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POLSKA AKADEMIA NAUK

Arch. Metall. Mater. **68** (2023), 4, 1519-1524

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ANALYSIS OF CHANGES IN THE PHYSICAL PROPERTIES AND STRUCTURE OF POLY(OXYMETHYLENE) AFTER AGEING IN NATURAL CONDITIONS AND ACCELERATED BY UVB-313 nm RADIATION

The paper presents the results of the analysis of physical phenomena associated with the degradation processes of the surface layer of polymeric materials. During the interaction disturbance of ultraviolet radiation, atoms are knocked out of the polymer chains, thus breaking the macromolecules, which leads to the disturbance in the structural stability of the materials. The standardised test samples obtained using the injection moulding method were subjected to the degradation process in natural and accelerated conditions in the UV Test device. The degradation process in laboratory conditions was carried out during 750 hours with the use of lamps with a wavelength of 313 nanometers and an irradiation level of 0.76 W/m^2, which corresponds to a period of 2 years in natural conditions. Using of thermogravimetric TGA and differential scanning calorimetry DSC analysis, the influence of energy applied from lamps and the energy reaching the earth's surface on the change of melting enthalpy ΔH_m, quantitative index of the crystalline phase and the temperature of phase changes were determined.

Keywords: poly(oxymethylene); natural weathering; UV ageing; thermal analysis

1. Introduction

In recent decades, the use of polymers, compared to many materials, has increased significantly due to their good mechanical properties and durability [1]. Plastics are subject to ageing processes, losing their physical and functional properties over time. As a result of the impact of these processes, strength decreases, brittleness increases, and tendency to delamination appears [2-4]. Structural changes in polymeric materials may be the result of chemical or physical changes during processing, storage and exploitation. Factors impacting on the ageing process of plastics include: heat, light radiation and the influence of various substances (e.g. moisture). Often, in order to improve the resistance to UV radiation, various types of light stabilisers are added in the processing processes, whose task is to limit or delay the degradation processes occurring in the material [1,5].

Due to the increasing use of polymeric materials in applications in which plastic elements are exposed to the effects of UV radiation and other environmental degradation processes, it is necessary to know the impact of these factors on the mechanical properties of the used polymeric materials [1,6]. There are many factors in the natural environment that can contribute to the degradation of polymeric materials. These include, among others: solar radiation, gases and elements present in the air (nitrogen, oxygen, ozone, carbon dioxide, nitrogen oxides NOx), precipitation and temperature changes. The interaction of many factors may contribute to the intensification of degradation processes [7,8]. The interaction of these factors also causes difficulties in capturing the intensity of the action of individual factors on the changes in properties occurring in the polymer. Photooxidation is the most important factor in the natural degradation of weathering [9]. Testing the durability of polymeric materials in natural conditions is not only a labour-intensive process, but also including uneven changes and a slow degradation rate. In order to be able to observe noticeable changes in polymer materials, long-term exposure to environmental factors is necessary. In order to obtain the same average effectiveness of the action of climatic factors, long-term studies must last for at least several complete climatic cycles. The necessity to use such long research periods is also due to the slow rate of changes and the need to obtain certain information. The development of new products and their introduction to the market requires fast and reliable accelerated durability tests that can predict the service life of materials [10]. In order to accelerate the degradation phenomena and to predict the changes occurring under the influence of factors, ageing in laboratory conditions (accelerated

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ageing) is used [6,11]. In such procedures, the long-term preservation of polymeric materials is usually predicted by subjecting them to alternating cycles of radiation, temperature changes, steam condensation and other external factors with much greater intensity than that occurring under real conditions [12]. Due to the fact that changes in the properties of polymers are mainly caused by photochemical reactions, with the participation of heat, most correlations between artificial and natural exposure assume a close relationship between the decomposition rate and UV radiation and an increased temperature of the performed tests [6,13,14]. In accelerated ageing tests, samples are exposed to action of higher radiant intensity, temperature and humidity than is likely under natural ageing conditions in order to achieve rapid degradation of the polymer in a convenient short time [15].

