Ice rock-resembling PHB thin films doped with TiO₂ NPs as photocatalyst

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Abstract

This study is to evaluate the performance of TiO₂ as a photocatalyst for polyhydroxybutyrate (PHB) in different concentrations. Five different concentrations of TiO₂ nanoparticles (0.001–0.005 wt%) have been added to PHB blend to produce modified PHB films. The conducting characterizations using FTIR, UV, SEM and optical microscope confirmed the photocatalytic activity of TiO₂ on the surface of PHB films. The SEM analyses after irradiation reports show that the PHB thin films doped with different concentrations of TiO₂ nanoparticles have piece of ice rock-resembling structure nature with heterogeneous surface morphology. After irradiation, the photodecomposition rate constant showed the highest value in the presence of TiO₂ with concentration (0.005 wt%). Therefore, TiO₂ nanoparticles, in particular high concentration (0.005 wt%), are considered as a photocatalyst for PHB films (30 μm thickness) photodegradation.

Keywords PHB · Photocatalytic · Titanium dioxide · Morphology · Scanning electronic microscope · Ice rock resembling

1 Introduction

Applications within the chemical synthesis field remain nevertheless rare even though variety of studies have been reported targeting new photocatalytic processes via synthesizing of composite or doped catalyst. Wide range of reaction types has been presented by different authors, which includes oxidations [1–3], reductions [4], isomerizations [5], additions [6], cyclizations [7] and so on. As a fact, conventional industries tactics in this area rarely meet the present day sustainability requirements, environmental safety and power performance essentially for a green processes [6]. TiO₂ inspected for photocatalytic techniques because of its economic manufacturing costs, lengthy-term stability upon corrosion photochemical affects and nontoxicity [7]. During the last decades, diverse TiO₂ structures

have been reported, like TiO₂ fibers, hollow sphere and tubes and tested for photocatalytic reactions [8, 9]. TiO₂ photocatalytic activity remains weak, that's because of week seen mild responsiveness because of its high b and gap (3.0–3.2 eV) and rapid recombination of electron-hollow pairs [10], and in order to enhance capacity of TiO₂ absorption for seen mild (43% of the whole sunlight), numerous techniques were deployed [11]. Polyhydroxybutyrate (PHB) is insoluble in water as a thermoplastic, while it decomposes in acids or bases. PHB tainted at when it be exposed to temperatures beyond its melting point (175 °C) [12]. Carbon dioxide, methane and water generally are the outcome of PHB biodegradation which can be done or achieved utilizing microorganisms in soil [13, 14] and could be accelerated utilizing plasticizers [15]. However, titanium dioxide (TiO₂) is considered as the most widely used photocatalyst for the photocatalytic reactions

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even though it comes with its own limitations such as it is only active when irradiated by UV light, due to its wide band, which makes it not as effective under sunlight, since the solar spectrum only consists of about 4% of UV light. Adding to that, TiO_2 has a high electron/hole pair recombination rate compared to the rate of chemical interaction with the adsorbed species for redox reactions [15]. The objective from the presented work was to observe PHB films photodegradation with different conditions and study the surface morphology of PHB films.

2 Materials and methods

Chemicals, reagents and solvents were supplied from Sigma-Aldrich Chemical Company (Gillingham, UK). The bacterial isolate of our study (*Rhodococcus* sp.) was isolated from soil sampled at Gunung Lang, Perak, Malaysia [16–18].

2.1 Preparation of PHB

PHB was extracted from *Rhodococcus equi* in existence of chloroform and crude palm kernel oil (CPKO; 1%) as a carbon giver [14, 19, 20], and the structure was authenticated using FTIR, $^1\text{H-NMR}$ and GC techniques as shown in Fig. 1 [20].

2.2 Thin films preparation

A solution of PHB in tetrahydrofuran was stirred at 25 °C for 30 min; various concentrations of TiO_2 (0.001, 0.002, 0.003, 0.004 and 0.005 wt%) were added to the PHB solution, and these mixtures were stirred at 25 °C for 30 min. Each sample was cast onto glass plates, and the formed films were left for 24 h at 25 °C under a vacuum to dry [20, 21].

