature, an increase in the stiffness of the material after the ageing process can be noticed. Near the glass transition temperature, an increase in the dynamics of the viscoelastic properties of the aged and non-aged material was observed.

4. Conclusions

The influence of thermal ageing on changes in physical and mechanical properties of PC/ABS samples was investigated. The conducted preliminary tests showed that heating the material at 90°C causes the smallest loss of its mass. When analysing the thermogravimetric curves, it can be noticed that the accelerated thermal ageing environment contributed to the deterioration of the thermal stability of the PC/ABS blend. The temperature of the onset of thermal degradation of the aged sample has shifted significantly towards lower values. Heating the material at 90°C for 5000 h increased the stiffness of the PC/ABS blend moulding. It was noticed that the nature of the changes is the same for the frequencies of 1 and 10 Hz. The results of the research carried out indicate that thermal ageing at 90°C contributes to changes in the physical and thermal properties of the PC/ABS blend, which initially occur in the outer layers of the material.

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