Application of photocatalytic oxidation process using modified TiO₂/PBS biocomposite film for dye removal

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Abstract. Polybutylene succinate (PBS) has been applying as one of the most recognizable biopolymers for fabrication as a biocomposite film for photocatalyst in the photocatalytic oxidation process. This research, the biocomposite film, was composed of PBS and TiO₂ particles, which was used as a model substrate such thyltriethoxysilane in order to modify the photo-catalytic degradation efficiency of the TiO₂ embedding throughout the PBS matrix. The results found that the photocatalytic activity efficiency of the TiO₂ in the degradation of black dye in wastewater from the textile industry in photoreactor had occurred on the TiO₂/PBS biocomposite film at a high amount of TiO₂ in the PBS matrix. The physical properties and chemical structures of developed photocatalyst biocomposite films were characterized using XRD, FTIR, UV-visible absorption spectra and SEM analysis. The SEM images indicated the presence of high homogeneity of the deposition of TiO₂ on the PBS matrix along with the RD patterns exhibited of anatase form. In addition, the photocatalytic results showed that the capacity of black dye removal was 40%, 32% and 18% of 100 ADMI, 300 ADMI and 500 ADMI respectively.

1. Introduction
Wastewater effluent from dye manufacturing and consuming in industries has always been an issue in environmental concern. It can be seen that the expansion of the textile sector invariably has brought about environmental degradation due to the discharge of diverse chemicals used in manufacturing consuming processes [1]. Usually, the problem of wastewater from textile dye industrial waste has been removed by physical, chemical and biological methods. Nowadays, advanced oxidation processes (AOP) have been widely applied on the removal of dye from wastewater due to their advantages such as being eco-friendly, economical and capable of degrading many dyes or organic pollutants present in water. Photocatalysis is one of the advanced oxidation processes, mainly carried out under irradiation of light and suitable photocatalytic materials [2]. The photocatalytic activity of the photocatalytic materials mainly depends on the band gap, surface area, and generation of electronhole pair for degradation dyes present in water. It has been observed that the surface area plays a major role in photocatalytic degradation of dyes similarly with the physical method as using activated carbon or resin [3] by providing higher surface area, which leads to the higher adsorption of the dye molecules on the surface of the photocatalyst and enhances the photocatalytic activity. The method of TiO₂ photocatalyst production and its physical form are among the most determining parameters influencing the overall photocatalytic ability.
However, a number of practical problems have arisen from the use of TiO$_2$ powder during the photocatalytic oxidation process and have been reported. For example, the separation of insoluble catalyst from the suspension is difficult. Also, the suspended particle tends to aggregate especially at higher concentrations. Moreover, it is challenging to apply the suspension in continuous flow systems. TiO$_2$ has been extensively studied for environmental purification applications, due to the distinguished characteristics of its powerful oxidation strength, chemical stability, non-toxicity and inexpensiveness. Nevertheless, TiO$_2$, which represents a high photocatalytic activity and a significant quantum effect commonly found in nanometer size, creating the problem of separation and recovery of photocatalyst from the reaction medium. An alternative method is to immobilize the TiO$_2$ powder on an inert and suitable supporting matrix.

In this research, the modification of TiO$_2$ coupling with ethyltriethoxysilane (ETES) was investigated with Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). ETES-TiO$_2$/PBS film was investigated in a photocatalytic oxidation process. In addition, the morphology of the photocatalyst was used for the dye degradation under the irradiation of light along with the prospects of highly adsorptive photocatalytic material and their applications in the photocatalytic removal of dye from wastewater.

2. Materials and methods

2.1. Chemical reagents

The TiO$_2$ powder was purchased from the Willson Company. The commercial grade polybutylene succinate (Grade: FZ91PD) used in this study was supplied by the Mitsubishi Chemical Corporation. Certain Melt Flow Index, MFI (2.16 Kg. at 190°C) of the resin, provided by the manufacturer are 5.5 g/10 min. (ETES) with purity 96.0% (Aldrich) was used as coupling agents.

2.2. Photocatalyst TiO$_2$/PBS biocomposite film preparation

The TiO$_2$ powder with 10% wt. contents was incorporated in molten PBS resins utilizing a twin screw extruder. Certain TiO$_2$ powders were modified with ETES to improve the dispersal of the TiO$_2$ and enhance the compatibility between TiO$_2$ and PBS matrix [4]. The TiO$_2$/PBS biocomposite films with a thickness of 30 µm were obtained from the blown film technique while using operating temperatures ranging from 110 °C to 140°C.

