Optimizing Photocatalytic Activity of Biodegradable PHB-TiO_2 Films: Proposing a Double Layer Structure

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The incorporation of self-cleaning and antimicrobial properties in polymeric films opens up new possibilities for the production of urban furniture that will require less maintenance and, at the same time, be safer for the population. So, the production of hydrophobic and self-cleaning biodegradable films of polyhydroxybutyrate (PHB) with titanium dioxide (TiO_2) is being proposed. Film photocatalytic activity was measured using a batch reactor, and Rhodamine-B (RhB) was the target molecule. Also, Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) were done. The highest value for the pseudo-first-order apparent kinetic constant (K'_{obs}) was found in films with the lowest investigated concentration of polymer and catalyst. A new preparation methodology is being proposed to improve the photocatalytic activity of materials: the construction of double layer films and for them k'_{obs} were 70% higher.

Introduction

Polymeric films are widely used in various industrial sectors and the incorporation of self-cleaning and antimicrobial properties in it opens up new possibilities. For instance, the production of urban furniture will require less maintenance and, at the same time, be safer for the population. These properties can be achieved by the addition of photocatalysts, which lead to the degradation of the compounds present on their surface when moisture and radiation of the correct wavelength are also present. In this regard, titanium dioxide (TiO_2) is the most commonly used catalyst, and its incorporation is done through methods such as sol-gel or electrospinning [1]. Alternatively, this study proposes the incorporation of TiO_2 during the solubilization of polyhydroxybutyrate (PHB) granules for the production of biodegradable, hydrophobic, and self-cleaning films.

Material and Methods

TiO2 P-25 from Aeroxide, Rhodamine-B, and chloroform P.A. were used in the experiment along with PHB from Good Fellow in the form of 5 mm granules. The PHB, solvent, and catalyst solution were stirred and heated on a shaker for 16 hours at 225 rpm and 60ºC, followed by ultrasonication for thirty minutes at 22ºC. Subsequently, the mixture was poured onto a 20 x 30 cm glass plate, and films with controlled thickness were produced using a spreader. They were then dried at room temperature with forced convection (60 m³/min) for one minute and subsequently placed in a container with one liter of distilled water until they were detached from the glass. Different mass ratios of polymer (3 to 11% w_{PHB}/w_{CHCl3}) and TiO_2 (3 to 20% w_{TiO2}/w_{PHB}) were investigated to identify the best result. Based on the best PHB and TiO_2 ratio, a film called 'double layer' was prepared. In this film, a 100 µm thick layer was first formed without the catalyst, and after one minute of exhaustion, a solution of polymer and catalyst was spread over the first layer, with 50 µm. To determine the photocatalytic activity of the synthesized materials, tests were carried out in a batch reactor, described in detail in [2], which is equipped with a solar simulator lamp (5.5 mW.cm-² at 365 nm) and an initial concentration of 40 mg L^{-1} of Rhodamine-B. The tests started without radiation, to achieve adsorption equilibrium. After 45 minutes, the lamp was turned on, and then the photocatalytic reaction started. Samples of 0.75 mL were collected at times 0, 5, 15, 30, and 60 minutes of reaction. The absorbance decay was measured in a UV-Vis spectrophotometer at the maximum wavelength of Rhodamine-B (553 nm). The color decay due to photolysis was also analyzed, i.e., promoted only by irradiation, without catalysts. At least three parts of each film were tested and a 5% maximum difference in the arithmetic mean of results was accepted. Using the pseudo-first-order model, the apparent kinetic constant (k_{obs}) was calculated. The films were characterized by Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS). Furthermore, their wettability was analyzed by measuring the contact angle of a water droplet.

Results and Discussion

Maintaining 9% of w_{PHB}/w_{CHCl3}, proportions of TiO_2 (3 to 20% of w_{TiO2}/w_{PHB}) were investigated. The results are shown in Figure 1, which reveals that the increase in the catalyst mass added to the material is not accompanied by an increase in its photocatalytic activity. Therefore, the catalyst's lower concentration proved to be the better option, a fact emphasized by the analysis of k'_{obs} (k_{obs}/w_{TiO2}). The micrographs (Figure 2) indicate that the film is dense and a large part of the added catalyst is not reached by radiation.

