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PHB-TIO_2 Composite Films: Study of Polymeric Extraction in Alternative Solvents and Methodologies for Production

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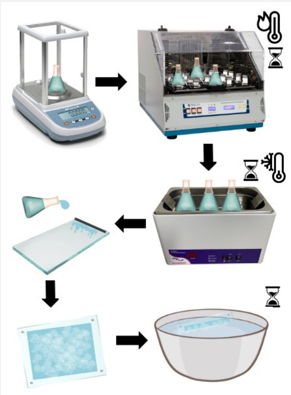

Self-cleaning films of polyhydroxybutyrate (PHB), a biodegradable polymer, were developed through TiO_2 incorporation. The possibility of using alternative solvents to chloroform, which is traditionally used, was evaluated. Composite films were prepared by casting and controlled thickness drawdown, followed by Non-solvent Induced Phase Separation (NIPS) and Evaporation Induced Phase Separation (EIPS) methods. Photocatalytic activity tests were conducted in a batch reactor using rhodamine-B (RHB) as the target molecule and solar simulator lamp. The films were also analyzed by Scanning Electron Microscopy (SEM). The results showed that while complete solubilization of PHB granules was achieved with acetone and aniline, film formation only occurred when chloroform was used. NIPS in water did not produce usable films, but ethanol proved to be a suitable substitute. Both ethanol-based NIPS and EIPS films showed similar photocatalytic results.

Introduction

Coatings that provide self-cleaning and antimicrobial properties can be applied in various industries, such as healthcare and food, adding value to materials. This study aimed to produce polymer composite films with titanium dioxide (TiO_2), which enables the pollutant's oxidation as long as there is moisture and radiation with an appropriate wavelength. Furthermore, TiO_2 has antimicrobial properties [1]. Polyhydroxybutyrate (PHB), a biodegradable polymer was chosen. It can be synthesized by microorganisms under unfavorable conditions [2] and, in this case, the solvation method using chloroform, is the most commonly used [3]. Guided by the predictions of Hansen Solubility Parameters [4] we searched for a more environmentally friendly method to solubilize PHB. To form the composite films, three methodologies were considered: casting; and controlled thickness followed by NIPS (Non-solvent Induced Phase Separation), or EIPS (Evaporation Induced Phase Separation).

Material and Methods

The experiments utilized TiO_2 P-25 from Aeroxide, Rhodamine-B, P. A. solvents, and PHB in the form of 5 mm granules from Good Fellow. Initially, the solvation of polyhydroxybutyrate granules was studied, and acetone, ethyl acetate, and aniline were chosen based on the literature for having a lesser impact on human health and the environment compared to chloroform. The solvents were compared by adding 0.1 g of polymer to 5 mL of solvent, and the mixture was stirred for eight hours at a constant temperature, which corresponded to 90% of the boiling temperature of each solvent. To form the film, the catalyst, PHB granules, and solvent were heated and stirred at 225 rpm until it became a homogeneous solution. The resulting solution was then spread on a glass surface and controlled thickness samples were formed using a spreader. Then they were submerged in water or ethanol for phase inversion (NIPS). The study analyzed proportions of 8%, 10%, 12%, and 15% wPHB/wsolvent, with and without the addition of 12% and 15% wTiO2/wPHB, at thicknesses of 100 µm, 150 µm, and 200 µm. Films were also prepared by evaporation (EIPS) and casting on Petri dishes. The film's photocatalytic activity was assessed in a batch reactor, isolated from the external environment, magnetically stirred, and provided with air bubbling, and temperature control, as described in detail by [5]. Rhodamine B (RhB) at 4.10^{-2} $g.L^{-1}$ was chosen as the model molecule. Irradiation was performed by a 300W solar simulator lamp which emitted 5.5 $mW.cm^{-2}$ a 365nm. The experiments started in the dark, to achieve adsorption equilibrium. After 45 minutes the lamp was turned on and then the photocatalytic reaction began. To quantify the dye concentration variation, 0.75 mL samples were collected at 0, 5, 15, 30, and 60 minutes of reaction. The concentrations were calculated using the absorbance measured in a UV-vis spectrophotometer at the rhodamine maximum wavelength, 553 nm. The dye concentration decay due to photolysis, i.e., without films and catalyst, was also evaluated. All experiments were conducted at least in triplicate. The films were also analyzed by Scanning Electron Microscopy (SEM).

