

Novel EPS/TiO₂ Nanocomposite Prepared from Recycled Polystyrene

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ABSTRACT

The synthesis and characterization of a new nanocomposite material that was prepared from recycled expanded polystyrene (EPS) and titanium dioxide (TiO₂) is reported here. The EPS was obtained from chemical reagent box insulation. To obtain the nanocomposite, these materials were dispersed in a solvent, mixed with TiCl₄ and heated. The resulting new material was characterized with SEM, TEM, TGA, BET, Raman and IR techniques. The Raman and IR spectra provided complementary information regarding the structure of the nanocomposite. The Raman spectra were used to identify the crystalline structure of TiO₂ in the nanocomposite. In contrast, the IR spectra were used to identify the organic portion of the nanocomposite. The TEM images indicated that the nanocomposites had an average particle size of 6 - 12 nm. In addition, the adsorption and photocatalytic properties of the new material were evaluated. The EPS/TiO₂ nanocomposite was efficient at degrading methylene blue (MB) dye solutions under UV irradiation. Furthermore, according to thermal analysis, this material had greater polymer stability due to the incorporation of TiO₂.

Keywords: Nanocomposite; Expanded Polystyrene; TiO₂; Photodegradation; Methylene Blue

1. Introduction

Titanium dioxide (TiO₂) is a common material that is used daily and is present in paints (as a pigment), cosmetics and foods. TiO₂ is inexpensive, non-toxic, and thermally stable, and it has a high refractive index and does not absorb visible light [1]. In addition, TiO₂ has three different crystalline forms including anatase, rutile and brookite [2]. TiO₂ is a semi-conductor material with well-established photocatalytic activity, especially when used in its anatase crystalline form [3-7]. Furthermore, TiO₂ is a strong oxidant that can be used to mineralize organic contaminants [8,9]. In recent years, TiO₂ was extensively used in the development of new water and air treatment technologies because it is easy to implement and operates across a broad temperature range. However, because of its size, TiO₂ must be fixed on a suitable substrate to improve the effectiveness of the oxidation process. Several different types of materials have been used as substrates including metals [10], glass, ceramics [11-13] and polymers [14]. One specific polymer that has been used for this purpose is polystyrene (PS) [15,16]. However, polymers like PS can cause serious environmental and economic problems because they do not bio-

degrade well and may be pollution sources. Thus, various polymer recycling methods were developed in the last few years [8,13,16-22]. Very small beads of extruded polystyrene (EPS) can be manufactured that contain between 4% and 7% of the blowing agent (usually pentane or butane). Due to its versatility, dimensional stability, cleanliness and low cost, EPS is widely used, especially in insulation and packing materials.

Several studies have focused on the synthesis of nanocomposites, such as PS/TiO₂. These studies have captured a great deal of attention in the past few years [23-27]. The use of reagents and monomers to produce these nanocomposites generates high energy and, in some cases, produces more contaminated waste [28-35]. This study introduces the use of an alternative material for creating new nanocomposites from TiO₂ and recycled expanded polystyrene (EPS).

Because EPS usually ends up in landfills or is incinerated, the large physical volume of EPS poses a severe contamination problem. In the past few years, EPS has been manually recycled as a hardwood replacement for garden furniture, as a slate replacement for roofing tiles and as a medium for new plastic items, such as coat hangers, CDs and video cases [36-40].

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This study presents a new and simple way to recycle EPS into a EPS/TiO₂ nanocomposite. This new material was characterized by TEM, SEM, TGA, FT-IR and Raman spectroscopy. Photocatalytic experiments were conducted to evaluate the catalytic properties of this new material. In addition, the results were compared with those from commercially available TiO₂.

2. Experimental

2.1. Reagents

Reagent grade titanium tetrachloride (TiCl₄), benzene and methylene blue (MB) were used in these experiments. The EPS was obtained from the insulation and packaging materials that were used to ship solvent grade acetone bottles. This recycled material was the main reagent in the synthesis of the EPS/TiO₂ nanocomposite material.

2.2. Preparation of the EPS/TiO₂ Nanocomposite

The method for synthesizing nanocomposite EPS/TiO₂ was simple. The first step of dispersing the recycled polymeric material in benzene was conducted at room temperature. A suitable amount of TiCl₄ was slowly added to the EPS that was dispersed in benzene. This mixture was heat treated at 300°C for approximately 3 h. After the mixture was allowed to return to room temperature, a black powder product was obtained.

2.3. EPS/TiO₂ Nanocomposite Characterization

Particle size and shape distribution are two important nanoparticle characteristics. Thus, the size, shape, surface area and spectroscopic properties of the nanoparticles were determined. Each of the obtained nanocomposite materials was characterized by using a combination of the following techniques.