2.3 UV light exposure

Ultraviolet light with below specifications was supplied to conduct the irradiation on PHB films samples: $\lambda_{\text{max}} = 365 \text{ nm}$ and light intensity = $6.2 \times 10^{-9} \text{ ein dm}^{-3} \text{ s}^{-1} \text{ nm}$. The PHB films were rotated consistently to ensure uniform supplying of light intensity on all the samples sides [20, 21].

Fig. 1 PHB structure

2.4 Observation of the photodegradation of PHB films

2.4.1 FTIR spectroscopy

Below equation was used to calculate the indices for carbonyl ($I_{\text{C=O}}$), polyene ($I_{\text{C=C}}$) and hydroxyl (I_{OH}) groups based of the data extracted from FTIR testes which have been performed to study the IR absorption bands amendments for carbonyl (1722 cm^{-1}), polyene (1602 cm^{-1}) and hydroxyl (3500 cm^{-1}) groups. The functional group index (I_s) as it is known depends on two conditions or variables which they are: peak absorbance in study (A_s) and as well, the reference peak (A_r) [22].

$$I_s = \frac{A_s}{A_r} (1).$$

2.4.2 Weight loss method

The percentage of PHB films weight loss (during processing the irradiation) was estimated based on the weight changes of the sample (before and after irradiation (W_1 , (W_2), respectively) as in Eq. (2).

$$\text{Weight loss \%} = \left[\frac{W_1 - W_2}{W_1} \right] \times 100 (2).$$

2.4.3 UV spectrophotometer

Spectrophotometer (by A Shimadzu UV-Vis 160A-Ultraviolet) had been ran to record the UV-visible spectra changes of PHB films during irradiation (where $\lambda_{\text{max}} = 313 \text{ nm}$) [20]. k_d factor which is known as photodecomposition rate constant for each prepared PHB sample was calculated using Eq. (3).

$$\ln(A_t - A_\infty) = \ln(A_0 - A) - k_d t (3).$$

The plot of $\ln(A_t - A_\infty)$ versus irradiation time (t) gave straight line. The slop is equal to k_d , indicating that the photodecomposition of PHB obeys to first-order kinetics which is in line with Khan et al. finding [23].

2.5 The surface morphology

The scanning electron microscopy (SEM) of PHB surface spotted utilizing voltage up to 15 kV, while PHB films

Fig. 2 I_{CO} for PHB films containing different concentrations of TiO₂ nanoparticles at 250 h of irradiation

Fig. 4 I_{OH} for PHB films containing different concentrations of TiO₂ nanoparticles at 250 h of irradiation

Fig. 3 I_{PO} for PHB films containing different concentrations of TiO₂ nanoparticles at 250 h of irradiation

Fig. 5 Weight loss of PHB films containing different concentrations of TiO₂ nanoparticles at 250 h of irradiation

depth (ca. 30 μ m) deliberated utilizing Digital Vernier Caliper 2610 A micrometer apparatus.

3 Results and discussion

Generally, photocatalysis is the changes of decomposition reaction under radiation within the sight of photocatalyst substance that retains under light as IUPC has defined it. This process is engaged with chemical transformation of the response accomplices [24]. The relationship between carbonyl (I_{CO}), polyene (I_{PO}) and hydroxyl (I_{OH}) indices with irradiation time for PHB films photodegradation which containing different concentrations (0.001–0.005 wt%) of TiO₂ nanoparticle photocatalysts as shown in Figs. 2, 3 and 4. All the results investigate PHB films, in the existence of TiO₂ nanoparticles, have a higher growth rate with 250 h of irradiation time compared to blank films. Figures 2, 3 and 4 show that indices (I_{CO} , I_{PO} and I_{OH}) were the highest when the concentration (0.005 wt%) was and lowest when the concentration

(0.001 wt%) of TiO₂ nanoparticles as a photocatalysts. Therefore, TiO₂ nanoparticles, in particular high concentration (0.005 wt%), considered as a photocatalyst for PHB films (30 μ m thickness) photodegradation.

The weight reduction of PHB films treated samples (30 μ m thickness), at different TiO₂ nanoparticles concentrations (0.001–0.005 wt%) against irradiation (250 h), extracted and referred to that acquired for unmodified PHB film. Figure 5 represents those changes in PHB weight loss percentage. Evidently, the PHB films with different concentrations of TiO₂ nanoparticles show higher weight loss compared to blank PHB. Therefore, TiO₂ nanoparticles, in particular high concentration (0.005 wt%), demonstrate the most photocatalytic effectiveness with PHB photodegradation.

