



Article Poly(butylene adipate-co-terephthalate)/Poly(lactic acid) Polymeric Blends Electrospun with TiO₂-R/Fe₃O₄ for Pollutant Photodegradation

Alessandra Ruyz Medeiros¹, Fabiana da Silva Lima¹, Andressa Giombelli Rosenberger¹, Douglas Cardoso Dragunski^{1,2}, Edvani Curti Muniz^{2,3,4}, Eduardo Radovanovic² and Josiane Caetano^{1,*}

- ¹ Universidade Estadual do Oeste do Paraná—UNIOESTE, Toledo 85903-000, Brazil
- ² Department of Chemistry, State University of Maringá, 5790 Colombo Avenue, Maringá 87020-900, Brazil
- ³ Department of Chemistry, Federal University of Piauí, Campus Petronio Portella, Ininga, Teresina 64049-550, Brazil
- ⁴ Department of Material Science, Federal University of Technology—Parana, Estr. dos Pioneiros, 3131, Jardim Morumbi, Londrina 86036-370, Brazil
- * Correspondence: caetanojosi@gmail.com

Abstract: This work aimed to use the electrospinning technique to obtain PBAT/PLA polymer fibers, with the semiconductors rutile titanium dioxide (TiO_2 -R) and magnetite iron oxide (Fe_3O_4), in order to promote the photocatalytic degradation of environmental contaminants. The parameters used in the electrospinning process to obtain the fibers were distance from the needle to the collecting target of 12 cm, flow of 1 mL h $^{-1}$ and voltage of 14 kV. The best mass ratio of semiconductors in the polymeric fiber was defined from a 2² experimental design, and the values obtained were 10% TiO₂-R, 1% Fe₃O₄ at pH 7.0. Polymer fibers were characterized by Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA) and Fourier Transform Infrared (FTIR) techniques. SEM measurements indicated a reduction in fiber diameter after the incorporation of semiconductors; for the PBAT/PLA fiber, the average diameter was $0.9466 \pm 0.2490 \ \mu\text{m}$, and for the fiber with TiO₂-R and Fe₃O₄ was $0.6706 \pm 0.1447 \ \mu\text{m}$. In the DSC, DRX, TGA and FTIR analyses, it was possible to identify the presence of TiO₂-R and Fe₃O₄ in the fibers, as well as their interactions with polymers, demonstrating changes in the crystallinity and degradation temperature of the material. These fibers were tested against Reactive Red 195 dye, showing an efficiency of 64.0% within 24 h, showing promise for photocatalytic degradation of environmental contaminants.

Keywords: polymeric matrix composites; environmental contaminants; electrospinning; semiconductors

1. Introduction

Currently, one of the great problems that has been pointed out in developed or developing countries is environmental pollution. In recent years, humanity has faced environmental problems, of which the concern with water is extremely relevant. This special attention to water bodies is due to the fact that the demands are growing more and more due to the accelerated increase in population, which generates a greater consumption of quality water. However, the quality of water has decreased alarmingly, and one of the factors that contributes most to this is the incorrect disposal of waste [1].

The absence of standardized procedures that can be applied in the treatment of contaminated water requires that their treatments must be carried out in isolation due to the complexity of pollutants. Thus, the search for new alternatives that allow not only the removal of the pollutant, but the complete mineralization of the contaminants has been studied [2].

Among the commonly used methods are physical-chemical and biological treatments, however, these methods require additional steps at the end of the process, which increases



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the cost. In view of this, advanced oxidative processes (AOPs) stand out for the possibility of transforming complex compounds into simpler substances with less toxicity through the generation of highly reactive species that can be produced by using strong oxidizing agents, semiconductor metals or radiation [3].

In this context, titanium dioxide (TiO₂) is a semiconductor that has been extensively studied in AOPs, especially in heterogeneous photocatalysis due to its high chemical stability, low toxicity and low cost. This semiconductor is an insoluble oxide capable of acting in the degradation of microorganisms, such as bacteria and viruses, in addition to organic and inorganic contaminants, as it has the capacity to produce hydroxyl radicals and superoxides from the absorption of ultraviolet light. It has three polymorphic phases, anatase, rutile and brookite. The rutile phase is considered the least photoactive, and one of the possible factors pointing to this is the low oxygen adsorption capacity. However, despite its low photocatalytic activity, rutile has some advantages over the anatase phase, such as the band gap value, which is lower than that of anatase, being 3.0 eV and 3.2 eV, respectively [4–7].

