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Effect of Radiation with Wavelength of 313 nm on Changes in Physical Properties and Structure of Polymers

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The aim of this work is to examine the thermomechanical and structural properties of thermoplastic materials. Standardised test samples were subjected to the ageing process under accelerated conditions with a lamp length of 313 nm and an irradiation level of 0.76 W/m^2. On the basis of the literature data, the radiation dose necessary to obtain the value of energy reaching the earth surface in the European zone corresponding to a period of 2 years under natural conditions was determined. The research included the determination of the quantitative crystalline phase index, temperatures of phase transformations using the differential scanning calorimetry method and thermomechanical analysis at dynamically changing loads. The variability of physicomechanical characteristics of the tested samples in the range of storage modulus and tangent of mechanical loss angle as a function of temperature was determined.

topics: polymeric materials, UV ageing, thermomechanical properties

1. Introduction

In terms of the ageing processes, in addition to long-term tests, short-term (accelerated) tests are also applied. They are carried out in special laboratory devices, in which basic climatic factors such as UV radiation, water or increased temperature are used. In accelerated tests, materials are exposed to higher intensity of radiation, temperature or humidity than in natural environment in order to obtain fast decomposition of polymer in the shortest possible time [1]. In the case of long-term (natural) tests, the choice of factors depends only on weather and environmental factors. Such tests are carried out in a climate typical of the country and the specimens are exposed in open and unshaded places, facing south at an angle of 45° [2–5].

Both the natural and accelerated ageing induce comparable changes in polymeric materials. In view of the fact that depending on the climate zone the weather conditions under which materials are tested vary, short-term tests are a reliable method for assessing colour change as well as durability properties [6–9]. For example, it was shown [10] that the acceleration of photooxidation ranged from 2.5 to 10 times compared to outdoor exposure, depending on the accelerated room conditions.

The aim of this study was to analyse the dynamic changes of mechanical and structural properties of polymeric materials subjected to accelerated UV ageing, corresponding to a period of 2 years in natural conditions.

2. Materials and methods

Research specimens of poly(acetal) (POM) and acrylonitrile-butadiene-styrene terpolymer (ABS) were made using a KraussMaffei KM65-160C4 injection moulding machine. In addition, a 3 wt% GRAFE colour concentrate was added to all materials in a carrier appropriate for each polymer.

The radiation source was eight fluorescent lamps with a wavelength of 313 nm UV-B. Intensity of radiation is measured in kLy (kilo Langley), i.e., the units used to measure sunlight. The literature data show [11, 12] that the average radiant intensity in the European zone is 120 kLy/year, at a radiation intensity of 1.33 W/m^2, which corresponds to 100 h of ageing tests under laboratory conditions. Assuming radiation intensity of 0.76 W/m^2, the total test time was 600 h, which is equivalent to 2 years of ageing in natural conditions.

The Differential Scanning Calorimetry (DSC) was used to evaluate changes in the structure of polymeric materials. This method makes it possible to observe and measure thermal effects accompanying the phenomena occurring in the studied samples. This technique takes advantage of differences in the flow of heat fluxes between the furnace and the tested substance as well as between the furnace and a reference sample under the influence of a given temperature. One then uses

$$\Phi_m = \Phi_S - \Phi_R, \tag{1}$$

where Φ_m — the difference of heat fluxes, Φ_S — the heat flux between the furnace and the tested substance, Φ_R — the heat flux between the furnace and the reference sample.

DSC tests make it possible to determine the degree of crystallinity, melting and crystallisation temperatures, glass transition temperature and more other parameters. The tests were performed on a DSC 214 Polyma from Netzsch. The heat transfer rate is the amount of heat transferred per unit time ($\mathrm{d}Q/\mathrm{d}t$), expressed in watts [W] and milliwatts [mW]. The crystalline phase content (α_j), on the other hand, is determined from the following relationship:

$$\alpha_j = \frac{\Delta H_j}{\Delta H_{\mathrm{tot,th}}} \times 100\% \tag{2}$$

where ΔH_j — the enthalpy of sample melting [J/g] determined from the thermogram, $\Delta H_{\mathrm{tot,th}}$ — the theoretical enthalpy of melting of the completely crystalline polymer.

Dynamic mechanical properties tests by the DMTA method were used to evaluate the transformations that take place in the polymers as a result of their degradation. The aged and reference specimens were subjected to periodically varying mechanical loads as a function of temperature (Fig. 1). The obtained graphs allowed for the determination of the values of the storage modulus E' and the angle of mechanical loss $\tan(\delta)$. Specimens of dimensions $56 \times 10 \times 4$ mm^3 were prepared and subjected to three-point free bending. Sinusoidal variable force interactions with frequency of 1 and 10 Hz and constant amplitude were introduced. The specimens were heated from ambient temperature to 160 °C for poly(acetal) and 140 °C for ABS. The obtained results were developed using the Proteus Analysis software.

3. Results

Figures 1 and 2 show DSC thermograms of the samples before and after ageing. In order to remove the thermal history of the tested samples and the influence of their processing, a program in which there is a second heating in addition to the first heating of the tested samples was used.