2.3.1. Surface Area

Nitrogen adsorption isotherms and surface area measurements were performed with nitrogen at 77 K. First, the samples were degassed by heating at a rate of 5 K/min and by evacuating at a rate of 50 mm Hg/s for 6 h. The specific surface area was determined by using the Langmuir method with a relative pressure range of 0.01 - 0.20 Torr. A static volumetric adsorption unit (ASAP 2020 Micrometrics, Norcross, GA, USA) was used for these analyses.

2.3.2. FTIR and Raman Spectroscopy

Raman spectra were collected with a Renishaw RM2000 microspectrometer that was equipped with 532 and 785 nm excitation sources. Raman spectra were acquired under the following conditions: a spectral range of 100 - 3200 cm⁻¹; an accumulation of 2; an acquisition time of

20 s; and laser power levels of 10 - 60 mW. A Bruker Optics IFS 66 series FT-IR spectrometer coupled to a Hyperion Infrared Microscope and the OPUS™ 4.0 data acquisition and analysis suite was used to obtain the IR spectra of the starting materials and the prepared nanocomposites.

2.3.3. SEM and TEM Images

Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) images were used to determine the average particle size and morphology of the prepared nanocomposites. The SEM images were obtained with a JEOL JSM-541 OL SEM microscope. The TEM images were used to observe the morphologies of the nanocomposite particles. First, the nanocomposite samples were dispersed in benzene. Next, a portion of the dispersed sample was placed (using a dropper) on a copper grid that was coated with Formvar and a carbon film. The solvents were allowed to evaporate on the grid. The TEM images were recorded by a model 1011 Transmission Electron Microscope that had a lattice resolution of 0.2 nm and a magnification between 50 and 10⁶ at an accelerating voltage of between 40 and 100 kV (JEOL, Peabody, MA). The samples were prepared by placing 1.0 μL of the Ag-NPs solution on ultrathin carbon film/holey carbon 400 mesh copper TEM grids (01824, Ted Pella, Inc., Redding, CA). The solvents were allowed to evaporate at room temperature. The grids were stored in a desiccator to provide a dust free environment. White light images were obtained with an Olympus America, Inc. (Center Valley, Pa, USA) model BH2-UMA high resolution optical microscope that was equipped with 10 - 250× magnification and a 6.0 MB PAX-Cam image capturing CCD camera controlled by PAX-it!™ Software (Midwest Information Systems, Inc., Villa Park, IL, USA).

2.3.4. TGA Analysis

The thermal degradation behavior of the samples was analyzed with a thermal gravimetric analyzer (TGA), model Q-500 (TA Instruments, New Castle, DE, USA). Aluminum pans (5 mm I.D.) were used to hold the standards, and platinum sample holders were used to hold the nanocomposites. Approximately 5 mg of dried material was heated from 20°C to 600°C at a scan speed of 10°C/min.

2.3.5. Photocatalytic Degradation Capability of EPS/TiO₂

The nanocomposite photodegradation capability was evaluated by using a discoloration method with the methylene blue (MB) dye. For these tests, 30 mg of the EPS/TiO₂ composite were mixed with 10 mL of a 14 ppm MB solution. A 2.0 mL aliquot of this reaction mixture was removed with a syringe at pre-determined time intervals.

The sampled aliquots were filtered through 0.45 nm Millipore membranes before analysis with a UV/Vis spectrophotometer (Agilent 8453 UV-Visible). The MB concentration was monitored by measuring the absorbance of the sample filtrate at 663 nm. All the experiments were performed in batches. The catalytic efficiency of the nanocomposite was evaluated by measuring the decolorizing efficiency of the MB solutions. All the samples were analyzed in triplicate and commercial TiO₂ was used as the control or blank.

3. Results and Discussion

The new EPS/TiO₂ nanocomposite was characterized with various analytical techniques. The TEM images are shown in **Figures 1(a)** and **(b)** and indicate that the particles were nearly spherical in form. The darker areas in the images correspond with TiO₂, and lighter gray and white areas correspond with the recycled EPS. These images confirm the presence of these two materials in the final product. The average nanoparticle sizes were between 5 and 15 nm. In addition, the TEM images show the morphology of the formed nanocomposite. The TiO₂ occurred in the form of islands within the polymeric matrix and was agglomerated in some regions. The SEM images (**Figures 1(c)** and **(d)**) show a granular morphology with a size of less than 100 μm. In **Figure 1(d)**, the SEM image focuses in on one EPS/TiO₂ grain. In this case, a smooth particle surface was observed.

