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SELECTED PROPERTIES OF POLYPROPYLENE-TiO₂ COMPOSITES AFTER EXPOSURE TO UV RAYS – PRELIMINARY STUDY

In this study the mechanical properties of polypropylene (PP) with a small amount of TiO₂, after UV-C exposure were preliminarily analyzed. The effectiveness of titanium oxide was evaluated in two alternative applications: TiO₂ as the polymer filler and TiO₂ as a protective outer coating. The samples were exposed to UV-C rays for 1000 hours. It was found that an addition of 5 wt.% TiO₂ to PP matrix results in a 60% smaller decrease in R_g after 1000 h of exposure to UV-C than in the case of neat polypropylene. It was also found that the addition of TiO₂ to the polypropylene matrix is more effective than TiO₂ applied as a coating component. The R_g decrease after exposure is about 35% in this case. The research confirmed that TiO₂ submicrometric particles seem to be a very good component in reducing the sustainability of polypropylene to UV radiation.

Keywords: titanium dioxide, polypropylene, UV degradation

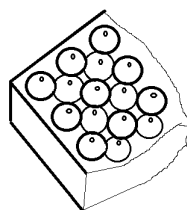
INTRODUCTION

The problem of polymer material degradation due to ultraviolet (UV) rays is one of the most frequently addressed for this product group [1, 2]. UV degradation is serious problem also in the case of highly responsible advanced polymer matrix composites (PMCs) based on curable resins [3-6]. Advanced polymer PMCs are employed in various new applications, among others in the transport and machine industries [7], where they are exposed to sun light. UV rays can also disrupt the functionality of special functional PMCs [8-11].

The degradation mechanisms caused by UV rays mainly consist in the defragmentation of polymer chains and acceleration of oxidation processes (synergy of degradation factors) [9, 12]. There are several strategies to improve the resistance of polymer materials to UV action [13-15]. The most popular method is the introduction of a suitable filler in the form of particles (introducing particles for functional purposes is a common practice in the case of plastics [16, 17]). It should be a substance that does not adversely affect the polymer, does not participate in oxidation reactions and does not catalyze such reactions. Some mineral oxides are a good solution here. The main task of the filler particles is to shield the deeper parts of the polymer material from UV radiation by absorbing the light. The filler content must therefore be high enough for the particles to screen the entire surface of the product in a relatively shallow section (Fig. 1). Moreover, the absorption coef-

ficient for the UV section in sunlight should be relatively high.

a)



b)

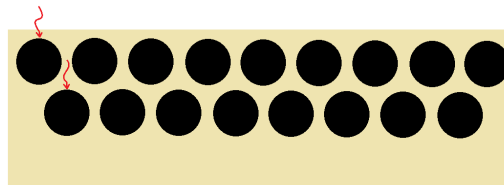


Fig. 1. Idea of shielding inside of plastic element by particles absorbing UV rays: a) spatial scheme of particle arrangement in layers, b) stereological scheme of layered arrangement of particles, showing absorption of rays by particles from different layers

For the absorption method given above, a gradient particle distribution (low inside, more at the surfaces exposed to the rays) would be advantageous. However, in most cases, plastics technology makes it impossible to achieve. Therefore, an outer protective coating with a high concentration of particles can also be a good solution [18, 19]. Micrometric titanium oxide powder ap-

pears to meet the physicochemical requirements mentioned above. In addition, it is white in color, which is not without significance for plastics from the utility point of view. It is a material often used as a filler for plastics, including protection against UV radiation [20]. A polymer material that is particularly sensitive to degradation caused by UV rays, and at the same time the most commonly used (perhaps, with the exception of polyethylene) is polypropylene (PP) [21]. Its effective protection against UV radiation could significantly expand its outdoor use, which is currently very limited.

In this study, we present a mechanical properties analysis of PP with a small amount of TiO_2 , after UV exposure. The effectiveness of titanium oxide was evaluated in two alternative applications: TiO_2 as the polymer filler and TiO_2 as a protective outer coating. In our research, we prepared three groups of PP samples exposed to 1000 hours of UV rays: unfilled PP samples, PP samples filled with TiO_2 powder, and unfilled PP samples covered with a protective coating with a high content of TiO_2 . A lamp emitting UV-C type radiation was used. After exposure, the samples were subjected to static three-point bending tests and visual assessment of the fractures. UV-C is high energy radiation occurring, among others, in water purification systems or disinfection chambers, where there is high applicability potential for PP.

MATERIALS AND METHODS

The investigated material was Moplen HP456J polypropylene (Lyondell Basell, Houston, USA). As the UV absorber, titanium oxide (Nr 865630428, Avantor Performance Materials Poland S.A., Gliwice, Poland) was used. The polypropylene granulates were mixed with TiO_2 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 for alcohol evaporation. The ratio between PP and TiO_2 was 95:5 by mass.

