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Analysis of the Influence of Time and Type of Ageing on Changes in the Physical Properties of Poly(Oxymethylene) (POM) Samples

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Polymeric materials are very widely used in the manufacturing of products in all industrial sectors. Their popularity is associated with a relatively low price, very good price–performance ratio and high availability, as well as significant possibilities of modification of physical and functional properties. Since one of the disadvantages of polymer materials is their susceptibility to changes in their properties under the influence of chemical and physical factors occurring in various industries, there is a need to test polymer materials in terms of these complex processes. This work presents experimental studies on changes in the physical properties of poly(oxymethylene) (POM) exposed to UVA and UVB radiation under accelerated conditions. Additionally, the ageing process was carried out under natural weathering conditions for 3 years and thermal ageing at elevated temperatures of 90 and 130°C. The effects of these factors were then analysed in terms of changes in tensile strength and impact strength. The research was supplemented with measurement of the weight of mouldings made of POM and aged in various conditions. The obtained results showed that ageing under accelerated conditions, in which they are used due to the increasing application of polymer materials, causes the greatest changes in the physical properties of the tested samples. Additionally, it was found that tensile strength and impact strength decreased with increasing ageing time.

topics: poly(oxymethylene) (POM), ageing of polymeric materials, mechanical properties

1. Introduction

During use, polymeric materials degrade as a result of various environmental conditions, which may result in irreversible changes in structure and thus changes in physical and chemical properties. The mechanisms of degradation depend on the main factor causing them. Typically, in the natural environment, two or more factors interact, accelerating the rate of degradation [1, 2]. Degradation initially occurs in the surface layers of materials, with visual effects such as colour changes and cracks appearing on the surface of the elements. Cracks expose the internal layers of the material to degrading factors, ultimately resulting in brittleness and physical disintegration [3].

Many authors conduct real-time ageing tests of polymer materials in natural conditions. The three most commonly used locations for these studies are Arizona, Florida, and Japan [4–7]. In laboratory conditions, accelerated ageing methods are often used in chambers with artificial light sources. These tests provide data in a much shorter time than tests in natural conditions. The most commonly used light sources are fluorescent or xenon lamps [8]. Many researchers have attempted to correlate the ageing of polymer materials in natural and accelerated (laboratory) conditions [9–12].

Studies on the mechanisms of thermal degradation of polymers not only aim to extend the lifespan of plastic elements but also contribute to a better understanding and increased rate of waste degradation in landfills. Thermal degradation (depolymerisation) can also play a role in the chemical recycling of plastics [13–15].

The aim of this study was to determine the influence of the type and duration of ageing on selected physical properties of poly(oxymethylene) moulding parts.

2. Materials and methods

The material used for the test was a homopolymer poly(oxymethylene) (POM) with a natural colour, commercially known as Delrin®500P NC010 from DuPont. The samples for testing

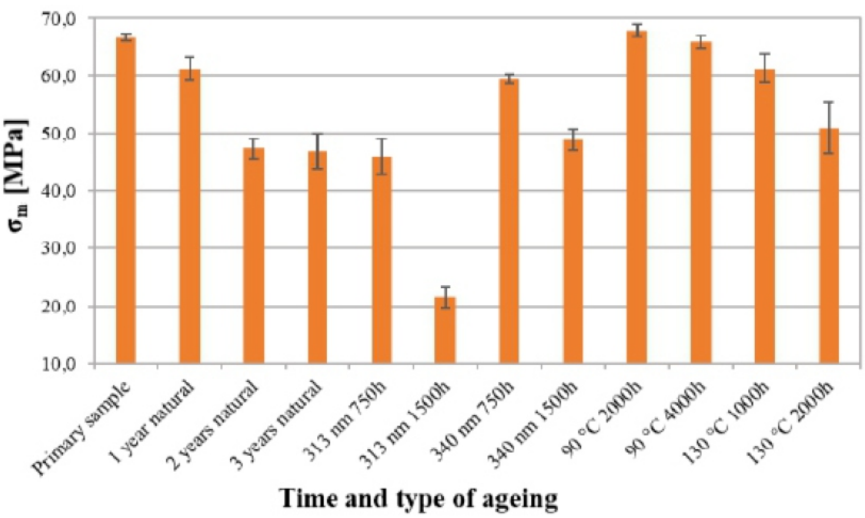

Fig. 1. Tensile strength of POM samples aged in various conditions.

were manufactured by injection moulding using a KraussMaffei KM65-160 C4 injection moulding machine with a mould closing force of 650 kN.