Despite the advantages, the use of these semiconductors has disadvantages such as the removal of particles from the medium and the recombination of electron-hole charges, mainly from the rutile phase, whose recombination occurs easily and reduces the photocatalytic efficiency. Therefore, the combination of semiconductors with different band gap values has been extensively studied in order to make the photocatalysis process more efficient, making charge recombination difficult [8–10].

Thus, the use of iron oxides in photocatalysis has become favorable due to their semiconductor properties, their low cost, high selectivity, high ratio between surface area and volume, possibility of changing the surface and variable band gap of 2.2 to 3.0 eV depending on the oxide used and which facilitates the use of visible light absorption. Iron oxide occurs mainly in the hematite phase (Fe₂O₃) and is one of the most used oxides in industrial and scientific fields. However, the magnetite phase (Fe₃O₄) is also very promising for photocatalytic studies due to its multiple vacancies. In addition, the magnetic properties can help the separation of the reaction medium and possible reuse of the oxide [11–17].

However, despite the efficiency of using semiconductors in heterogeneous photocatalysis, some points have become unfavorable, such as the fine suspensions used. These suspensions, as in the case of TiO_2 , require an additional step in the treatment process, as it becomes necessary to separate the photocatalyst to avoid losses. Thus, the immobilization of these photocatalysts has gained relevance due to the ease of separation and reuse capacity [18,19]. Therefore, the use of the electrospinning technique to produce polymeric fibers with large surface area and high porosity containing semiconductors has been highlighted [20].

In the work of Aksimentyeva and collaborators, one can observe the advantage of producing a composite formed by an oxide and a polymer. The authors used nanoparticles of magnetite encapsulated with polymeric casings and modified by barium zirconate and polyaniline and verified, through the characterization of the composite, improvements in the properties of the materials together compared to those separated due to the interactions that reorganize the chemical bonds of the materials. In addition, it is highlighted the fact that the composite formed showed potential for varied applicability such as the development of sensors and materials for the area of medicine [21].

In recent times, polymeric fibers are being developed based on sustainability and the preservation of the environment. Therefore, the use of natural and biodegradable polymers has increasingly attracted the interest of researchers, such as poly(lactic acid) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT), which together form a polymer blend of Ecovio[®] [22].

Studies show several applications, both for pure polymers and for the PBAT/PLA polymer blend. Rocha [23] incorporated calcium carbonate in Ecovio[®] fibers to check their behavior and obtained better mechanical properties. Sheikh [24], on the other hand, studied the degradation of Congo Red dye using electrospun fibers of polyvinylpyrrolidone (PVP)

incorporated with rutile TiO_2 and Fe_2O_3 , and the fibers showed photocatalytic potential degrading about 75% of dye.

Therefore, this study aimed to use the electrospinning process for the development of a PBAT/PLA polymeric fiber incorporated with rutile titanium dioxide and magnetite iron oxide to evaluate its photocatalytic potential in the degradation of the azo dye Reactive Red 195.

2. Experimental

2.1. Material

The polymer used consists of a polymer blend of 55% poly (butylene adipate-coterephthalate) (PBAT) and 45% poly (lactic acid) (PLA), manufactured by Basf (Ludwigshafen, Germany), under the name Ecovio[®] F C2224. This was solubilized in Chloroform (CHCl₃) and N-N-dimethylformamide (C₃H₇NO) available from Neon Comercial (São Paulo, Brazil). The two semiconductors used were obtained from Sigma-Aldrich (St. Louis, MO, USA) with the following characteristics: titanium dioxide-rutile (TiO₂-R) with 99.9% purity (particle size smaller than 5 µm) and iron oxide-magnetite (Fe₃O₄) with 98.0% purity (particle size smaller than 50 nm). The dye used was Reactive Red 195, commercially named Red BF-4B (M_w = 1136.31 g mol⁻¹; C₃₁H₁₉N₇Na₅O₁₉S₆Cl).