The FT-IR spectra of the TiO₂, EPS and EPS/TiO₂ were compared to observe the vibrational pattern changes of the nanocomposite spectra relative to those of the parent compounds. **Figure 2** shows the FT-IR spectra of the rutile-TiO₂, untreated EPS films and EPS/TiO₂. Nearly all of the vibrational information that was observed in the starting materials was observed in the nanocomposite. Persistent vibrational signatures that corresponded to phenyl ring vibrations were identified at approximately 1630, 1490 and 1450 cm⁻¹.

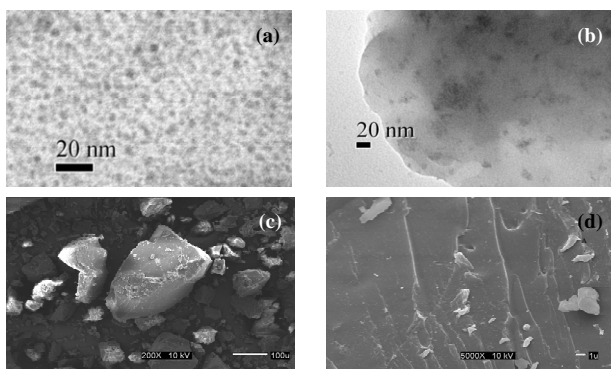


Figure 1. SEM and TEM images of the EPS/TiO₂ nanocomposite. Micrographs of the TEM images (a) and (b) and the SEM images, (c) and (d).

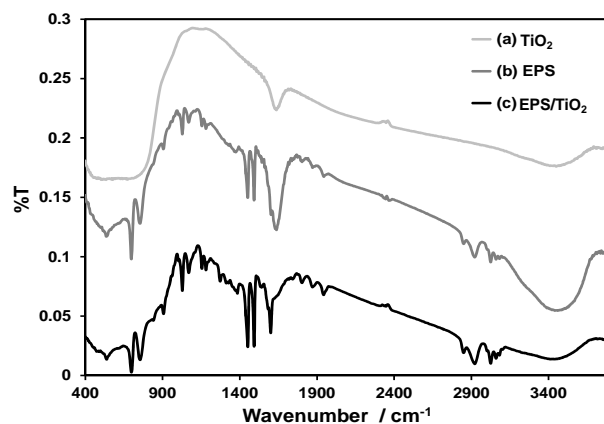


Figure 2. FT-IR spectra of the (a) rutile TiO₂; (b) EPS; and (c) EPS/TiO₂ nanocomposite.

A broad band at approximately 3400 cm⁻¹ was attributed to surface hydroxyl bending vibrations. **Figure 3** shows the Raman spectra of the TiO₂ in the anatase and rutile phases and in the nanocomposite. These spectra were obtained to identify which of the bands from these crystalline forms were present in the final product. The main signal corresponded to the anatase phase. The Raman spectra of the new material and TiO₂ shows bands that correspond to TiO₂, which supports the presence of this material in the final product and indicates that no significant changes in the vibrational profile of the polymer occurred in the low frequency region (**Figure 3**).

The thermal behavior of the EPS/TiO₂ nanocomposite was measured and compared to that of the recycled EPS. TGA analysis of the EPS/TiO₂ and EPS resulted in different mass loss profiles at different temperatures. While the thermal degradation of EPS/TiO₂ begins at 344°C with a 5% of weight loss, that of the recycled EPS begins at 293°C, which is more than 50°C earlier than that of the EPS/TiO₂ nanocomposite. This shift reflects that the incorporation of TiO₂ into the polymer improves its thermal stability. The EPS and nanocomposite curves in a nitrogen atmosphere are shown in **Figure 4**.

These results were similar to those obtained by Dzunovic *et al.* [41]. The final synthesis product that was described in this paper (EPS/TiO₂) had similar thermal properties to those of the nanocomposite that was formed by the polymerization of styrene. Thus, this new chemical process provides an important contribution to industrial sustainability and embraces its challenges.

In addition, the absorbent and catalytic properties of EPS/TiO₂ were studied and evaluated. The gas adsorption results showed that the new material had a poor adsorption capacity. This result was confirmed by the BET analysis results, in which the surface area was relatively low (BET surface area of 5.11 m²/g). **Figure 5** contains the EPS/TiO₂ composite adsorption results.