The samples for testing were injected into a steel mold with a diameter of $\phi 50$ mm and thickness 6 mm (Fig. 1). The injection molding temperature was 230°C . In total, 15 samples (9 neat PP and 6 PP/ TiO_2) were made. Additionally, a coating based on a 7% polyvinylpyrrolidone solution in water (PVP K90 supplied by Sigma-Aldrich, St. Louis, MO, USA) mixed with TiO_2 was made. The ratio of the solution to TiO_2 particles was 2:1. The coating was applied with brush on three neat PP samples.

Three of each type of samples were placed in a UV chamber (authors' own construction, oblong UV-C lamp 36 W) for 1000 h, while the reference samples were kept in absence of light for the same time. In the UV chamber the samples were exposed only from one side, as presented in Figure 2. The areal energy density in the applied conditions was about 0.01 W/cm^2 . The list of samples is presented in Table 1.

TABLE 1. List of samples

| Samples | Mass ratio PP: TiO_2 | UV exposure [h] | Coating |
|-------------------------|-------------------------------|-----------------|----------------------------------|
| PP | 100:0 | 0 | – |
| PP – UV | 100:0 | 1000 | – |
| PP/ TiO_2 | 95:5 | 0 | – |
| PP/ TiO_2 – UV | 95:5 | 1000 | – |
| PP+ TiO_2 – UV | 100:0 | 1000 | 7% PVP solution + TiO_2 |

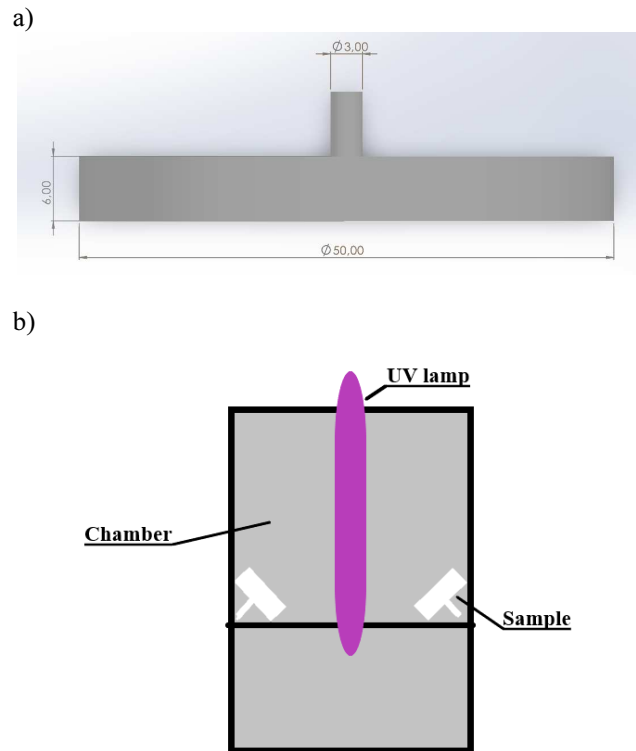


Fig. 2. Samples: a) standard test sample, b) scheme of placing samples in UV-chamber

After UV exposure, the standard samples were cut to rectangular shaped 20 mm wide specimens. To evaluate the strength of the specimens, three-point bending was performed. The flexural strength (R_g) and bending strain (ϵ_{flex}) were ascertained at room temperature on a Shimadzu AGX-V machine (Japan). The support spacing was 34 mm and the deformation speed was 5 mm/min. The specimens were tested with the UV-exposed side facing up, as presented in Figure 3.

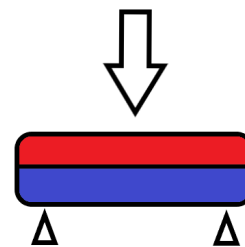


Fig. 3. Scheme of sample placement (red side UV exposed, blue side was not) and corresponding load-support conditions during three-point bending

Micrographs of the fracture surfaces were obtained by means of a scanning electron microscope (SEM) HITACHI 3400N. Low vacuum conditions were applied for the imaging procedure.

RESULTS AND DISCUSSION

The results of the three-point bending test (Fig. 4) reveal significant degradation of the polypropylene after 1000 h of exposure to UV-C rays.

