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Polystyrene fibers recycled waste produced by Solution Blow spinning with TiO_2 incorporation.

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Abstract
This study attempted to produce polymeric microfibers with low-cost and photocatalytic properties, making it possible to remedy two modern problems, plastic disposal and irregular effluent disposal, for which we used the solution blows pinning (SBS) technique to produce recycled polystyrene (PS) microfibers (recycled waste from transparent barrel pen), the use of the SBS also has good mobility for the benefit of fibers, allowing the fibers to be produced directly under the surface where intend to be used, through the SEM was found the ideal concentration to produce uniform microfibers. With the minor average diameter, FTIR analysis of the fibers showed peak characteristics of PS, demonstrating that most of the transparent barrel pen is composed of PS. The as-prepared fibers of recycled PS were incorporated into their polymer solution with a TiO_2 Degussa P25 concentration of 10% (w/w) concerning the polymer mass. For the study of photocatalytic activity, the dye Rhodamine B was used as an indicator. Excellent photocatalytic activity, XRD pattern of PS and PS/TiO_2-10% fibers showed PS and TiO_2 in two phases, anatase and rutile.

Keywords: Recycled polystyrene, solution blows pinning, polymer fiber, TiO_2

1. Introduction

The industrialization process over the years has brought several benefits to society, but along with it many environmental problems have come, such as the propagation and accumulation of waste.[1-3] Part of this waste is often mistakenly disposed of, according to recent research. Industries are contaminated by paints, resins, phenol, fatty acids, dyes, and plastics. [4-5] One of these commonly found dyes is Rhodamine-B, which is soluble in water and belongs to the class of xanthenes, it is widely used in textile, cosmetics, and printer cartridges. Still, it is highly toxic to humans and animals, which may irritate the eyes and respiratory tract. Studies show that it has both carcinogenicity and neurotoxicity. [6-8]

Conventional processes for treating waste in water and eliminating these dyes are generally high-cost and complex, such as ionization[9], extraction[10], electrochemical method[11], and sonocatalytic degradation[12]. The photocatalysis process is currently being highly studied because it is a simple process to be applied, a compound used in this process is titanium dioxide (TiO_2), which is a semiconductor non-toxic, low cost and stable, its energy GAP to the anatase phase is in the range of 3.2 eV, thus an energy range that corresponds to UV light.[13-14]

To improve the efficiency and application of the TiO2 photocatalytic it is attractive that the semiconductor is distributed in polymeric nanofibers to increase its surface area. The most common technique for producing polymeric nanofibers is electrospinning, but because of its use of high electric fields, it becomes a dangerous and expensive method[15-16]. A recently developed method was called Solution Blow Spinning (SBS), and it is possible to produce nanofibers more efficiently and without the use of high voltages, only by extrusion of the solution by blow and creating a region of difference in pressure [17-18].

Different polymers can be used in the SBS technique; one of them is polystyrene (PS). PS is a polymer widely used in packaging, e.g., disposable cups, plates, and construction materials, as it has an excellent cost-benefit and good mechanical properties. There are about 21 million tons of polystyrene produced in the world[19].

In this work, sustainable polystyrene was used, acquired through transparent pens discarded by society. The Solution Blow Spinning technique produced the PS / TiO2 nanofibers, and their photocatalytic activity was evaluated through the degradation of the dye Rhodamine B.

2. Experimental

2.1. Materials

Polystyrene was obtained through the recycling of transparent pen barrel, ethyl acetate was purchased from Sigma-Aldrich, dioxide titanium (TiO2) Degussa (P25) were obtained from Nippon Aerosil CO LTD, the reagents were was used without purification.

2.2. Preparation of solution blow spinning recycled PS and PS/TiO_2

To get the PS, the transparent barrel pen was used. After washing and macerate, the pen was dissolved in ethyl acetate at four different concentrations 10; 13.5; 15 and 17.5% w/v ratio. The solution was vigorously stirred for 1 hour at room temperature, and after mixing the prepared solutions were poured into a 5 ml syringe and inserted in the SBS technique. To produce PS-TiO2 fibers we used the 13.5% PS solution and added 0.05 g of TiO_2 nanoparticles with an average diameter of 25 nm. The solution was poured into a syringe and inserted in the SBS technique.