Natural weathering is determined by the location, weather and climatic conditions, the day and night cycle and the change of seasons [16]. Contrary to natural conditions, ageing under accelerated conditions is carried out at elevated temperatures, which under environmental conditions are achieved only with intense radiation in the warm season [13]. Laboratory ageing tests only partially simulate natural ageing, as demonstrated by the authors in [17]. The differences between the tests may be caused by different microclimates in relation to standardised laboratory tests. Under appropriate research conditions, it is possible to obtain a high correlation between natural and accelerated ageing [18-20]. In work [21] it was shown that the structural and mechanical properties change faster at higher temperatures and levels of UV radiation. Weathering in different climatic zones affects the rate of degradation of polymer materials, but does not change its mechanism [22]. During both types of ageing, modifications in the material occur mainly in the surface layers, causing fogging and micro-cracks. Their presence has a destructive effect on the polymer as it allows of the penetration of volatile substances, such as oxygen and liquids, in the deeper layers of the material, which contributes to the intensification of chemical degradation processes [23]. During weathering, loose, degraded polymer particles are also washed away, which in turn reveals further areas and layers of the native material.

Plastic products should maintain their chemical, physical, mechanical and aesthetic properties throughout their useful life, often for many years. However, they are exposed to influence of light, oxygen, elevated temperature and water during their use. Understanding the processes of destruction and degradation and the possibility of preventing them is very important for both plastics processors and users of products. Assessment of polymer ageing is very important to the long-term efficiency of polymeric materials, but correlating accelerated assessments with real-time procedures remains a challenge [24].

2. Research material and methods

The aim of the study was to assess the impact of degradation processes in natural and accelerated conditions on changes in the properties of poly(oxymethylene) (POM) injection mouldings

parts. The homopolymer under the trade name DuPont ™ Delrin® 500P NC010 with a melt flow rate (MFR) of 15 g/10 min was used for the tests. The tests were carried out with a load 2.16 kg and 190°C. Poly(oxymethylene) is a thermoplastic structural polymer characterised by high hardness, good mechanical and sliding properties, as well as abrasion and creep resistance. It is widely used in the engineering and automotive industries as well as in construction. This material is also used in the production of friction bearings, rollers, gears and gear components.

The test specimens, in the shape of A1 paddles in accordance with the PN-EN ISO 527-2:2012 standard, were made using a Krauss-Maffei KM65-160 C4 injection moulding machine with a mould clamping force of 650 kN. The material was pre-dried at the temperature of 80°C for 4 hours with the use of a laboratory shelf dryer Shini CD-09. The samples were injected into a thermostated two-cavity injection mould with a parallel arrangement of the feed channels using the following process parameters:

- Injection temperature T_w = 210°C,
- Mould temperature T_f = 90°C,
- Injection pressure (maximum) p_w = 120 MPa,
- Injection time t_w = 0.58 s,
- Injection speed v_w = 50 mm/s,
- Holding pressure p_d = 65 MPa,
- Holding time t_d = 20 s.

After the test samples were produced, they were aged in natural and laboratory (accelerated) conditions. The obtained mouldings were exposed to the effects of weather conditions in special holders, set at an angle of 45°C to the ground for 2 years in the conditions of the European zone. Artificially simulated (accelerated) ageing was performed in the Atlas UVTest device. The source of the radiation was eight fluorescent lamps emitting radiation with a wavelength of UVB-313 nm. The test program was established in accordance with the ISO 4892-3 standard, and the conditions were selected in accordance with the climatic conditions of Poland. The entire cycle has been extended to include rainfall (simulating rain in natural conditions). The research assumed the average intensity of solar radiation in the European zone at 120 kLy/year (kilo Langley), with the intensity of radiation 1.33 W/m². With the radiation intensity of 0.76 W/m² assumed for the tests and the total test duration of 750 hours, the tests performed are approximately the equivalent of 2 years of natural ageing.