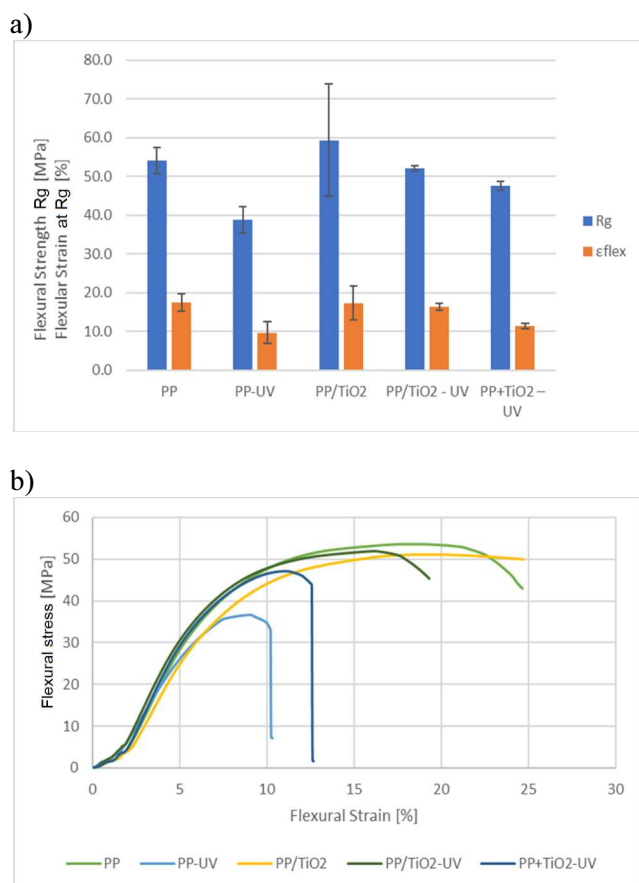


Fig. 4. Results of three-point bending test (a) and exemplary stress-strain curves (b)

The flexural strength (R_g) and strain at R_g (representing the plasticity of the material) decreased by 28.3% and 44.7 correspondingly. Furthermore, a drastic increase in the fraction of brittle fracture surface after UV exposure was observed on the fracture surface of the SEM micrographs (Fig. 5). The addition of TiO₂ to PP reduced the effect of UV radiation, which resulted in only a 12% loss in R_g and around 6% in plasticity. Nevertheless, the difference in the obtained data for the composite are insignificant due to the high standard deviation. That observation confirms the effectiveness of titanium oxide as a UV-C protector. On the other hand, comparing the unexposed PP with PP/TiO₂-UV, the difference between samples is insignificant.

The specimens with the protective PVP/TiO₂ coating have significantly lower values of R_g and ϵ_{flex} .

The reduction in strength and plasticity was 12.1 and 35.3% correspondingly. Such a result indicates that a protective coating is indeed suitable for anti-UV applications; however, comparing to the PP/TiO₂ composite, the coating is significantly less effective. The reason could be in the coating defects, its inhomogeneity, degradation of the binding agent (PVP) or lack of 100% absorption efficiency of the thin TiO₂ layer.

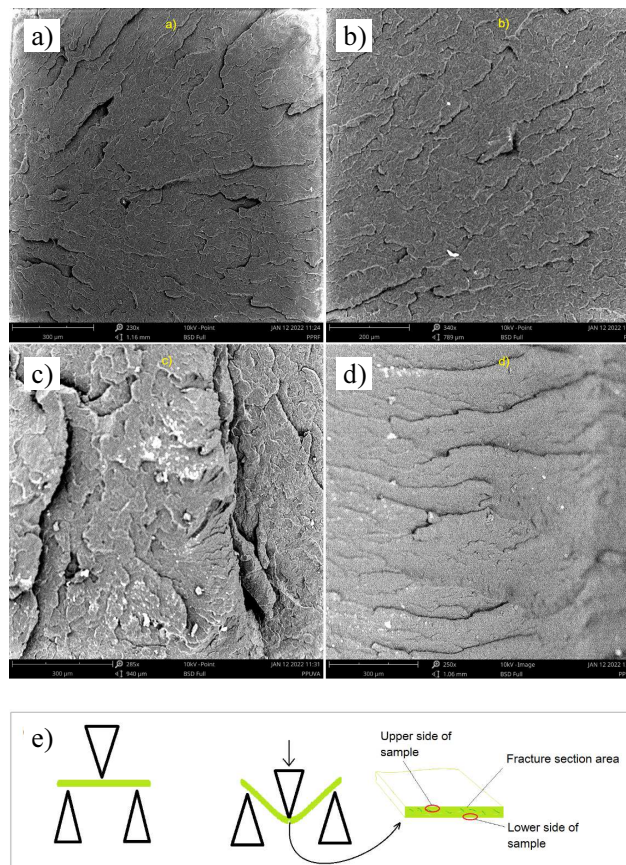


Fig. 5. Fracture surface after bending – SEM micrographs: a) unexposed PP – upper side of sample, low brittleness effects b) unexposed PP – lower side of sample, low brittleness effects, c) PP-UV – upper side of sample, increased brittleness effects clearly visible, d) PP-UV – lower side of sample, low brittleness effects, e) diagram of imaging areas

CONCLUSIONS

The obtained results allow the following conclusions to be drawn:

- The addition of 5 wt.% TiO₂ to the polypropylene matrix results in a 60% smaller decrease in R_g after 1000 h of exposure to UV-C radiation than in the case of neat polypropylene.
- The addition of TiO₂ to the polypropylene matrix is more effective than TiO₂ applied as a coating component – the R_g decrease after exposure is about 35% in this case.
- TiO₂ submicrometric particles seem to be a very good component to improve the sustainability of polypropylene to UV radiation.

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