2.2. Preparation of Polymer Solution

A 2.5 mL solution was prepared using 15% (w/v) PBAT/PLA solubilized in a mixture of chloroform and DMF (85:15% v/v). Subsequently, different percentages of semiconductors were added; for TiO₂-R, the concentration was varied from 10% to 25% (w/v), and for Fe₃O₄, from 1% to 10% (m/m in relation to the mass of TiO₂). The solution was subjected to magnetic stirring for 24 h before electrospinning.

2.3. Obtaining Polymeric Fibers

Polymeric fibers were obtained from the electrospinning process; for this, the polymeric solution was inserted into a 10 mL glass syringe with a Hamilton needle (Reno, NV, USA) with an internal diameter of 1.5 mm. To control the flow, an SP100I Syringe Pump (Sarasota, FL, USA) was used with an applied flow of 1.0 mL h⁻¹. The distance between the needle and the collecting target was 12.0 cm, and the potential difference applied to the high voltage source (Bertan, 30-R, Rio de Janeiro, Brazil) was 14.0 kV. Humidity and temperature were controlled to an average of $45 \pm 5\%$ and 25 ± 3 °C, respectively.

2.4. Experimental Design

To obtain the polymeric fibers, the mass proportions of the semiconductors were defined using a 2² experimental design with triplicate at the central point. For this, three levels and two factors were considered, as presented in Table 1.

Table 1. Experimental design.

| Factors | (-1) | (0) | (+1) |
|-------------------------------------|------|------|------|
| TiO ₂ -R (% <i>w/w</i>) | 10.0 | 17.5 | 25.0 |
| $Fe_{3}O_{4}$ (% <i>w/w</i>) | 1.0 | 5.5 | 10.0 |

2.5. Polymeric Fiber Characterization

To evaluate the morphology of polymeric fibers, samples were subjected to Scanning Electron Microscopy (SEM) (Quanta 250, Waltham, MA, USA). In order to measure the fiber diameter, the software Quantikov Image Analyzer 10.1 (Belo Horizonte, Brazil) was used, and 10 fibers were randomly measured from the SEM images at a magnification of 20 k×.

To identify the structural characteristic of the polymeric fiber and its modifications, it was analyzed by Fourier Transform Infrared (FTIR) spectra, using the Attenuated Total Reflectance (ATR) module. The spectrometer used was a Perkin-Elmer FTIR (Waltham, MA, USA), and the conditions for analysis were a temperature of 25 °C, in the region of 650 to 4000 cm⁻¹, with a resolution of 1.0 cm⁻¹.

Thermal properties were evaluated by differential scanning calorimetry (DSC). The equipment used was a Shimadzu DSC 60 (Kyoto, Japan), under an inert nitrogen atmosphere with a flow rate of 50.0 mL min⁻¹. The heating and cooling rate was 10 °C min⁻¹, with heating starting at a temperature of 25 °C to 200 °C, and cooling starting at a temperature of 200 °C to 25 °C. For calculations of the heat involved in the processes and the melting and crystallization temperatures that occurred during heating and cooling, TA60WS software (Kyoto, Japan) was used. The calculation of polymer crystallinity was also performed using Equation (1), conceived by Rossin and Aldhafeeri [25,26].

$$X_c = (\Delta H_m - \Delta H_c / \Delta H^\circ_m) \times 100 \tag{1}$$

where X_c is the degree of crystallinity of the polymer, ΔH_{cc} is cold crystallization enthalpy of the sample, ΔH_m is fusion enthalpy of the sample, ΔH°_m is theoretical fusion enthalpy of the 100% crystalline sample; in the case of PBAT, $\Delta H^\circ_m = 114 \text{ J} \cdot \text{g}^{-1}$, and, for PLA, $\Delta H^\circ_m = 93.7 \text{ J} \cdot \text{g}^{-1}$.

Thermal stability of the fibers was verified by thermogravimetric analysis (TGA) with Perkin-Elmer STA 6000 equipment (Waltham, MA, USA). The experimental conditions were a nitrogen atmosphere with a flow rate of 50 mL min⁻¹ at a heating rate of 10 °C min⁻¹ and temperature varied from 25 to 545 °C.