The aged and non-aged samples were subjected to comparative analysis. The method of differential scanning calorimetry (DSC) was used to assess changes in the structure of polymeric materials. Thanks to it, it is possible to observe the thermal effects accompanying the phenomena occurring in the tested samples. The research was performed with the use of the DSC 214 Polyma device by Netzsch. The samples weighing about 10 mg were sealed in aluminium crucibles and were initially heated from 20 to 220°C at a rate of 10°C/min (first heating), then cooled to 20°C at the same rate and reheated to 220°C (second heating). From the obtained thermograms, the degree of crystallinity, the enthalpy of melting (ΔH_m), the peak melting point (T_m), the crystallisation temperature (T_c) and the crystallisation enthalpy (ΔH_c) were determined. Thermal decomposition along with thermal

stability were investigated by means of thermogravimetric analysis (TGA) using the STA 449 F5 Jupiter coupled analysis device from Netzsch. The samples were heated in the temperature range from 35 to 750°C with a heating rate of 10°C/min under an argon atmosphere. On the basis of the obtained results, the temperature of the beginning and end of weight loss, the percentage of the remaining residue and the temperature at the maximum decomposition rate determined from the curve of the first TGA derivative were defined. In addition, the research was extended to microscopic observations at ×200 magnification using the Keyence VHX-7000 digital microscope.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC)

The DSC analysis was carried out to assess the change in thermal effects resulting from ageing in natural and laboratory conditions in the structure of POM samples. The influence of radiation in natural and laboratory conditions on the melting and crystallinity of the tested samples was assessed. The results of all tested samples are presented in TABLE 1. In order to remove the thermal history of the tested samples and the influence of their processing, the H-C-H program (I heating-cooling-2 heating) was used. The enthalpy of melting was used to calculate the degree of crystallinity of the tested samples.

Fig. 1 shows the DSC thermograms from the first heating, which present three graphs – the primary sample (blue), aged for 2 years in natural conditions (green) and aged in accelerated conditions UVB-313 nm 750 h (violet). The results of the first heating show the direct influence of exposure to UV radiation and atmospheric conditions on the melting and the degree of crystallinity. In the samples subjected to the ageing process, both in natural and laboratory (accelerated) conditions, a drop in the melting point was observed in relation to the samples not subjected to ageing. The enthalpy of melting and hence the degree of crystallinity increased significantly. Under the influence of UV radiation, it is likely that unstable crystals were formed during the recrystallisation process, which were too weakened during the reheating process to crystallise into more stable forms. The changes in the value of the degree of crystallinity in the first heating directly showed that the conditions under which the ageing processes were carried out, directly affect the degree of polymerisation of the material.

Fig. 2 shows thermograms from cooling of all tested materials. The enthalpy of crystallisation decreased after ageing both under natural and accelerated conditions, which may indicate an overall decrease in the degree of crystallinity. All types of ageing (natural and accelerated) showed an increase of about 1°C in the crystallisation temperature as compared to the temperature value of the non-aged sample

The analysis of the obtained results after removing the thermal history of the tested samples (Fig. 3) showed a significant

TABLE 1

Degree of crystallinity, melting and crystallization temperatures and enthalpies of primary and aged samples obtained by DSC method