In the case of poly(acetal) (Fig. 1), a decrease in the enthalpy of melting was observed after the accelerated UV ageing process. Based on this value, it was possible to calculate the degree of crystallinity, which was 47.9% for the original sample and 27.3%

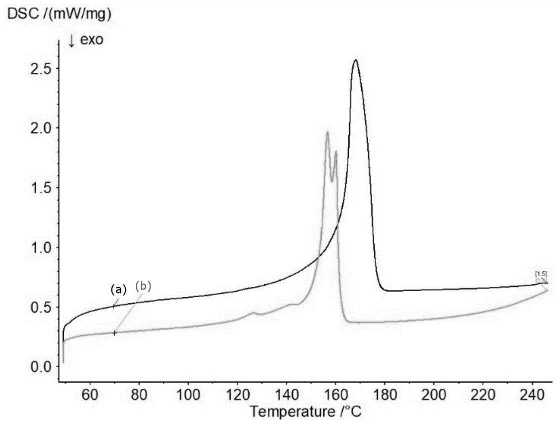

Fig. 1. DSC thermograms for POM: original sample (a), aged sample (b).

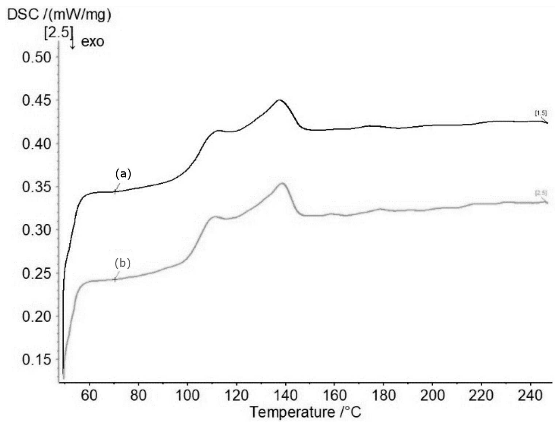

Fig. 2. DSC thermograms for ABS: original sample (a), aged sample (b).

for the aged sample. The degradation resulted in the formation of shorter, irregular sections of macromolecules, which led to a weakening of the nucleation process, that can be observed in the form of an increase in the proportion of the amorphous phase in relation to the crystalline phase. The melting temperature range also narrowed. Significant shifts of the melting and crystallisation temperatures towards lower values were observed too, which could be caused by a change in the molecular weight distribution of the studied material. Furthermore, an additional peak can be observed.

Samples, which are made of acrylonitrile-butadiene-styrene terpolymer (Fig. 2), were characterised by a slight decrease in glass transition temperature (by about 2 °C) after ageing. An increase of ΔC_p was also observed, which may indicate a strengthening of the material. The obtained results show that amorphous polymers are less susceptible to UV radiation than partially crystalline ones.

Table I presents the collective results of the values of the storage modulus (E') and the mechanical loss angle $\tan(\delta)$ for the samples before and after

TABLE I

Values of storage modulus and tangent of the mechanical loss angle for polymers before and after UV ageing.

Material	E' at 50 °C [MPa]	E' at 100 °C [MPa]	$\tan(\delta)$ at 50 °C	$\tan(\delta)$ at 100 °C
POM_org	2250	1085	0.067	0.130
POM_600h	2021	984	0.048	0.109
ABS_org	2839	800	0.040	0.081
ABS_600h	3246	1039	0.090	0.095

UV ageing. Due to the equal nature of the changes in the E' and $\tan(\delta)$ values at 1 Hz and 10 Hz, the higher frequency was omitted.

UV ageing of poly(acetal) caused a decrease in the value of the storage modulus. At temperature of 50 °C, the difference was about 230 MPa. As the temperature increased, the difference between the values of the storage modulus of the original and aged samples decreased. The maximum value for the non-aged material was 2597 MPa and for the UV-exposed material — 2361 MPa. A slight shift in the temperature at which the maximum occurs in the case of aged POM can also be observed. In turn, analysing the changes in the mechanical loss angle $\tan(\delta)$ and the storage modulus E', no clear changes can be seen in the material under the influence of temperature. The damping properties of aged and non-aged POM increase with increasing temperature.

Analysing the course of changes of storage modulus E' and the mechanical loss angle $\tan(\delta)$ as a function of temperature for acrylonitrile-butadiene-styrene terpolymer unaged and aged in accelerated conditions, it can be observed that UV radiation caused an increase in the value of storage modulus by about 400 MPa. This may indicate an increase in the stiffness of the studied material. In the case of the tangent of the mechanical loss angle, it can be noted that ageing caused a shift in the temperature at which the maximum value occurs. In the temperature range $95 \div 120$ °C, a sharp decrease in the value of the storage modulus can be observed. For aged specimens, this decrease is sharper and more rapid than for the reference material.

4. Conclusions

The analysis of the obtained results allows concluding that UV radiation influences the change of properties and structure of polymeric materials. The research has shown that after ageing the values of such effects as melting point, glass transition temperature or degree of crystallinity decrease. The samples made of amorphous polymers are characterised by greater resistance to UV radiation — their degradation proceeds much more slowly than in the case of samples made of semi-crystalline polymers.

An important factor in accelerated tests using laboratory methods is also the comparison of their results with similar tests in natural conditions. This is due to the fact that then, in addition to the effect of UV radiation to a greater extent, there are also changes in temperature, humidity or the effect of rainfall and other chemical substances present in the atmosphere.

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