X-ray diffraction analysis was performed to verify the crystallinity of the samples. For this, a Bruker[®] diffractometer (Billerica, MA, USA) was used, with diffraction at a 2 θ angle, ranging from 7° to 80°, with an increment of 0.01°, using Cu_{K α} radiation of λ = 1.5406 Å, as a graphite monochromator.

2.6. Photocatalytic Degradation

To assess the photocatalytic capacity of the fibers obtained, an aqueous solution was prepared, at a concentration of 35 mg L⁻¹, of the azo dye Reactive Red 195, and 30 mL of solution was placed in a beaker containing the polymeric fiber in a steel support of 3.0 cm^{-1} in diameter. Subsequently, the dye solution was irradiated by an Osram Ultra-Vitalux 300 W UV-A/UV-B Xenon lamp (Munich, Germany) with a measured intensity of 46 W m⁻² for a period of 1440 min. The distance between the lamp and the solution was measured at 28.5 cm, and a thermostated bath kept the temperature of the study system controlled at 21.0 °C.

Dye solution degradation was evaluated using a Shimadzu-1800 UV/VIS spectrophotometer (Kyoto, Japan) in the 200–800 nm spectral region. For this analysis, aliquots were taken at defined times up to 1440 min. All aliquots taken for analysis were returned to the irradiated solution.

3. Results and Discussion

3.1. Preliminary Tests

The mass proportions of semiconductors (TiO₂-R/Fe₃O₄) with higher photocatalytic efficiency were defined using a 2^2 factorial design. For this study, preliminary degradation tests were performed using the reactive dye Reactive Red BF-4B in order to obtain the values to be applied in the design. A small variation in the pH of the medium was also produced to check the influence on the analyte degradation. Figure 1 illustrates the preliminary tests, together with the dye photolysis and the study with the polymeric fiber with the PBAT/PLA polymer alone.

Within 24 h of exposure to light, there was no dye degradation and the pure PBAT/PLA fiber also did not show photocatalytic activity in dye degradation. A lower percentage of Fe_3O_4 caused an increase in degradation of approximately 30% for the 40% TiO_2 -R + 1% Fe_3O_4 fiber. According to the catalytic regime, the degradation speed is generally proportional to the catalyst mass, but there is a limit on the amount of mass to be used, and, after reaching it, the process becomes independent of it. This maximum amount depends on some factors,

such as the experimental conditions, light irradiation and also the amount of dopant, which, if excessive (above 1%), causes a greater number of defects in the doped structure, and, thereby, the degradation response decreases [27,28].



Figure 1. Degradation of BF-4B Reactive Red dye (35 mg L^{-1}) for polymeric fibers of pure PBAT/PLA; incorporated and the photolysis of the dye at pH 7 under luminous intensity of 46 W m².

Furthermore, there was little difference in dye degradation when comparing the fiber containing 40% TiO_2 -R + 5% Fe_3O_4 at pH 6.0 and 8.0. Due to the small difference between the pH tested, it was decided to carry out the experimental design at pH 7.0, as more acidic or alkaline pH values can favor the hydrolysis of polymer fibers; in addition, in acidic pH, iron solubilization can occur.

After these tests, fiber containing 40% TiO₂ was visibly dry and fragile, therefore, we decided to do a test with 25% TiO₂ mass, setting the Fe₃O₄ mass at 1%. The degradation obtained was almost 60% of dye and, visually, the fiber produced was more resistant.

From the preliminary tests, it was possible to set the levels of TiO_2 and Fe_3O_4 applied in the 2^2 design. The experiments were performed randomly and irradiated for 24 h; the evaluated response was the percentage of degradation of the dye Reactive Red 195. The results are listed in Table 2.

| Order of Experiments | TiO ₂ -R Mass (%) | Fe ₃ O ₄ Mass (%) | Dye Degradation Percentage (%) |
|----------------------|------------------------------|---|--------------------------------|
| 3 | 10.0 | 10.0 | 20.7 |
| 5 | 17.5 | 5.5 | 28.7 |
| 6 | 17.5 | 5.5 | 32.3 |
| 2 | 25.0 | 1.0 | 39.6 |
| 1 | 10.0 | 1.0 | 63.9 |
| 7 | 17.5 | 5.5 | 26.1 |
| 4 | 25.0 | 10.0 | 33.9 |

Table 2. Matrix of the 2^2 experimental design.