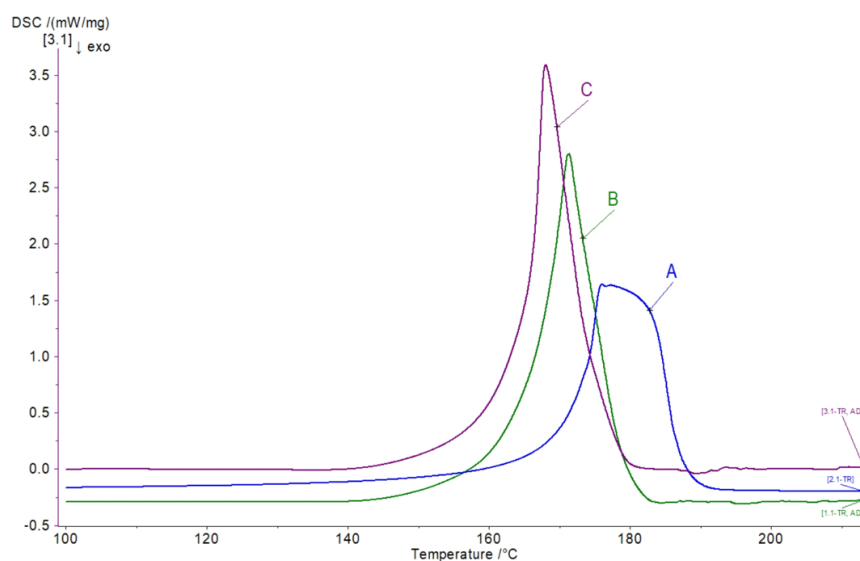| Sample	1 heating			cooling		2 heating		
	T_m, °C	ΔH_m, J/g	Degree of crystallinity, %	T_c, °C	ΔH_c, J/g	T_m, °C	ΔH_m, J/g	Degree of crystallinity, %
Primary (reference)	176.0	149.3	45.81	148.6	165.2	180.2	158.9	52.66
2 years of natural ageing	171.3	189.7	58.18	149.8	103.0	169.6	100.1	31.99
750 h, UVB-313 nm	168.0	197.4	60.55	149.4	113.4	166.8	116.5	36.84

Fig. 1. DSC thermograms for POM – 1 heating: primary sample (A), sample aged in natural conditions (B), sample aged in accelerated conditions (C)
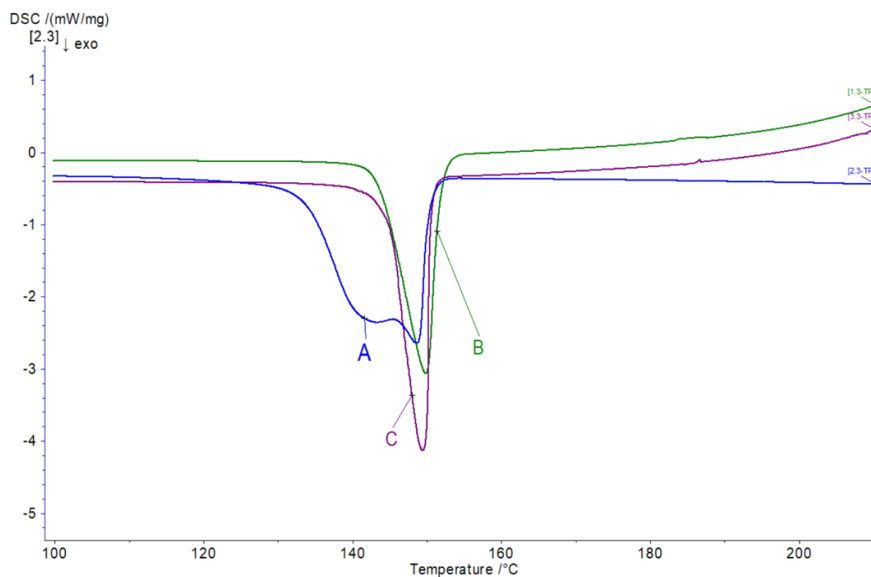
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Fig. 2. DSC thermograms for POM – cooling: primary sample (A), sample aged in natural conditions (B), sample aged in accelerated conditions (C)
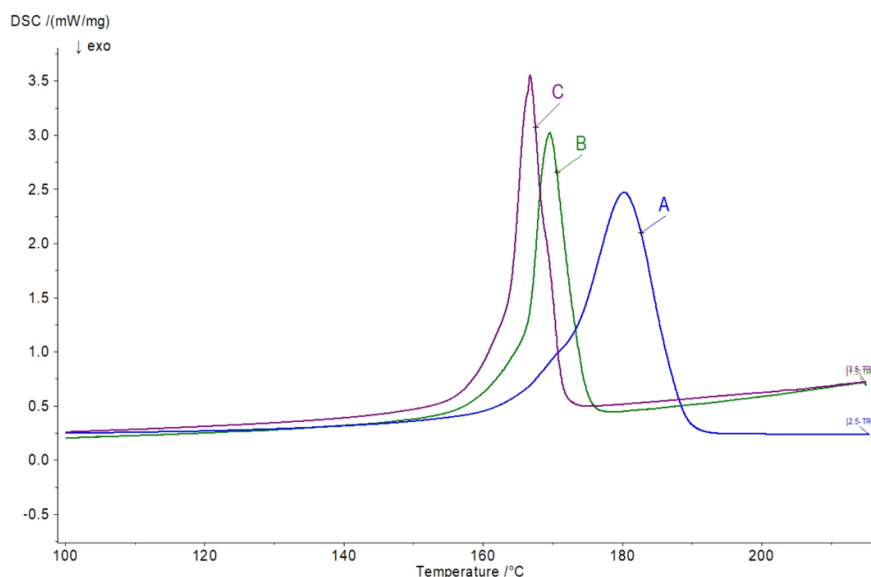