The parameters used were 120 µl/min for feed rate, 150 rpm in the rotate collector counterclockwise, 35 cm between the needle tip and collector, the pressure used in the system was 140 kPa, all fibers were obtained at room temperature. The fiber membrane was collected on aluminum foil and then peeled off. The apparatus used in the SBS technique is illustrated in Fig. 1.

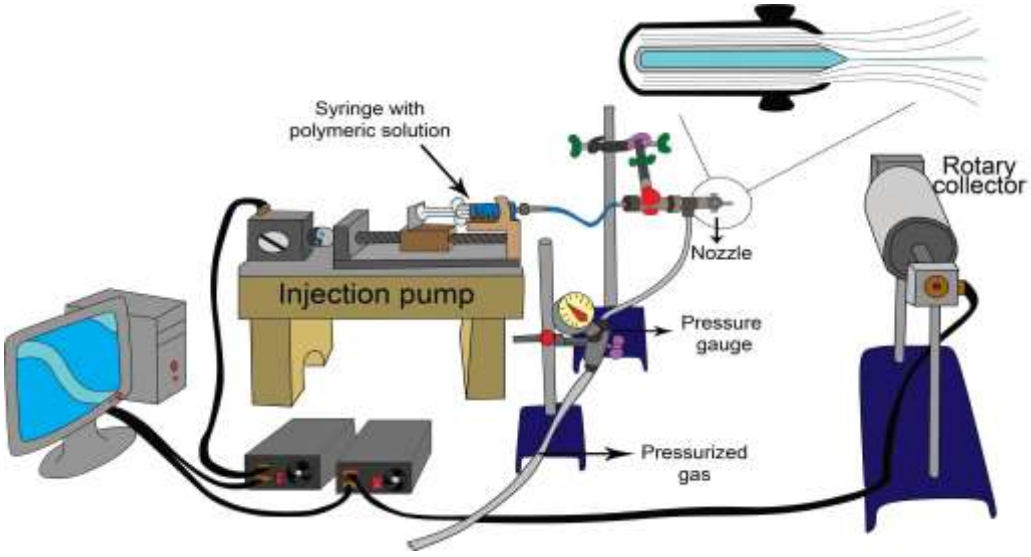

Figure 1. Apparatus used in SBS technique to produce PS and PS/TiO_2 fibers.

2.3. Characterization

Scanning electron microscopy (SEM, Zeiss EVO LS15) was used to evaluate the fiber's morphology and diameter, performed at a voltage of 10 KV. X-ray diffraction (XRD) was used to define the structures and phases of the samples using equipment (Shimadzu, XRD-6000) CuKα (λ=1,54 Å). Uv-vis spectra were collected by (Varian Cary 50 Scan) to analyze the peak decay in maximum dye absorption. The FTIR Nicolet 5DXB (Nicolet Instruments, Madison, WI) was used to discover the composition of the PS recycled.

2.4. Photocatalytic activity evaluation

The photocatalytic activity of PS/TiO_2 was evaluated by the degradation of RhB in water solution under UV irradiation. In the photocatalytic assay was used in a closed box with a UV mercury lamp (150 W), and a magnetic stirrer, the distance between the lamp and the surface of the solution was 25 cm. A RhB solution (0,02 mol/l) was prepared and the fibers were immersed in the solution with a ratio of 0.08 g to 100 ml. After the UV irradiation, 3 ml of sample drawn in regular intervals of 5 min to be analyzed in the UV-vis spectrophotometer.

3. Results and Discussion

3.1. Structure and morphology of PS fibers obtained from SBS technique

Initially, to produce the fibers, we chose to use four different concentrations of PS with ethyl acetate. Was sought to obtain fibers with the smallest diameter to proceed with the photocatalyst characterizations as discussed by Huang et al.20, the more minor the surface area, the larger the contact area, which is highly desirable for photocatalysis.