The adsorption capacity of the composite was also

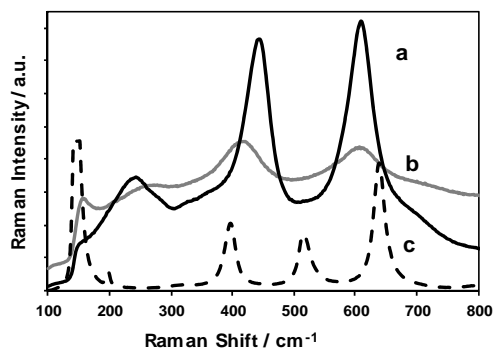


Figure 3. Raman spectra of the (a) anatase phase of TiO₂; (b) EPS/TiO₂ nanocomposite; and (c) rutile TiO₂.

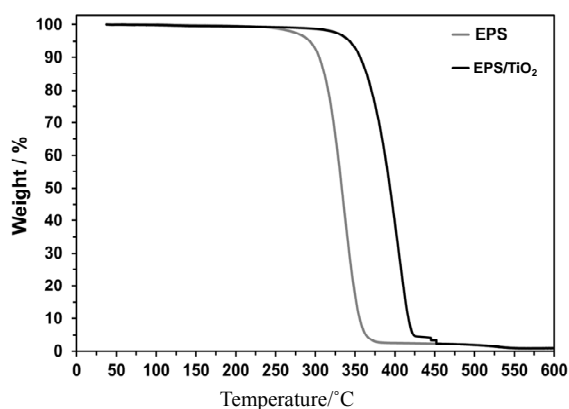


Figure 4. Thermogravimetric curves of the EPS (gray trace) and EPS/TiO₂ (black trace).

determined to ensure that adsorption was not the only process that occurred. However, this process is important for heterogeneous photocatalysis. The adsorption capacity of EPS/TiO₂ was analyzed by using methylene blue (MB). Approximately 0.01 g of the EPS/TiO₂ sample were added to aqueous MB solutions and magnetically stirred for 2 h. The samples were placed in the dark to prevent photodecomposition by white light irradiation. After various contact times, the MB concentration was measured to evaluate its dependency on the contact time with EPS/TiO₂. The MB concentration remained constant during nearly 12 h of contact. The Freundlich Isotherm model best fit the results. The well-known linear form of the Freundlich model is shown below.

$$x/m = K_F C_{eq}^{1/n} \quad (1)$$

or

$$\log(x/m) = \log K_F + 1/n \log C_{eq} \quad (2)$$

where K_F is the “Freundlich” equilibrium constant and $1/n$ is a constant that can be evaluated with the linearized Freundlich equation (Equation (2)). The amount of analyte that is adsorbed at equilibrium (mg, MB) is represented by x/m , where m is the mass of the adsorbent (g) and C_{eq} is the equilibrium concentration of the adsorbate

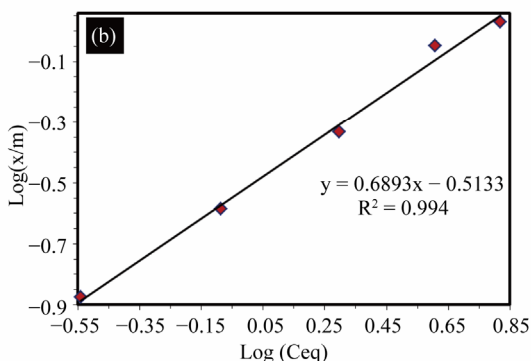
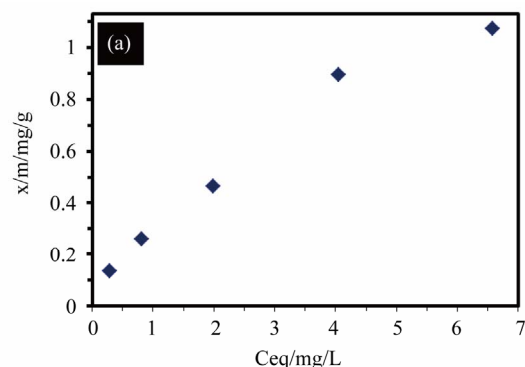


Figure 5. The adsorption capacity of several MB aqueous solution concentrations including (a) normal plot of amount adsorbed vs equilibrium concentration; and (b) the Freundlich plot of the data represented in (a).

(MB).

If $(1/n)$ approaches 1, then the equation is linear. This linear equation occurs for a limited range of the adsorbance values. For the complete range of values, the non-linear isotherm data can be plotted in a linear form by taking the log of both sides of the equation. The linear fit of the adsorption data that is shown in **Figure 5(b)** is $\log(x/m) = 0.689 \log(C_{eq}) - 0.513$ (with a coefficient of determination of $R^2 = 0.994$, $1/n = 0.689$ ($n = 1.45$ and $K_F = 0.307$)). The value of $1/n$ is related to the heterogeneity of the materials surface. Based on these results, the adsorption in this composite is semi-heterogeneous. Another way to evaluate the adsorption efficiency of the material is with a cross comparison experiment that is designed to evaluate the photocatalytic activity of EPS/TiO₂ and TiO₂. The results of these experiments are presented in **Figure 6**. A similar degradation time was observed for EPS/TiO₂ and the commercial TiO₂ when 30 mg of material were added to the MB solutions.