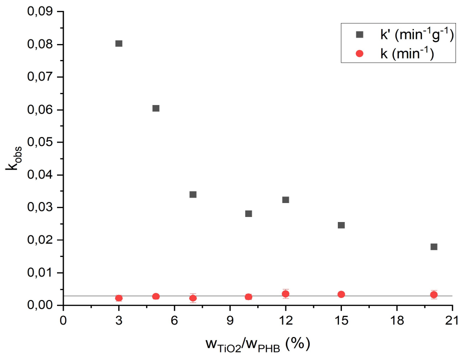

Figure 1. k_{obs} results of the different proportions of TiO_2

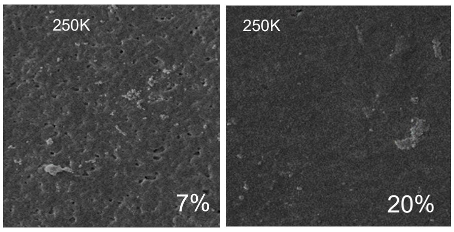

Figure 2. SEM micrographs for 7 and 20% w_{TiO2}/w_{PHB}

So, we decided to investigate the impact of polymer concentration on photocatalytic activity, evaluating proportions of 5 to 11% of w_{PHB}/w_{CHCl3} (the limit for the formation of a viable film). In all cases, 12% of w_{TiO2}/w_{PHB} was used. According to Figure 3, the lower amount of PHB resulted in the highest value of k'_{obs}. Therefore, it was possible to conclude that the best film would be with 5% of w_{PHB}/w_{CHCl3} and 3% of w_{TiO2}/w_{PHB}, which was effectively confirmed and presented a k'_{obs} of 0.1468 ± 0.0015 $min^{-1}g^{-1}$. These finds were corroborated by Sökmen et al [3], who immobilized TiO_2 in a biopolymeric polycaprolactone (PCL) film and demonstrated better photocatalytic activity with lower TiO_2 proportions (5% compared to 10% w_{TiO2}/w_{PCL}). The results demonstrated that the film's photocatalytic activity is limited because the polymer is an effective barrier to radiation. Thus, two alternatives to increase the amount of catalyst achieved by irradiation were identified. The first was changing the film production method, seeking to produce a more porous film composite. This alternative did not solve the problem because the radiation does not reach the interior of the material's pores, as proven and discussed in another work by the same research group presented at CIPOA 2024. The second alternative was to minimize the film thickness, respecting the minimum required for handling. However, this minimum thickness still did not lead to sufficiently active films.

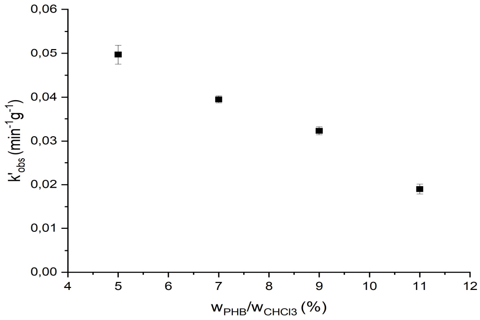

Figure 3. k'_{obs} results of the different proportions of PHB

So, a material named 'double layer' was created. The first layer contained 9% of w_{PHB}/w_{CHCL3}, free of catalyst, and the second layer consisted of 3% of w_{PHB}/w_{CHCl3} and 3% of w_{TiO2}/w_{PHB}, the same mass of titania as the best film with a single layer. As a result, a k'_{obs} of 0.2506 ± 0.0019 $min^{-1}g^{-1}$ was achieved, a value 70% higher than the monolayer. Figure 4, generated by EDS, illustrates the difference in the TiO_2 concentration on the surface of the monolayer film (A) and the bilayer film (B). Thus, the development of bilayer films is an effective approach for obtaining biodegradable films with self-cleaning and antimicrobial properties.

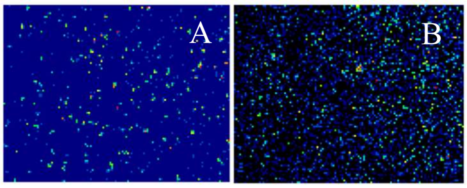

Figure 4. EDS results showing the TiO_2 concentration for the monolayer (A) and double layer (B)

Additionally, it was observed that the films presented a hydrophobic surface. The polymeric matrix without the catalyst showed the same contact angle as the films with TiO_2 incorporated (96.4° ± 0.8°).

Conclusions

Lower TiO_2 concentrations provided better photocatalytic activity. MEV showed a dense film with TiO_2 dispersed throughout the polymer matrix, which is an effective barrier to radiation. So, films with lower PHB content performed better k'_{obs}. To improve TiO_2 availability on the film surface, a double layer structure was created, which showed a k'_{obs} 70% higher than the monolayer. The double layer film effectively dispersed the catalyst on their surface, enhancing their photocatalytic activity. Additionally, the film exhibited a hydrophobic surface, which is a desirable characteristic for various applications.

References

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