A fiber analysis was performed using SEM and the results are shown in Fig. 2. Figure (a) we have fibers obtained with a concentration of 10% (m / v). We can observe fibers with diameters between 5-25 µm, not dispersed and with some granules. Fig. 1. (b) and (c) show fibers with 13.5 and 15% concentrations, respectively. We can observe fibers with smoother aspects and better disperses where we can highlight the concentration of 13.5% with the best dispersion and with low diameter variation as shown in figure (e). Figure (d) shows that the fibers obtained with a concentration of 17.5% have diameters between 6 and 22 µm. We observe that most fibers are joined together. This morphology is due to the high concentration of polymers that prevent the fibers from dispersing in production and drying before reaching the collector.

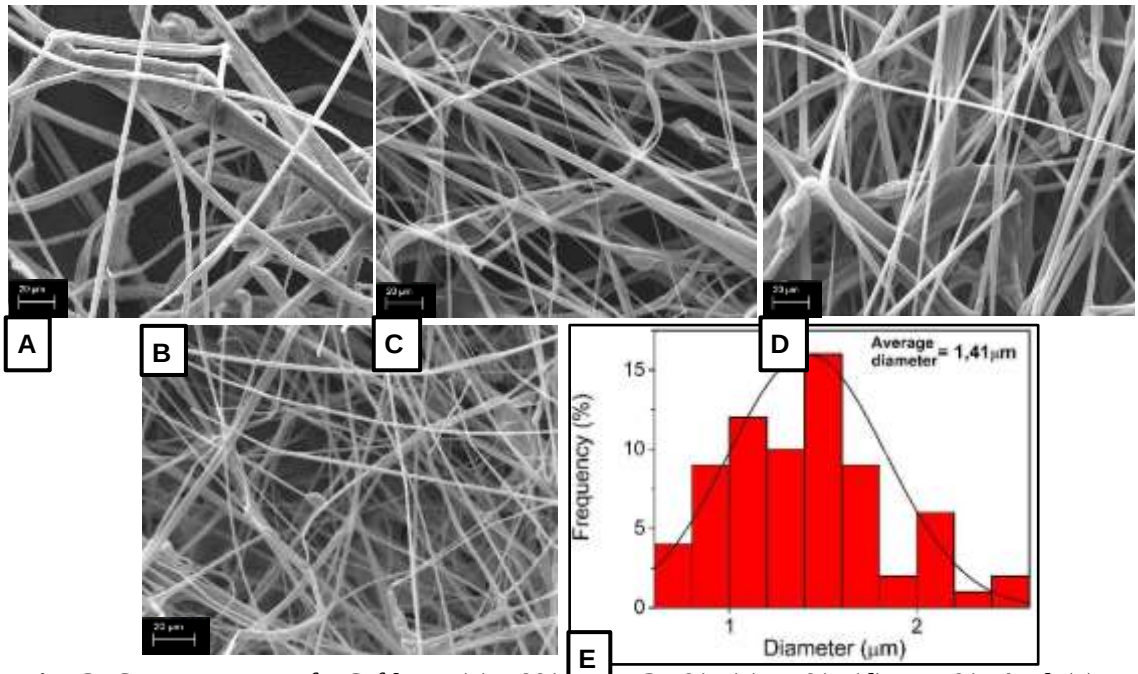

Fig. 2. SEM images of PS fibers (a) 10%, (b) 13.5%, (c) 15%, (d) 17.5%. And (e) a diagram of average diameter for fiber 13.5%.

Fourier transform infrared spectroscopy (FTIR) was used for quantitative fiber analysis. Fig. 3 shows the infrared spectrum of 3200-400 cm^{-1}as a way to improve the visualization of the absorption bands, we used a baseline to correct the intensity of the result.