Natural weathering was conducted over approximately three years (from 9 August 2019 to 30 September 2022) in Poland, in the Silesian Voivodeship. The weathering station was prepared in accordance with the PN–EN ISO 877-1:2010 standard [16] and positioned facing the equator at an angle of 45° to the ground elevation. Samples for further testing were taken from the station at yearly intervals.

Accelerated ultraviolet (UV) ageing was carried out in an Atlas UVTest chamber. This ageing chamber is equipped with eight fluorescent UV lamps, enabling the exposure of polymer materials to alternating cycles of radiation, sample spraying, and condensation. Samples for further testing were taken every 750 h. The tests used UVA-340 nm and UVB-313 nm lamps.

Thermal ageing was carried out using a SANYO MOV-212S laboratory convection oven at a constant temperature of 90°C for 2000 and 4000 h and at 130°C for 1000 and 2000 h.

The mechanical properties were evaluated through uniaxial tensile testing using a Shimadzu EZ-LX testing machine. The tests were carried out in accordance with the PN–EN ISO 527-1 standard [17]. The samples were in the shape of A1 tensile bars.

Impact strength (a_{cU}) testing by the Charpy method was performed using a Zwick/Roell HIT5.5P impact tester with testXpert III software. Samples with a length of 80 mm were cut from the tensile test paddles. The tests were conducted in accordance with the PN–EN ISO 179 standard [18].

The mass of the moulded parts before and after ageing was measured with an accuracy of ±0.01 mg using a Sartorius CP225D laboratory scale with a closed measuring space.

3. Results

Samples aged under natural, accelerated, and thermal conditions were subjected to tensile strength testing at a test speed of 50 mm/min after the specified ageing cycles were completed. Figure 1 presents the average tensile strength results for all series of samples.

Ageing of moulded parts made of POM in natural conditions resulted in a decrease in tensile strength. As the ageing time increased, the tensile strength value decreased more and more. The most significant decrease was observed after 2 years. POM samples after ageing in accelerated conditions are characterised by lower tensile strength compared to the original sample. The worst tensile strength ($\approx$ 22 MPa) was observed with UVB-313 ageing for 1500 h. With prolonged UVB exposure, the tensile strength decreased further. UVA-340 ageing did not cause such significant changes in tensile strength as UVB-313. After 1500 h, the tensile strength was 27 MPa higher compared to the same ageing duration using 313 nm wavelength lamps. In turn, increasing the temperature during the thermal ageing of POM moulded parts led to a deterioration of tensile strength. A similar trend was observed with the extension of the process at 90°C. Only ageing for 2000 h at 90°C resulted in a minimal increase in tensile strength compared to the unaged sample.

Figure 2 presents the average impact strength results from 10 measurements of samples subjected to different types and times of ageing.

The impact strength of the POM moulded parts decreased significantly after just 1 year of ageing in natural conditions. With increasing ageing time, the impact strength decreased more and more. After 3 years of natural weathering, the impact strength of the POM samples was 95% lower compared to the original samples. This indicates the degrading

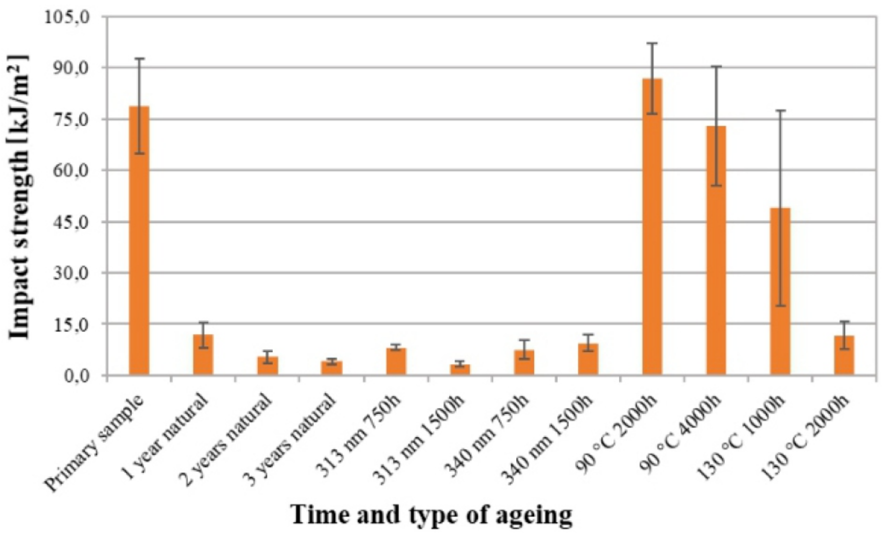

Fig. 2. Average impact strength values of POM moulded parts subjected to ageing under different conditions.