Only experiment 1 presented a degradation percentage higher than 50%. Thus, to assess which factor has the greatest influence on the response variable, Table 3 was analyzed.

| | Effects | Standard Error | t-Value | p *-Value |
|---|---------|----------------|---------|-----------|
| Intercept | 35.028 | 1.176 | 29.766 | 0.001 |
| (1) TiO_2 -R mass | -5.550 | 3.113 | -1.782 | 0.216 |
| (2) Fe ₃ O ₄ mass | -24.450 | 3.113 | -7.853 | 0.015 |
| 1 by 2 | 18.750 | 3.113 | 6.022 | 0.026 |

Table 3. Effects for dye degradation percentage response.

* Values in red show the significant variables at the 95% confidence interval (*p*-value < 0.05%).

Table 3 shows that the interaction effects related to the TiO_2/Fe_3O_4 ratio, as well as the Fe₃O₄ mass, are significant, noting that iron oxide is an important factor for dye degradation. These results can be interpreted according to the algebraic signs of the effects. For the main effects with negative values, there is an indication that the response increases when the factor moves towards its minimum level. For interactions, positive values show that the two factors must go towards the same level, being this lower or higher, for the response to increase. Therefore, the surface graph was constructed, as shown in Figure 2.



Figure 2. Surface graphics for TiO₂-R/Fe₃O₄ ratio.

It can be seen in Figure 2 that the increase in degradation occurs with the decrease in the percentage of Fe_3O_4 and TiO_2 -R mass, which corroborates the studies shown in Table 2, with the polymeric fiber with TiO_2/Fe_3O_4 at 10:1% with better photocatalytic activity.

3.2. Polymeric Fiber Characterization

After obtaining the polymeric fibers, SEM analyses were performed (Figure 3) in order to assess diameters, morphologies and their possible alterations.

Analyzing the images, it can be seen that both the fibers with embedded semiconductors and the pure PBAT/PLA fiber presented a uniform and continuous appearance. Moreover, it is noted that there is evidence that TiO₂-R and Fe₃O₄ are found inside the fibers. In addition, in the presence of semiconductors, there was a reduction in their diameter, and, for the PBAT/PLA fiber, the mean diameter was $0.9466 \pm 0.2490 \ \mu\text{m}$, for TiO₂-R, $0.5890 \pm 0.1707 \ \mu\text{m}$, for Fe₃O₄, $0.7102 \pm 0.2479 \ \mu\text{m}$ and for TiO₂-R with Fe₃O₄, $0.6706 \pm 0.1447 \ \mu\text{m}$. When analyzing the standard deviation of the pure PBAT/PLA fiber ($\pm 0.2490 \ \mu\text{m}$) and the fiber incorporated with the two semiconductors ($\pm 0.1447 \ \mu\text{m}$), it was observed that there was an increase in homogeneity with their presence. This occurs because the presence of semiconductors possibly increases the electrical conductivity of the polymer solution [29]. In addition to SEM images, photographs were taken (Figure 4) of polymer fibers with and without TiO₂-R and Fe₃O₄.



Figure 3. Scanning Electron Microscopy (SEM) images of (**a**) pure PBAT/PLA polymeric fibers; (**b**) with 10% TiO_2 -R + 1% Fe_3O_4 ; (**c**) with 10% TiO_2 -R; and (**d**) with 1% Fe_3O_4 . All at 20,000× magnification.



Figure 4. Images of polymeric fibers of PBAT/PLA (**a**) with 10% TiO_2 -R; (**b**) with 1% Fe_3O_4 ; (**c**) pure; and (**d**) with 10% TiO_2 -R + 1% Fe_3O_4 .

From the images, fibers 4-a and 4-c showed little difference in color, both of which have a white color due to the characteristics of the materials. However, in the 4-a image, the white color is more intense due to the presence of TiO₂-R. Fibers 4-b and 4-d, on the other hand, exhibited a gray coloration, whereas fiber 4-b had a darker color because it contains only Fe₃O₄. Given this and the SEM images, it can be said that the fibers are possibly found in the presence of semiconductors [30,31]. To prove the semiconductors in polymer fibers, FTIR analyses were performed, as illustrated in Figure 5.