The irradiation led to a notified changing in modified PHB films samples, and dissociation had taken place. Figure 6 shows the changes in the $\ln(A_t - A_\infty)$ in 250 h of irradiation time for PHB films that containing different concentrations (0.001–0.005% by weight) of TiO₂ nanoparticles. The photodecomposition rate constant (k_d) was

Fig. 6 Changes in $\ln(A_t - A_{\infty})$ for PHB films containing different concentrations of TiO₂ nanoparticles at 250 h of irradiation

highest for PHB film which contains TiO₂ with high concentration (0.005 wt%) [20].

Figures 7 and 8 represent microscopic images for PHB films containing different concentrations of TiO₂ nanoparticles before and after irradiation. Discoloration and degradation could be noticed on the surface of PHB that containing the nanoparticles after irradiation via the optical images (Fig. 8), as indication for photodegradation. PHB (blank) and those samples treated with TiO₂ before

irradiation demonstrated a round cross section using optical microscopy with a relatively smooth surface; it has been observed formation of fine pigment particles with uniform distribution. Treated PHB after irradiation revealed characteristic surface cracks. Notwithstanding surface affected with the cracks, the sporadic and surfaces rakish states, particularly apparent at the edges, is steady with the mechanical breakage of bigger chains, maybe made weak through oxidative weathering.

SEM gives clear idea about morphology of the polymers' surface which reflects their internal structures [25]. The surface morphology of the PHB thin films doped with various concentrations of TiO₂ nanoparticles has been analyzed using SEM characterization from 5 to 200.00 Kx magnifications. Figure 9 shows that the PHB surface was damaged after 250 h of irradiation.

It can be observed from Figs. 10, 11, 12, 13 and 14 the formation of ice rock structure with sturdy feature and tiny mist morphology [26]. The presented SEMs morphology for PHB thin films doped with different concentrations of TiO₂ nanoparticles illustrates entirely rough surface structures was increased with increases in concentration of TiO₂ for the prepared samples.

Figures 10, 11, 12, 13 and 14 show damages on the sample surfaces that treated with TiO₂ particles after

Fig. 7 Microscopic images for PHB films containing different concentrations of TiO₂ nanoparticles before irradiation

Fig. 8 Microscopic images for PHB films containing different concentrations of TiO_2 nanoparticles after irradiation

Fig. 9 SEM images for PHB films after 250 h of irradiation

irradiation. These damages were more noticeable compared to the ones containing TiO_2 nanoparticles beside the cracks that been discussed earlier.

Fig. 10 SEM images for PHB + 0.005% TiO_2 nanoparticles after 250 h of irradiation

Basic mechanism built on the ROS formation which signifies i , the radical reactive oxygen forms as superoxide anion radical ($-\text{O}^{2-}$) and highly reactive hydroxyl radical

Fig. 11 SEM images for PHB + 0.004% TiO₂ nanoparticles after 250 h of irradiation

Fig. 13 SEM images for PHB + 0.002% TiO₂ nanoparticles after 250 h of irradiation

Fig. 12 SEM images for PHB + 0.003% TiO₂ nanoparticles after 250 h of irradiation

Fig. 14 SEM images for PHB + 0.001% TiO₂ nanoparticles after 250 h of irradiation

(-OH). Non-radical hydrogen peroxide (H₂O₂) is formed and singlet oxygen (¹O₂), ozone (O₃) [13, 27] (Schemes 1, 2).

4 Conclusions

TiO₂ photocatalysts exhibit photocatalytic activity for PHB under UV excitation. The photocatalytic degradation of polyhydroxybutyrate was at minimum for the PHB which

Scheme 1 Photodegradation of PHB

Scheme 2 Photodegradation and oxidation of PHB

has been treated by introducing some additives compared to the ones containing TiO₂ nanoparticles films. This trend can be attributed to the various concentrations of TiO₂. After irradiation, the SEM images revealed that the PHB thin films doped with different concentrations of TiO₂ nanoparticles have piece of ice rock-resembling structure nature with heterogeneous surface morphology.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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