In addition, an alternative method was used to determine the photocatalytic activity of EPS/TiO₂. This method was conducted using the discoloration efficiency value (D) of the MB solution as a comparative parameter and was used by Su *et al.* in 2007 [42]. The catalytic reaction was performed in a flask under UV irradiation at

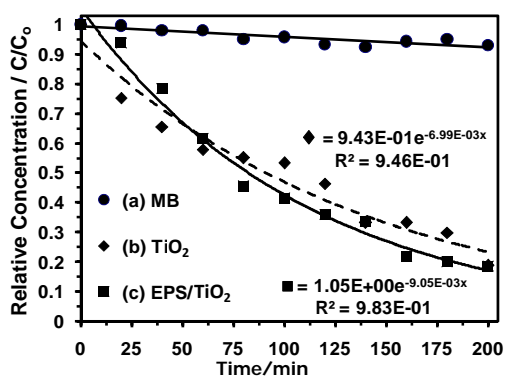


Figure 6. Photocatalytic degradation of MB under UV light irradiation. (a) MB without TiO₂; (b) 30 mg of TiO₂ in contact with MB; and (c) 30 mg of EPS/TiO₂ in contact with MB.

254 nm. Exactly 50 mg of powder were added to 10 mL of a 14 mg/L MB solution. Next, the system was stirred for under UV irradiation at 254 nm before measuring the absorbance as a function of time.

The discoloration efficiency values were calculated by using the MB solution absorbance that was determined after it was in contact with the EPS/TiO₂. The discoloration efficiency was evaluated using Equation (3) in terms of percent discoloration (D).

$$D(\%) = \left\{ \frac{C_o - C_t}{C_o} \right\} \times 100\% \quad (3)$$

where, D represents the discoloration efficiency (%) of the MB solutions, C_o and C_t represent the absorption values of the MB solutions at the initial time $t = 0$ and at a particular time t , respectively. Commercial TiO₂ was used as a reference material. **Figure 7** shows the representative discoloration for MB with the EPS/TiO₂ and TiO₂ photocatalysts.

The best discoloration behavior was observed in the EPS/TiO₂ nanocomposite. The percent discoloration of the MB solutions reached 98% (data not shown). Poor discoloration of the MB solutions was observed when the photocatalysts were not added to the solutions (control runs), which confirmed the photocatalytic activity of the nanocomposite.

4. Conclusion

A new nanocomposite made with extruded polystyrene (EPS/TiO₂) was synthesized from recycled polymer sources. The new material was characterized by various techniques, such as SEM, TEM, BET, FT-IR, and Raman spectroscopy. No differences in vibrational spectra were observed between the EPS and EPS/TiO₂, which indicated that TiO₂ was attached to the polystyrene and produced a black nanocomposite with an average particle size of between 5 and 12 nm. Raman spectroscopy was used as a complementary tool to evaluate the inorganic portion of

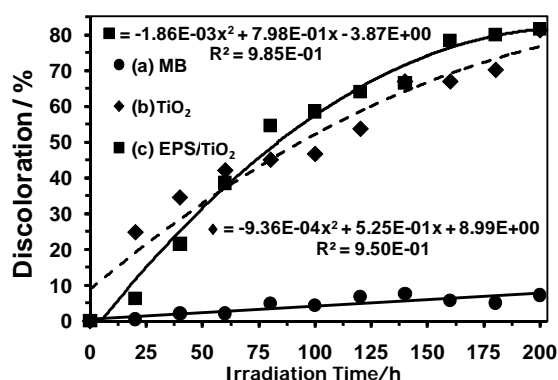


Figure 7. Discoloration of the MB solutions under UV light irradiation. (a) MB with EPS/TiO₂; (b) MB with TiO₂; and (c) MB without TiO₂ or EPS/TiO₂ (control).

the new nanocomposite including the anatase phase of the TiO₂. The EPS/TiO₂ nanocomposite had a high discoloration efficiency for aqueous methylene blue (MB) solutions. The percent of discolorization reached 98% in the MB solution. Better results were obtained for the new nanocomposite than for the commercially available one. Thus, EPS/TiO₂ will be used in future degradation tests of persistent organic pollutants that occur in water.

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