A summary of the peaks observed in the FTIR analysis are presented in Table 4.

| Polymer | Wave Number (cm $^{-1}$) | Functional Group |
|---------|---------------------------|---|
| PLA | 1759 | C=O |
| PBAT | 2948 and 2886 | C–H sp ³ and sp ² |
| PBAT | 1710 | C=O |
| PLA | 1453 and 1392 | C–H sp ² |
| PLA | 1182 | C-O-C |
| PBAT | 1083 | C-O-C |

Table 4. Absorption band in the infrared region for PBAT and PLA.



Figure 5. Fourier Transform Infrared (FTIR) vibrational spectra from attenuated reflectance (ATR) for PBAT/PLA polymer fibers.

From the infrared spectra, it was possible to observe the characteristic bands of PBAT and PLA polymers, the bands being presented for the ester group for PBAT at 1083 cm⁻¹, and for PLA at 1182 cm⁻¹. Furthermore, another characteristic band is the carbonyl of polymers, which is presented for PBAT and PLA at 1710 cm⁻¹ and 1759 cm⁻¹, respectively. The band observed at 2950 cm⁻¹ refers to the stretching of C–H bonds [32]. Regarding the incorporation of semiconductors, no characteristic bands were observed. However, there was an increase in the intensity of the carbonyl band of both polymers, especially the C=O band of PBAT, when compared to the pure polymer fiber, which may show that the semiconductors are found inside the fibers.

In order to assess the thermal stability of the fiber containing the semiconductors, DSC analyses were performed (Figure 6).



Figure 6. (a) Heating and (b) cooling thermograms for PBAT/PLA polymeric fibers.

According to thermograms, it is possible to identify three endothermic peaks (Figure 6a), referring to the PBAT/PLA blend; these being peak 1 (\approx 62.0 °C), peak 2 (\approx 90.0 °C) and peak 3 (\approx 150.0°). Peak 1 is associated with the glass transition temperature (T_g) of PLA,

that is, the passage from a rigid material to a more organized material. Peak 2 refers to the melting temperature (T_f) of PBAT, and peak 3 to T_f of PLA [33,34].

 T_f of PBAT has a broader and less intense peak compared to T_f of PLA, which has a more intense behavior. This may indicate that PBAT has less crystallinity, that is, it has less rigidity. Studies report that PBAT has two melting temperatures, one referring to the melting of the aliphatic part (close to the T_g of PLA (peak 1)), and the other temperature referring to the aromatic part (peak 2). Therefore, due to a possible interaction between PBAT/PLA, the T_f of PBAT, referring to the aliphatic part, may have been overlaid by the T_g of PLA [35,36].

In addition to the endothermic peaks, it was possible to observe in Figure 6b the presence of one exothermic peak for polymer fibers at approximately 95 °C. This peak is related to the crystallization temperature (T_{cc}) of PLA [35]. The melting and crystallization temperatures and the heat involved in the processes are described in Table 5.

Table 5. Temperatures and heat involved in the fusion and crystallization of polymer fibers.

| | Peak 1 | | Peak 2 | | Peak 3 | | Peak 4 | |
|---|-----------------------------|------------------------------|-----------------------------|------------------------------|-----------------------------|------------------------------|--------------------------------------|------------------------------|
| Polymer Fiber | T _{fusion} (°C) | Heat (J∙g ^{−1}) | T _{fusion} (°C) | Heat (J∙g ^{−1}) | T _{fusion} (°C) | Heat (J∙g ⁻¹) | T _{crystallization} (°C) | Heat (J∙g ⁻¹) |
| PBAT/PLA | 61.92 | 1.46 | 94.95 | 11.07 | 151.71 | 11.77 | 94.07 | -0.08 |
| PBAT/PLA/10% TiO2-R | 61.64 | 0.76 | 87.93 | 5.48 | 151.63 | 7.43 | 93.41 | -0.09 |
| PBAT/PLA/1% Fe ₃ O ₄ | 61.84 | 1.00 | 94.01 | 9.74 | 151.51 | 11.23 | 93.04 | -0.09 |
| PBAT/PLA/10% TiO ₂ -R/1% Fe ₃ O ₄ | 61.86 | 0.90 | 90.45 | 5.90 | 151.54 | 10.66 | 92.67 | -0.09 |

With the presence of semiconductors, both for the fibers containing the blend and for those containing the semiconductors separately, there was a decrease in the melting and crystallization temperatures of PBAT and PLA, but they were not very expressive. The heat involved in the melting process, on the other hand, decreased more sharply, which may indicate the interaction of TiO_2 and Fe_3O_4 with both polymers. To better assess this possible interaction, the degree of crystallinity related to the fusion process of PBAT and PLA was calculated. The results are listed in Table 6.