2.3. Photocatalysis experiments

The photocatalytic reactor was a plug flow type containing ETES-TiO$_2$/PBS film of the photocatalyst and dye solution of 25 mg/L placed in a continuously ventilated chamber. Irradiation in the UV-C region (254 nm) was provided by a 100 watt light source. The distance between the UV source and the reactor was 10 cm. The suspension was magnetically stirred during irradiation at a steady state. Before irradiation, the sample was stirred for 5 min to reach an adsorption–desorption equilibrium between the dye molecules and the catalyst surface as shown in figure 1 [5]. Dye removal is a diazo group-containing acid dye, as a black powder, which is soluble in water. The dye was supplied by a textile manufacturing company. A dye solution of 100 mg/L was prepared by dissolving black dye in distilled water. The pH of the solution was adjusted to 8.0 by the addition of diluted HCl or NaOH with employing a pH meter. 200 mL of the solution was put into a 250 mL flask, and various initial concentrations ranging from 100 to 500 ADMI unit were added. After irradiation for a certain period of time. Color removal was measured using a spectrophotometer for a color unit (ADMI).
2.4. Physical properties
The microstructure of the biocomposite film was examined using a Scanning Electron Microscope (SEM, Hitachi S-3400N). In order to prevent the charge build-up during SEM observation, samples were coated with gold, which was used as the ion sputter target. The sputter rate and time were set for 10 nm/min at 1 and 3 min, respectively. The gold film thickness was approximately 30 nm [6].

2.5. Optical property
Ultraviolet-visible spectra of the photocatalyst were recorded employing the UV-VIS spectrophotometer (Lamda 950, Perkin Elmer instrument) equipped with an integrating sphere. A BaSO₄ dye was used as a reference. The scan ranged from 300 to 800 nm. All spectra were monitored in the absorbance mode and acquired under ambient conditions. The band gap energy of TiO₂ thin film can be calculated from absorbance results [7].

2.6. Fourier Transform Infrared (FTIR) Spectroscopy
Adsorption of the unmodified and modified TiO₂ nanoparticles was studied using FTIR. FTIR spectra was obtained using a Model Perkin Elmer System 2000. The unmodified and modified TiO₂ nanoparticles were dried in an oven at 120 °C for 6 h, and then KBr pellets were prepared with the dried TiO₂ nanoparticles. The spectra was collected in the range from 400 to 4000 cm⁻¹ [8].

2.7. X-ray Diffraction (XRD)
The crystalline structures of photocatalyst were determined using the X-Ray Diffraction (XRD) technique. XRD patterns were obtained on the X-Ray Diffraction (JEOL JDX-353) using Cu Kα and radiation (=1.5418 Å). The scan ranges from 20° to 60° with a scan rate of 2° min⁻¹.

3. Results and Discussion
3.1. Characteristic of modified TiO₂/PBS biocomposite film
The morphological structure of TiO₂ particles was studied using the scanning electron microscope (SEM). Scanning micrograph of the unmodified TiO₂ particles was shown in Figure 2(a). SEM micrograph shows the agglomeration of the spherical-shaped particles with less than 0.2 µm of primary particle size. Figure 2(b) shows the XRD pattern of unmodified TiO₂ particles, which the XRD pattern shows clear broad peaks of 2θ as 25.36, 36.9, 37.86, 38.62, 48.08, 53.94 and 55.12,
which is matched with plane as (101), (103), (004), (112), (200), (105), and (211), respectively. This XRD data corresponds to the anatase phase of TiO$_2$ (JCPDS 65-5714). Typical diffraction peaks representing rutile or brookite are not presented in the pattern [9]. It can be concluded that surface modifications using modified TiO$_2$ can improve the sorption efficiency of targeted ions and organics as mentioned in the literature [10].

Figure 2. (a) SEM image of the unmodified TiO$_2$ particles and (b) XRD pattern of TiO$_2$ particles.