Results and Discussion

Regarding solubilization: it was found that PHB granules could be fully dissolved in acetone and aniline but not in ethyl acetate. However, during the film formation process, it was observed that the films were destroyed when they were exposed to water or ethanol in the coagulation bath (NIPS) regardless of their concentration or thickness. These results are represented in Figure 1. Therefore, as this study aims to produce a film, the use of the traditional solvent chloroform was necessary.

Regarding the use of chloroform: preliminary tests were conducted, which showed efficient solubilization after 16 hours at 60ºC. Investigating samples with the previously mentioned proportions and thicknesses, the best result by NIPS in water was found with 9% $wPHB/wCHCl_3$ and 12% $wTiO_2/wPHB$, with 100 µm. Although this was the best film obtained by this technique, it was not good enough as it had a heterogeneous surface and holes. Thus, casting, NIPS in ethanol, and evaporation-induced phase separation (EIPS) were also evaluated. The casting methodology proved to be unsuitable, as shown in Figure 2. On the other hand, NIPS in ethanol and EIPS produce intact films, as shown in Figure 3.

Regarding photocatalytic activity: Although NIPS provided more porous films than EIPS, as shown in Figure 4, both achieved the same absorbance reduction after one hour of testing (20,0 ± 2,2%). This indicates that the radiation does not reach the material internal pores and only the catalyst that is on the external surface is used. Similar results could be found in the literature [6]. This barrier was overcome using an innovative technique, which will be described in a future publication.
The EIPS method was preferred to avoid the ethanol use and the residues associated with coagulation baths. Additionally, photolysis showed an 8.0 ± 2.8% absorbance reduction after 60 minutes. Figure 5 illustrates the photocatalytic activity test results.

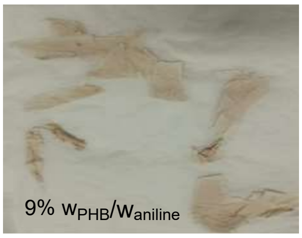

Figure 1. Film prepared by NIPS with aniline as solvent

Figure 2. Casting result

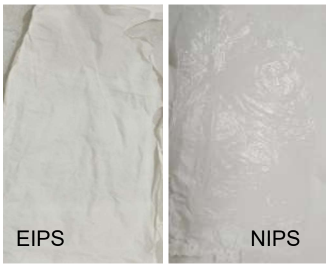

Figure 3. Film prepared by EIPS and by NIPS in ethanol

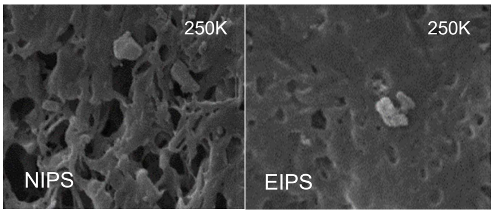

Figure 4. SEM results

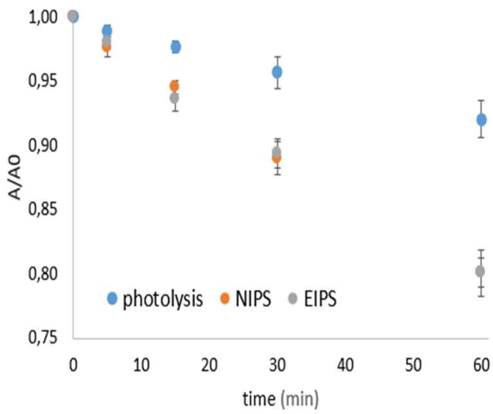

Figure 5. RhB degradation

Conclusions

This study demonstrated that PHB granules can be dissolved successfully in acetone and aniline but not in ethyl acetate. These solvents, however, do not lead to the formation of polymer composite films by any of the tested methods and, therefore, chloroform was necessary. Among the film formation methods, Casting was found to be unsuitable while NIPS with ethanol and EIPS led to homogeneous, sufficiently resistant, and hole-free film formation. NIPS resulted in more porous films than EIPS but these methods showed similar photocatalytic activities. EIPS was chosen as the preferred method due to its avoidance of ethanol use and residue formation.

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