Table 6. Crystallinity percentages calculated for the melting peaks of the polymeric fibers.

| Polymer Fiber | Crystallinity Peak 2 (%) | Crystallinity Peak 3 (%) |
|--|-----------------------------|-----------------------------|
| PBAT/PLA | 9.78 | 10.40 |
| PBAT/PLA/10% TiO ₂ -R | 5.15 | 6.60 |
| PBAT/PLA/1% Fe ₃ O ₄ | 8.62 | 9.92 |
| PBAT/PLA/10% TiO2-R/1% Fe3O4 | 5.25 | 9.42 |

After the incorporation of semiconductors, a decrease in the crystallinity of both PBAT and PLA was found, which may indicate that semiconductors interacted with both polymers. The polymeric fiber containing only TiO_2 has a lower crystallinity value, that is, the incorporation of this semiconductor makes the polymeric fibers less organized, which may indicate that it worked as a plasticizer. In addition, it is noted that, for PBAT, there was a reduction in crystallinity for both polymer fibers; this may be due to PBAT having aromatic chains and possibly they fold TiO_2 , unlike PLA, which has aliphatic chains and can therefore form clusters with the semiconductor [37].

To verify whether the degradation temperature of the PBAT/PLA fiber was changed in the presence of semiconductors, TGA measurements were performed, as can be seen in Figure 7.



Figure 7. Thermogravimetric curves (TGA) and derivative of degradation curves (DTGA) of pure (a) PBAT/PLA polymeric fibers; (b) with 10% TiO_2 —R; (c) with 1% Fe_3O_4 ; and (d) with 10% TiO_2 —R + 1% Fe_3O_4 .

Both polymer fibers lost mass in two thermal events defined by derivative curves, in which the first thermal event indicates the degradation of the PLA polymer and the second, the PBAT polymer [38].

Furthermore, it was possible to verify that the presence of TiO₂ and Fe₃O₄ modified the degradation temperature of polymeric fibers in relation to pure PBAT/PLA. For fibers containing only 10% TiO₂—R, there was an increase in the initial degradation temperature for both polymers, being \approx 9.0 °C for PLA and \approx 20 °C for PBAT, showing an increase in their thermal stability.

However, for polymer fibers containing Fe₃O₄, both pure and in the presence of TiO₂, there was a decrease in the initial degradation temperatures. For pure Fe₃O₄ fiber, this decrease was \approx 2.0 °C for PLA, and \approx 10.0 °C for PBAT, indicating a more pronounced decrease in stability for PBAT. In addition, a change in the DTGA profile in the presence of semiconductors is noted, indicating that Fe₃O₄ possibly interacts with polymers.

As for the polymeric fiber containing TiO₂ and Fe₃O₄, this decrease in the initial degradation temperature was \approx 15.0 °C for PLA, and \approx 4.0 °C for PBAT, indicating a lower stability for PLA. Therefore, these results can show that there is a more synergistic effect for PLA when the two semiconductors are combined, showing that, even in small amounts, iron can influence the characteristics of the polymeric fiber, corroborating the degradation tests. Furthermore, these results may indicate interaction between semiconductors and polymers, as also shown by DSC analysis.

XRD analyses (Figure 8) were performed to assess fiber crystallinity before and after addition of semiconductors.

In Figure 8, a change in the characteristics of the polymeric fiber can be seen after the incorporation of semiconductors [39]. Between the angles of 25.0° and 70.0°, there was an increase in crystallinity, which is probably due to the crystal structure of semiconductors, as can be seen in the diffractograms (Figure 8a,b) of the powder samples. However, when comparing polymer fibers in the presence of semiconductors separately (Figure 8d,e), it can be noted that the crystallinity of TiO₂-R is more evident than Fe₃O₄, corroborating Figure 8c, which shows crystallinity peaks similar to those of powdered TiO₂, indicating that rutile titanium dioxide is responsible for the increase in crystallinity of the fiber containing the semiconductor blend. These results, together with the SEM, TGA, DSC and FTIR analyses, indicate the presence of semiconductors in polymer fibers.