Fig. 3. DSC thermograms for POM – 2 heating: primary sample (A), sample aged in natural conditions (B), sample aged in accelerated conditions (C)

shift of the melting point of the materials after ageing towards lower values. The drop in melting points may be due to the shortening of the polymer chain length and thus chain breakage. Moreover, the melting enthalpy also changed under the influence of the factors causing the ageing of poly(oxymethylene) under natural and accelerated conditions. A significant decrease in the degree of crystallinity was observed, which may indicate an increase in the share of the amorphous phase and a decrease in the crystalline phase. The degradation of the material most likely resulted in the formation of shorter, irregular stretches of macromolecules, which weakened the nucleation process.

From the conducted research it can be concluded that the factors that contribute most to the degradation of poly(oxymethylene) are UV rays, increased temperature and humidity, which, thanks to their synergistic action, intensify the degradation processes.

3.2. Thermogravimetric analysis (TGA)

Fig. 4 shows the characteristics of the thermal decomposition for POM samples before and after ageing. The influence of natural and accelerated ageing on the thermal stability of the tested samples was determined, the results of which are presented in TABLE 2. No heterogeneity of the structure of the tested materials was observed, which is evidenced by one-stage decomposition processes.

For the unaged samples, the initial decomposition temperature was around 259°C with a weight loss of 99.13%. After natural and accelerated ageing, a significant shift of the initial decomposition temperature towards lower values was observed. For weathering the starting temperature was about 100°C, and for laboratory ageing about 108°C. The weight loss was successively 99.21% for natural weathering and 99.88% for UV

Results of thermogravimetric analysis for primary samples, aged in natural and accelerated conditions

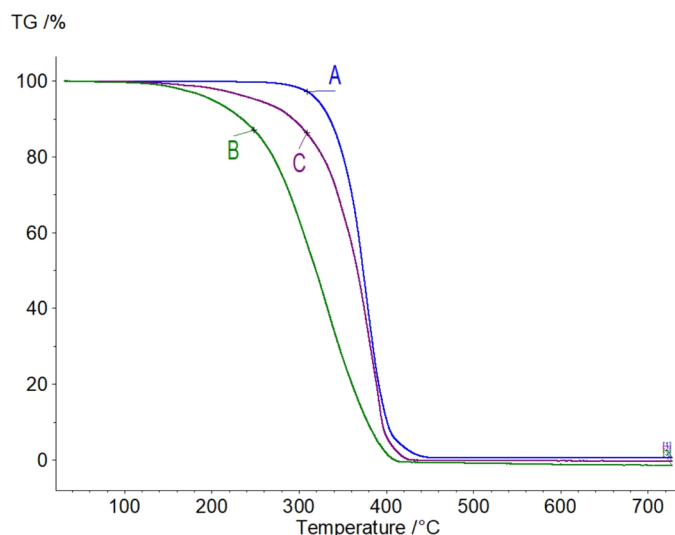| Sample	Temperature range, °C	Mass change, %	Residual mass, %	Temperature at which mass loss is fastest, °C
Primary (reference)	259.3÷448.8	99.13	0.87	384.9
2 years of natural ageing	100.6÷430.7	99.21	0.79	331.5
750 h, UVB-313 nm	108.6÷439.7	99.88	0.12	381.1

Fig. 4. TGA charts of POM samples before ageing (A), after natural ageing (B), after accelerated ageing (C)

the greatest impact on the deterioration of the thermal stability of samples made of POM. Ageing in laboratory conditions also significantly influenced the changes in the thermal stability of the material, however, the conducted research showed a slight influence on the temperature value, in which weight loss occurs most quickly.