Due to the use of a recycled material that went through unknown processes in the industry where it was manufactured, it can lead to some noise and some peaks that are not related to the PS. However, in Fig. 3,

some absorption peaks characteristic of PS, such as the peaks from 3200 to 2800 where we have the CH elongation modes, the 3060 and 3026 cm^{-1} peaks are related to the CH elongation vibrations aromatic. For peaks 2923 and 2848 cm^{-1}, the vibrations of asymmetric and symmetrical elongation of the methylene groups -CH2, respectively. The pattern of peaks in 1601, 1493, and 1452 cm^{-1} regions are related to The aromatic C=C stretching vibration absorption; these peaks indicate the presence of an aromatic ring probably coming from the PS; however, the 1452 cm^{-1} band can be a result of both of the deformation of -CH2 as the ring breathing of the benzene ring. The absorption peaks at 1028 cm^{-1} are related to in-plane C–H bending of the phenyl ring, and the peaks at the wavenumbers of 757 and 697 cm^{-1} correspond to C-H out-of-plane bending vibration absorption.

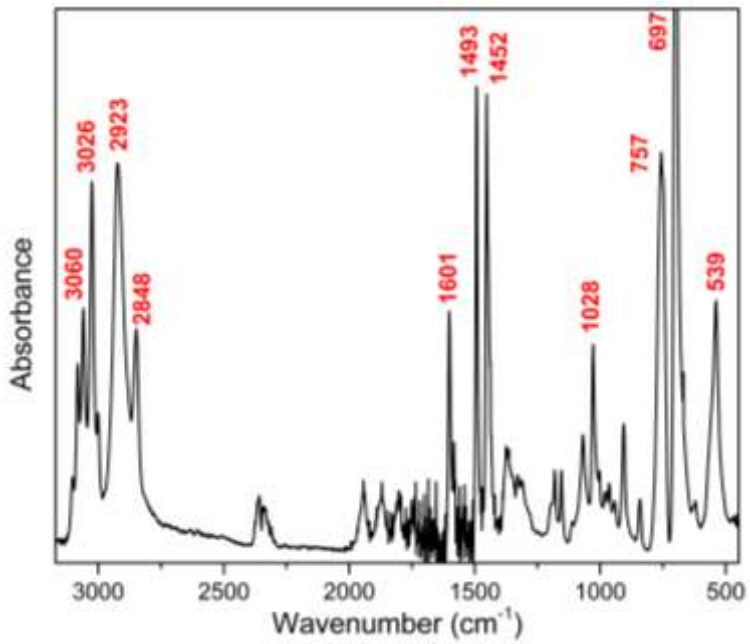

Fig. 3. Infrared spectrum of PS fibers produced PS recycled waste.

3.2. Photocatalytic performance and composition of PS/TiO_2.

For TiO2 incorporation, we used the fiber with a concentration of 13.5% (w/v) as it has the minor average diameter among all samples, and the amount of TiO_2 incorporated was 10% of polymer mass (w/w). After the incorporation of TiO_2 was investigated, the stability and photocatalytic activity of the composite fibers.

The photocatalytic activity was investigated by degradation of RhB dye. The fibers were cut into a circular shape with a mass of approximately 0.08 grams and fixed in support in the center of the beaker.

With the incidence of UV light the dye degradation was monitored by removing 2 ml aliquots in 10 min. The Uv-vis spectra were set between 450-610 nm being the λ_{max} of RhB dye at 540 nm. As we can see in Fig. 4 the graph refers to the photocatalytic activity of the PS/TiO_2 $\mathbf{C/C_0}$ versus the time equation where $\mathbf{C_0}$ is the initial concentration of RhB and **C** is the concentration of RhB that was degraded at time. TiO_2 Degussa p25 was choosing due to as a nanoparticle due to its degradation capacity, low cost and used as a reference in several works as a standard photocatalys[21-23] a considerable degradation of the dye during ultraviolet light irradiation, proving to be promising for using the fibers as a photocatalyst even with a small amount of TiO_2, degrading 65% of the dye during 100 minutes under UV irradiation, during non-photocatalysis there was breakage of the fibers and no particles that came detached during the photocatalytic test, showing good stability.

