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SELECTED PROPERTIES OF POLYPROPYLENE-BaSO₄ COMPOSITES AFTER UV EXPOSURE

The paper presents a preliminary study on the effect of an addition of barium sulfate (BaSO₄) particles on the mechanical properties of polypropylene (PP) and an evaluation of the effectiveness of this additive in protecting the material against UV rays. Tests were carried on PP samples filled with BaSO₄ powder and on samples covered with a protective coating based on BaSO₄. Samples of the materials were exposed to UV-C rays for 1000 hours. After exposure, specimens were subjected to static three-point bending tests and hardness examination. Based on the obtained results, it was concluded that BaSO₄ reduces the decrease in flexural strength and in hardness caused by exposure to UV-C rays by half in comparison with neat PP. The action of BaSO₄ particles as a filler of PP and as a component of a coating applied on the surface of the sample results in similar anti-UV protection of the material. BaSO₄ seems to be a commonly available and inexpensive anti-UV protector for plastics.

Keywords: barium sulfate, polypropylene, UV degradation

INTRODUCTION

The degradation of polymer materials and polymer-matrix composites (PMCs) by ultraviolet (UV) rays is one of the most important problems concerning constructions made from these groups of materials [1-3]. The problem of UV degradation is ever more significant because in recent years plastics have replaced traditional materials in many applications, including metals [4]. Additionally, increasingly more functional materials are based on various polymers [5, 6]. Moreover, polymer bases are widely involved in the recycling of various specific wastes [7] and in the production of ecological materials containing bio-degradable renewable components [8]. UV radiation also has a destructive impact on fiber reinforced polymer laminates, including responsible high-loaded primary constructions [9-12]. There are no doubts that protecting polymer materials against UV rays is a crucial technical challenge. There are a number of methods of protecting plastics against UV rays [13]. The most common method used is to fill the plastic with an appropriate particle filler [14]. The filler should not adversely affect the polymer, e.g. not be a substrate in oxidation reactions and not catalyze such reactions. The most common choice here is metal oxide powders [15]. They work by direct physical shielding of the deeper areas of the plastic from the rays by scattering or absorbing them. The filler content must be high enough for its particles to reveal the interior of the product even at a small depth (Fig. 1).

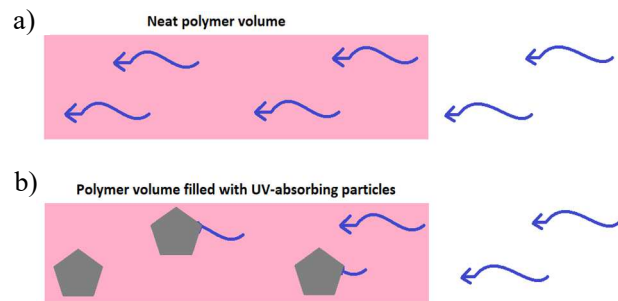


Fig. 1. Ideal scheme of absorbing UV rays by particle filler structure of polymer material: a) volume of neat polymer material, b) volume of polymer material filled with particles capable of absorbing UV rays

In some cases, if there is a possibility, and the additional technological steps do not significantly increase the cost of the product, an outer protective coating with a high content of protective particles may be a good solution. The coating is a solid barrier against UV rays [16, 17]. Micrometric barium sulfate powder is often used as a filler in thermoplastic polymer materials [18, 19]. Its positive effect on the mechanical properties of the material was found. It also exhibits a thermal stabilizing effect on the polymer, which may indicate a potential for protection against UV radiation. A polymer, which particularly often suffers from degradation caused by UV rays is polypropylene (PP) [20]. It is a very popular material, very easy to produce and easy

to recycle. The sensitivity of PP to UV rays causes a serious barrier against using it in outdoor applications [21]. Its improvement in terms of UV radiation resistance is of great importance for the global economy. Filling PP with barium sulfate is commonly practiced [22]; however, there are not many studies concerning the resistance of PP-barium sulfate composites against UV radiation.

The paper presents a preliminary study on the influence of the addition of BaSO₄ (barium sulfate) powder on the mechanical properties of PP and an evaluation of the effectiveness of this additive in protecting the material against UV. Three groups of PP samples were prepared for the tests: unfilled PP samples, PP samples filled with BaSO₄ powder, unfilled PP samples covered with a protective coating with a high content of BaSO₄. They were exposed to UV-C rays for 1000 hours. UV-C is high energy type of UV radiation (wavelength of 100–280 nm) used, for instance, in disinfection chambers. After UV exposure, the samples were subjected to static three-point bending and hardness tests. The results were analyzed and conclusions about the anti-UV protective effectiveness of BaSO₄ powder were drawn.

MATERIALS AND METHODS

The investigated material was Moplen HP456J polypropylene (Lyondell Basell, Houston, USA). As the UV absorber barium sulfate (Hadron Scientific, Kielce, Poland) was used. The polypropylene granulates were mixed with BaSO₄ in an ethanol solution (P.P.H. “Stanlab” Sp. z o. o., Lublin, Poland) in an ultrasonic bath for 15 min. After mixing, the mixture was held at 60°C until the alcohol evaporated. The ratio between PP and BaSO₄ was 95:5 by mass.

The samples for testing were injected into a round-shaped steel mold 50 mm in diameter and thickness of 6 mm. The injection molding temperature was 230°C. In total, 15 samples (9 neat PP and 6 PP/BaSO₄ composite) was made. Additionally, a coating based on a 7% polyvinylpyrrolidone solution in water (PVP K90 supplied by Sigma-Aldrich, St. Louis, MO, USA) mixed with BaSO₄ was made. The mixture contained 33% BaSO₄ by mass. The coatings were applied to three neat PP samples manually with use of a brush. Micrographs of the samples are presented in Figure 2.