3.3. Microscopic observations

The surface morphology of the samples after ageing in natural and accelerated conditions compared to the original sample is shown in Fig. 5. It can be seen that the surface of the untreated sample is smooth, with small scratches resulting from scratching the mould.

During natural ageing, as a result of the degradation processes, cracks spontaneously form on the surface of the sample in the direction parallel to the injection point, which gradually increase with the increase of the weathering time. Multiple cracks are parallel to each other and have a regular distance between them. Despite numerous cracks, the surface layer is compact and the chalking phenomenon does not occur. In the case of samples aged in laboratory conditions, the first small and irregular cracks begin to appear after 750 hours. A powder was formed on the surface of the samples, which may indicate the occurrence of the chalking phenomenon. At higher magnification, the surface of the tested samples shows numerous gaps in which there are loose particles of material, separated from the parent material. This means that the surface of samples made of poly(oxymethylene) under accelerated conditions is much more susceptible to degradation processes compared to the surface of samples exposed to weather conditions. It may be related to the relative higher humidity and constant influence of higher temperature than in the natural environment.

ageing in the chamber. During the ageing processes, the bonds in the molecular chains were probably broken, which in turn resulted in a significant reduction in the temperature of the onset of degradation. Ageing in natural and accelerated conditions influenced to a lesser extent to the temperature of the end of thermal degradation of the tested materials. The end of the degradation takes place at 449°C for the original material, 431°C for the material aged in weather conditions and 440°C for the material aged under accelerated conditions, respectively. The UV radiation in the chamber did not significantly affect the temperature at which weight loss occurs most quickly. On the other hand, the atmospheric conditions caused the temperature drop with the maximum coefficient of weight loss by more than 50°C in relation to the value of the unaged sample. The obtained results showed that ageing in natural conditions had

Fig. 5. Surface of POM samples: primary sample (A), sample aged in natural conditions (B), sample aged in accelerated conditions 750 h (C)

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4. Conclusion

The influence of natural and accelerated (laboratory) ageing on changes in structural properties and surface properties of samples made of poly(oxymethylene) was investigated. The main aim of the study was to evaluate and compare the effects of ageing in natural conditions for a period of 2 years and in laboratory (accelerated) conditions. The samples in the chamber were aged for a period equivalent to that of 2 years under natural conditions. It can be shown that similar degradation results were obtained in natural and artificial tests.

The thermal analysis by DSC was carried out to assessment of changes in the structure properties of the tested materials. Research has shown that after natural and accelerated ageing, the value of the enthalpy of melting, and thus the degree of crystallization, decrease. During the influence of the factors on the material, their phase composition most likely changed – the ratio of the amorphous phase to the crystalline phase increased in relation to the original samples. A decrease in the melting point and a slight increase in the crystallisation temperature were also observed.

When analysing the thermogravimetric curves, it can be noticed that both the atmospheric factors and the conditions in the ageing chamber significantly contributed to the deterioration of the thermal stability of samples made of poly(oxymethylene). The temperature of the onset of degradation of the aged samples has shifted significantly towards lower values.

The degradation of semi-crystalline materials most likely resulted in the formation of shorter, irregular stretches of macromolecules, which weakened the nucleation process and contributed to a decrease in thermal stability. From the conducted research it can be concluded that the factors that contribute most to the degradation of poly(oxymethylene) are UV rays, increased temperature and humidity, which, thanks to their synergistic action, intensify the degradation processes.

Microscopic observations showed that the surface of samples made of poly(oxymethylene) under accelerated conditions is much more susceptible to degradation processes compared to the surface of samples exposed to weather conditions. This may be due to the relative higher humidity and constant exposure to higher temperatures than in the natural environment.

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