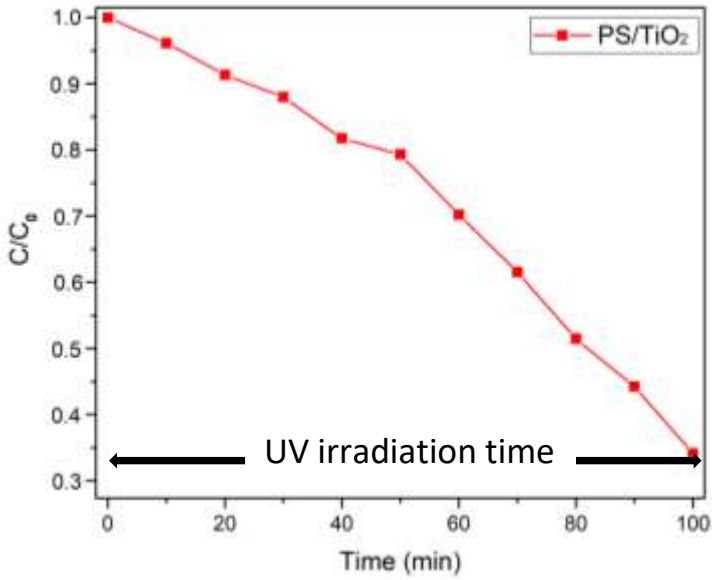

Fig. 4. Photocatalytic degradation of RhB dye using ultraviolet radiation and PS/TiO_2-10% fiber as photocatalyst.

Fig. 5. shows the XRD pattern of PS and PS / TiO2, we can see that the PS diffractogram is not well defined indicating a large amount of amorphous polymer, and as expected, the fibers present Anatase phase (peaks 25.2° (101), and 48.1° (200)) and Rutile phase (peaks 27.4° (110); 36.1° (101); 54.3° (221)).

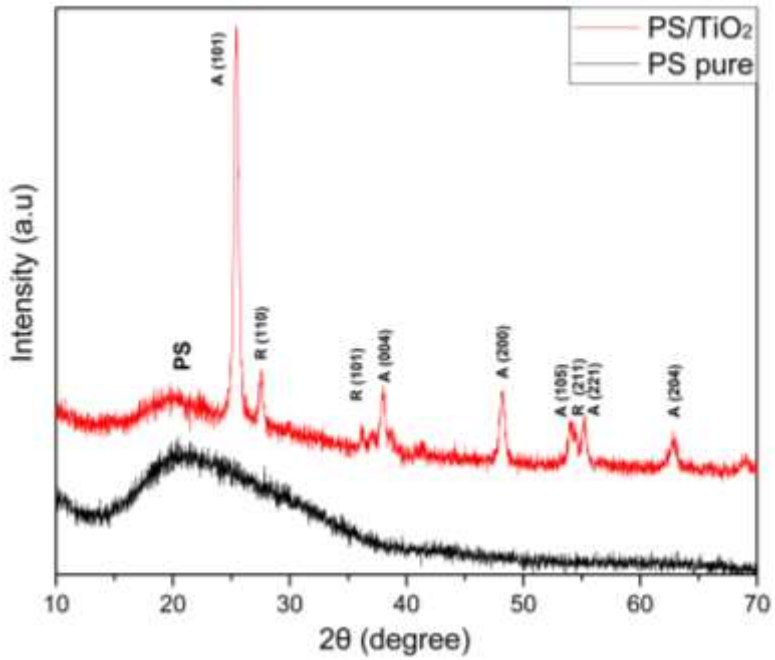

Fig. 5. XRD pattern of PS-13% and PS/TiO_2-10% fibers. (A) Anatase, (B) Rutile.

4. Conclusion

In summary, the solution blow spinning technique enabled the production of recycled PS fibers and the PS/TiO_2 composite. In the initial study, to determine the ideal concentration to produce PS fibers uniform and smaller diameter, was used the SEM and the ideal concentration was 13.5%, with an average diameter of 1,4 μm. Using the FTIR technique in the fibers produced, was possible to find several peaks characteristic of the PS. XRD showed peaks of the two phases of TiO_2 Anatase and Rutile as expected due to the use of TiO_2 Degussa P25 and the PS-related peak. Moreover, fibers with 10% (w/w) incorporations of TiO_2

Degussa P25 showed photocatalytic greatly efficiency, degrading 65% of the dye in 100 minutes under UV irradiation.

Acknowledgements

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