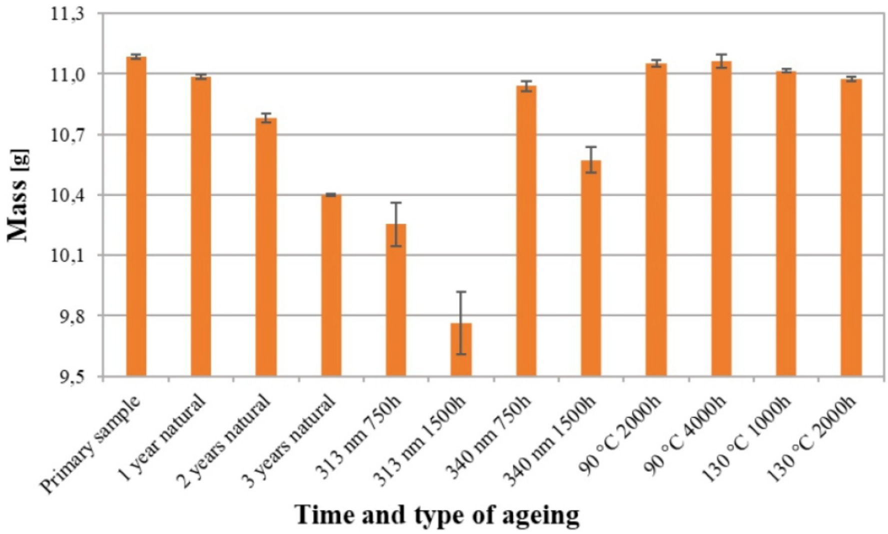

Fig. 3. The average weight of POM moulded parts subjected to ageing in different conditions.

influence of atmospheric factors on poly(oxymethylene).

Accelerated ageing, on the other hand, resulted in a significant decrease in the impact strength of the tested samples. UVB-313 ageing for 1500 h resulted in a reduction in the impact strength value by over 75 kJ/m^2. It can be observed that both types of accelerated ageing caused a significant decrease in impact strength after just 750 h. However, with UVA-340 radiation, a slight increase in impact strength was observed after 1500 h compared to shorter ageing times.

Analysis of the POM moulding parts results showed that ageing at 90°C initially contributed to the increase in impact strength. However, after ageing for 4000 h, a slight decrease in impact strength of $\approx$ 7% compared to the unaged sample was observed. In the case of ageing at 130°C, a proportional decrease in impact strength was observed with increasing ageing time. After ageing for 2000 h, the impact strength decreased by $\approx$ 67 kJ/m^2.

Figure 3 shows the influence of different types of ageing on the change in the mass of POM moulded parts.

As can be observed, in most cases, the weight of moulded parts decreases with the extension of the ageing cycle. The influence of atmospheric factors contributed to the loss of weight in the tested samples. With each additional year of ageing, the mass decreased progressively. The most noticeable loss of mass, amounting to 7%, was observed after 3 years of ageing. Accelerated ageing had the most significant impact on the change in mass of moulded parts made of POM. As the ageing time increased, the weight of the aged samples decreased. The samples aged for 1500 h with UVB-313 had the lowest weight compared to the unaged sample, where the weight loss was $\approx$ 12%. UVA-340 radiation had a lesser effect on the degradation of POM.

Organoleptic evaluation of the aged moulded parts allowed for the conclusion that, in addition to the weight, the width and thickness of the UVB-313 aged moulded parts also changed. In the case of thermal ageing, the samples aged at higher temperatures and for a longer time exhibited the lowest weight, with a mass loss of only about 1%. In the remaining cases, ageing at 130°C for 1000 h and at 90°C for 2000 and 4000 h, the mass loss was minimal and could be within the measurement error margin.

4. Conclusions

The conducted studies have shown the varied impact of individual degrading factors on the changes in mechanical properties and the weight of the tested mouldings. The most significant influence on the change in tensile strength, impact strength, and mass of all tested mouldings is observed during accelerated ageing. It has been observed that the interaction of different factors (UV radiation, increased temperature, water) leads to the formation of microcracks and the detachment or leaching of loose material particles, directly contributing to the alteration of mechanical properties and weight of the moulded parts. In natural conditions, due to the variability of atmospheric conditions, the effect of factors causing changes in properties is less intense and uneven throughout the cycle. Therefore, these processes are prolonged and cause less damage.

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