Figure 8. X-ray diffractograms of powder samples of (a) TiO—R and (b) Fe_3O_4 and polymeric fibers of PBAT/PLA (c) with 10% TiO₂—R + 1% Fe_3O_4 ; (d) with 10% TiO₂—R; (e) with 1% Fe_3O_4 ; and (f) fiber in the absence of semiconductor.

3.3. Photocatalytic Degradation of Reactive Red 195

The potential of the polymeric fiber was tested by photocatalytic degradation, using the dye Reactive Red 195 as a model molecule. The tests were performed with the polymeric fibers in the absence of semiconductors (photolysis), in the presence of each one separately and in the fibers containing the blend, as shown in Figure 9.



Figure 9. (a) Degradation of Reactive Red 195 for pure PBAT/PLA fibers and incorporated PBAT/PLA fibers. (b) Images of membrane nanostructure of PBAT/PLA after 1400 min of photodegradation ((1) with 10% TiO₂—R; (2) with 1% Fe₃O₄; (3) pure; and (4) with 10% TiO₂—R + 1% Fe₃O₄).

From these tests, it is observed in Figure 9a that there was no dye degradation with light irradiation, and that the pure PBAT/PLA polymeric fiber and that with 1% Fe₃O₄ did not present photocatalytic activity.

Furthermore, the polymeric fiber containing the blend of TiO_2 —R/Fe₃O₄ semiconductors had greater photocatalytic activity (64.0%), compared to polymeric fibers containing

only TiO₂ (24.0%), for a degradation time of 1440 min. According to Zhan [40], the improvement in the photocatalytic efficiency of the polymeric fiber of titanium dioxide with iron oxide may occur because the iron oxide possibly increases the titanium dioxide absorption intensity in the visible light region and, consequently, more electrons and holes are generated and accelerate photocatalysis, in addition to decreasing the electron-hole recombination time.

Furthermore, in Figure 9b, it can be seen that, after a degradation time of 1440 min, all membranes used in the test were visually stable, which may indicate that they can be reused.

Another important factor is the onset of degradation, which only occurs after 300 min. This is possibly due to the hydrophobic character of the PBAT/PLA blend, making it difficult for semiconductors to contact the dye [41]. Therefore, it was decided to test the degradation with the polymeric fiber, after its immersion for 1080 min in distilled water, as illustrated in Figure 10.





The polymeric fiber immersed in water presented better photocatalytic efficiency compared to the fiber without immersion, being about 20.0% higher after 900 min. These results indicate that, with immersion in water, fibers may swell, causing the dye to come into contact with the semiconductors, promoting more rapid degradation.

These tests showed that fibers containing the semiconductor have the potential to promote photocatalytic degradation of environmental contaminants.

4. Conclusions

It was possible to obtain a polymeric fiber of PBAT/PLA/TiO₂-R/Fe₃O₄ with photocatalytic activity by the electrospinning process, using experimental design. The characterization of the fibers showed the presence of semiconductors with a decrease in the average diameter and an increase in uniformity, indicating possible interactions. These results demonstrated that semiconductors can be immobilized in polymeric fibers obtained by electrospinning without impairing their properties and photocatalytic characteristics. Moreover, that, because of this, the material produced has an interesting applicability in the degradation of pollutants with the possibility of reuse without considerable loss of its efficiency for more than one cycle of degradation, in addition to facilitating the separation of semiconductors from the reaction medium once they remain immobilized in the polymeric fiber. **Author Contributions:** Conceptualization A.R.M. and F.d.S.L.; methodology, A.R.M., F.d.S.L. and A.G.R.; software, A.R.M. and F.d.S.L.; investigation, A.R.M. and F.d.S.L.; resources, D.C.D., J.C., E.C.M. and E.R.; data curation, A.R.M. and F.d.S.L.; supervision, D.C.D. and J.C.; project administration, J.C.; funding acquisition D.C.D., J.C., E.C.M. and E.R. All authors have read and agreed to the published version of the manuscript.

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