In Figure 3 shown FTIR spectra of bio-composite films. The broad band at around 3400 cm$^{-1}$ was assigned to stretching vibrations of Ti-OH groups. The broad band between 400 cm$^{-1}$ and 900 cm$^{-1}$ should be due to the envelope of the phonon bands of Ti-O-Ti bond. The assignments for the main FTIR band of coupling agents modified TiO$_2$ are listed in Table 1. In the spectrum of TiO$_2$ modified with stearic acid, the bands at 2920, and 2850 cm$^{-1}$ assigned to alkyl group appeared. The peak of C=O stretching mode at 1720 cm$^{-1}$ of stearic acid (Figure 3) splits to the asymmetric vibration of (COO$^-$) and symmetric vibration of (COO$^-$) bands, 1505 and 1410 cm$^{-1}$, respectively.

Figure 3. FTIR spectra of TiO$_2$/PBS and ETES-TiO$_2$/PBS biocomposite file.

Figure 4 shows the morphology of unmodified and modified TiO$_2$/PBS biocomposite films. These images indicate the dispersion and interfacial adhesion of TiO$_2$ particles in a PBS biocomposite. In the case of unmodified TiO$_2$/PBS biocomposite films, the poor interfacial interaction between TiO$_2$ particle and PBS biocomposite appears on the cross section of the film. In both cases of modified TiO$_2$/PBS biocomposite films, the good dispersion of TiO$_2$ particle on the PBS biocomposite appear and the interfacial interaction between TiO$_2$ particle and PBS biocomposite is good. It indicates the
coupling agent can improve the dispersibility of TiO$_2$ particle on the PBS biocomposite and compatibility between the TiO$_2$ particle and PBS biocomposite. The surface modification of TiO$_2$ particle is successfully prepared.

### Table 1. Characteristic peak obtained from FTIR unmodified and modified TiO$_2$/PBS biocomposite

| Wave number (cm$^{-1}$) | Functionality                                      |
|------------------------|----------------------------------------------------|
| 400-900                | Stretch vibration band of Ti-O-Ti                  |
| 960-910                | Stretch vibration band of Ti-O–Si                  |
| 2850, 2920             | C-H symmetrical and a symmetrical stretching vibration |
| 3400                   | Stretch vibration band of Ti-OH groups             |

![Figure 4](image1.png) The SEM image of (a) TiO$_2$/PBS (unmodified), (b) ETES-TiO$_2$/PBS.

The result from the UV-Vis spectroscopy in Figure 5 shows that both the unmodified and modified TiO$_2$/PBS biocomposite film absorbs the range of the UV region. The energy band gap ($E_g$) of these TiO$_2$/PBS biocomposite films is calculated from the result. The energy band gap ($E_g$) of unmodified ETES are 3.18 and 3.26 eV, respectively. It found that surface modification strongly effects the energy band gap of TiO$_2$ powder [9]. In addition, the maximum absorption wavelengths of unmodified, ETES modified TiO$_2$/PBS biocomposite films were 360 and 350 nm, respectively.

![Figure 5](image2.png) UV–visible absorption spectra of TiO$_2$ biocomposite films.
3.2. Photocatalytic oxidation degradation of dye

Photocatalytic activity of the modified TiO$_2$/PBS biocomposite film for removal of black dye was investigated. It can be seen that Figure 6 the photocatalytic degradation of ETES-TiO$_2$/PBS yielded degradation efficiency of black dye by 40%, where as unmodified TiO$_2$/PBS film yielded degradation efficiency of black dye by 14% with the removal efficiency for a treatment time of 180 minutes. Because of the energy band gap and dispersion of modified TiO$_2$/PBS biocomposite films enhanced [11].

![Figure 6.](image.png)

**Figure 6.** The impact of initial black dye concentration 100-500 ADMI unit (the modified TiO$_2$/PBS biocomposite films 10% w/w, light intensity 5 mW.cm$^{-2}$).

4. Conclusion

ETES modified TiO$_2$/PBS bio-composite films were successfully prepared by the blown film process to evaluate the degradation of dye. The modification of TiO$_2$ with ETES strongly affects the dispersion of such particle in PBS biocomposite and the energy band gap of biocomposite film. The ETES particle exhibits uniform dispersion while unmodified TiO$_2$ exhibits evidence of agglomeration in a PBS matrix. In the photocatalytic activity, the degradation efficiency strongly depends on the energy band gap. The photocatalytic degradation of ETES-TiO$_2$/PBS film yielded degradation efficiency of black dye by 40%, for the treatment time of 200 min.

5. References

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