Three of each type of samples were subjected to UV-C rays in a chamber of the authors' own construction for 1000 h. The reference samples kept in conditions without light for the same time. In the UV chamber the samples were exposed to the rays only on one side, as presented in Figure 3. The list of samples is presented in Table 1.

After UV exposure, the samples were machined and 20 mm wide rectangular specimens were cut from each sample. To evaluate the mechanical properties of the materials the specimens were subjected to three-point bending tests. The flexural strength (R_g) and bending strain at R_g (ϵ_{flex}) were recorded at room temperature on

a Shimadzu AGX-V testing machine (Japan). The support spacing was 34 mm and the displacement rate was 5 mm/min. The specimens were tested with the UV-exposed side facing up (on the pressed part of the bent beam).

TABLE 1. List of samples

Samples	Mass ratio PP: BaSO ₄	UV exposure [h]	Coating
PP	100:0	0	–
PP – UV	100:0	1000	–
PP/BaSO ₄	95:5	0	–
PP/BaSO ₄ – UV	95:5	1000	–
PP+BaSO ₄ – UV	100:0	1000	10%PVP solution + BaSO ₄



Fig. 2. Samples with BaSO₄: neat (a) and coated (b)



Fig. 3. Diagram of sample exposure in UV-chamber

The hardness measurements were carried out using an HK460 (Heckert, East Germany) device based on the Brinell method. The tests were conducted under a 135 N load in accordance with the PN-EN ISO 6506-1 standard for the hardness of polymer materials.

RESULTS AND DISCUSSION

The results of bending test demonstrate that the addition of BaSO₄ does not significantly influence the strength or plasticity (represented by ϵ_{flex}) of polypropylene. Nevertheless, barium sulfate significantly reduces the photodegradation caused by the UV-C rays (Fig. 4, Table 2). The relative decrease in flexural strength and bending strain for neat PP was 28.3 and 44.7% correspondingly, while the decrease of PP/BaSO₄ was 13.5% and 35.7%. This confirms the UV protective action of the BaSO₄ particles in the polymer matrix.

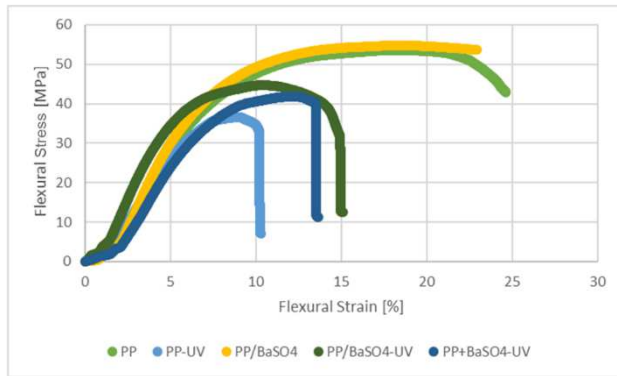


Fig. 4. Exemplary stress-strain curves obtained from bending test

TABLE 2. Three-point bending test results

	R_g [MPa]	ϵ_{flex} [%]
PP	54.1 (3.4)	17.5 (2.3)
PP – UV	38.8 (3.3)	9.7 (2.8)
PP/BaSO ₄	55.0 (2.7)	18.1 (1.1)
PP/BaSO ₄ – UV	47.6 (6.0)	11.6 (1.9)
PP+BaSO ₄ – UV	45.2 (5.2)	12.7 (2.1)

The coating applied on surface of the PP specimens significantly reduced the impact of UV radiation. In addition, the results of flexural strength and bending strain are not significantly different from the PP/BaSO₄ specimens. This means that barium sulfate is versatile as a UV absorber – it provides significant protection as a composite filler and as a coating component as well.

The hardness test results correspond well with the results obtained in three-point bending tests. The set of hardness results is presented in Figure 5.

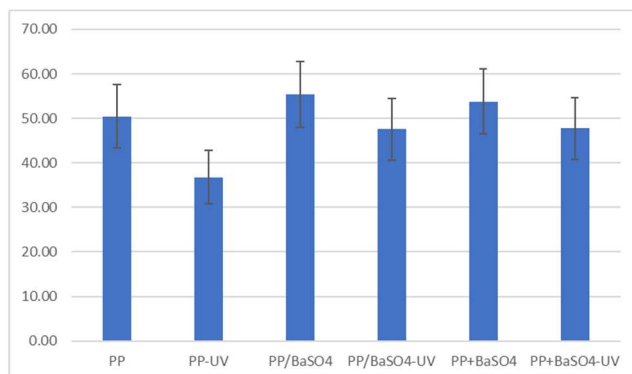


Fig. 5. Results of Brinell hardness tests for tested PP specimens

The change in hardness caused by UV exposure for neat PP was 26%. It is probably connected with the main mechanism of photodegradation – a decrease in the degree of polymerization, which usually means a decrease in hardness [20]. The decrease in hardness is evidently (by half) lower in the case of PP covered with BaSO₄ particles or composed in the mass (respectively – 11 and 14%). In general, BaSO₄ is a component that should be taken into account as protector of polymer materials against UV radiation.

CONCLUSIONS

Based on the obtained results and the performed observations, the following conclusions were drawn:

- BaSO₄ micrometric particles comprise a quite good anti-UV protector. They reduce the decrease in flexural strength and in hardness caused by exposure to UV-C rays by half, in comparison with neat PP.
- The action of BaSO₄ particles as a filler of PP-matrix composite and as a component of a coating covering the surface of the sample, results in similar an anti-UV protective influence on the material.
- BaSO₄ seems to be a commonly available and inexpensive anti-UV protector for plastics.

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