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Photodegradation and thermal properties of biopolymer nanocomposites based on poly(butylene succinate) and modified titanium dioxide

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In this research, poly(butylene succinate) (PBS)/titanium dioxide (TiO_2) nanocomposites were prepared by internal melt mixer and compression molding machine. The severe aggregation of TiO_2 nanoparticles in polymer matrix were reduced by the modification of TiO_2 surface with propionic acid and n-hexylamine. Photodegradation and thermal properties of biopolymer nanocomposites were investigated over a range of filler content 0-10 wt%. All samples with a wide range of filler addition exhibit the translucency. The surface morphology showed that a uniform dispersion of filler in the matrix existed when the nanoparticles content was less than 5 wt%. The results indicated that nanocomposites could be efficiently photodegraded by UV-A, UV-C and solar radiation in comparison with neat PBS. The photodegradability of composites can be efficiently promoted, and the photodegradation rate can be controlled by filler content. The materials exhibited elevated degree of crystallinity (X_c) and decreased melting temperature (T_m) as the nanoparticles concentrations were increased.

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1. Introduction

Nowadays, environmental friendly biodegradable polymers have become substitutes for petroleum-based plastics, owing to their biodegradability that could reduce plastic waste pollution. Apart from that, limited fossil resources and increasing oil price have accelerated the development of biodegradable polymers derived from renewable resources [1]. The biopolymers have been widely used in the fields of packaging, agriculture, medical service, and daily used goods, etc., which have attracted much interest in science research and industry due to the advantages of microbial degradation and alleviating the environmental pollution [2,3]. A great amount of works has already been carried out on biodegradable packing polymers, such as poly(butylene succinate) (PBS), poly(lactic acid) (PLA), and poly(ε-caprolactone) (PCL) [4].

PBS is one of the most promising biodegradable aliphatic polyesters, which was invented in the early 1990s by Showa Highpolymer in Japan [5]. It is a competitive material against other biodegradable plastics due to its superior mechanical and thermal properties, good processability, high chemical resistance, availability and lower material cost [6]. It is commercially available at lower cost than PLA and poly(3-hydroxybutyrate) (P3HB), which have been frequently studied as biodegradable polymer matrix in a biocomposite system. Therefore, PBS may be a good candidate material for utilizing as a polymer matrix of green composite materials [7]. However, with further development of PBS, it is expected to be applied in the engineering fields, such as in automotive components, electrical industry and the aerospace industry due to ecological and economical advantages [8]. Therefore, modification for PBS is urgent [9]. The modification of polymers using inorganic fillers is also common in the production of polymer composites [10,11]. The inorganic fillers have been more often used to fulfill a functional role, such as increasing the stiffness or improving the dimensional stability of the materials [9,12]. The biopolymer needs to be reinforced inorganic particles such as clay, silica, layered silicate nanoparticles. Among them, titanium dioxide (TiO_2) is one of the most important materials, because of its potential applications in the photocatalytic activity, photoelectric conversion, antibacterial activity and self-cleaning mechanism [13-15]. Such advantages make TiO_2 an ideal inorganic reinforcing component in manufacturing nanocomposites material with promising properties and applications [16,17].

The synthesis of inorganic-biopolymer nanocomposites has been intensely studied due to their unique combination of properties and widespread potential applications. A key factor associated with the construction of nanocomposites is to develop specific interactions between nanoparticles and polymer matrix [18,19]. The effects of nanofiller on the properties depend strongly on its shape, particle size, aggregate size, surface characteristics and degree of dispersion. The dispersion of nanoparticles is generally difficult to control, though property improvements have been achieved in a variety of nanocomposites [20,21]. In this study, the surface of TiO_2 nanoparticles was modified using propionic acid and n-hexylamine in order to disperse them into the PBS matrices without aggregation. The photodegradation and thermal properties of biopolymer nanocomposites were also investigated.

2. Experimental

2.1 Materials

TiO_2 nanoparticles (AEROXIDE® TiO_2 P 25) were supplied from Evonik Industries, Germany. PBS pellet (AZ71TN, Mitsubishi Chemical Corporation, Japan) was used as a thermoplastic matrix. Propionic acid and n-hexylamine were purchased from Sigma-Aldrich Chemistry and used as chemical agents of surface modification of TiO_2 nanoparticles. All other chemicals used were analytical grade reagents.

2.2 Modification of TiO_2 nanoparticles

20 g TiO_2 was directly added in excess amount of propionic acid 350 ml. After stirring as slurry for 24 h at ambient temperature, the precipitated solid was collected by centrifugation and washed with ethyl acetate. The TiO_2 nanoparticles were added to 350 ml methanol and sonicated for 1 h. The precipitated solid was easily dispersed into methanol. Afterwards, excess amount of n-hexylamine 350 ml was added to the solution. After stirring for 1 h, precipitated solid was obtained by centrifugation, and washed with ethyl acetate. The precipitated solid was dried at 120 °C for 12 h in an oven [19,22]. Fig. 1 illustrated the modification of TiO_2 surface with propionic acid and n-hexylamine.

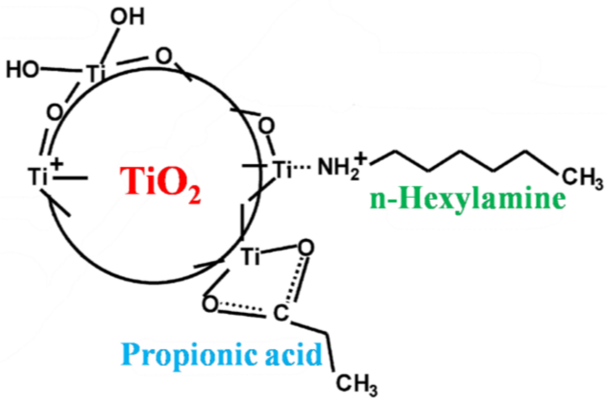


Fig. 1. Surface of TiO_2 nanoparticle modified by propionic acid and n-hexylamine [22].

2.3 Preparation of biopolymer nanocomposites

All samples were prepared by internal melt mixer and compression molding machine. The weight content of fillers varied from 0 to 10 wt%. TiO_2 and PBS pellets were fed into a Brabender Mixer Docking Station (W50EHT), and a uniform temperature of 160 °C was maintained inside the machine. The screw speed and the mixing duration were set to be 40 rpm and 13 min, respectively. The biocomposites were then compression molded (Scientific, Labtech) to make the mechanical testing specimens at 170 °C and 100 bar for 10 min.

2.4 Characterization

2.4.1. Field emission scanning electron microscopy (FE-SEM)

The surface morphology of biopolymer nanocomposites was conducted using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800). The distributed state of TiO_2 nanoparticles in material was checked by SEM micrograph. The sample surfaces were sputter coated with platinum to avoid charging and make them conductive prior to SEM observation.

2.4.2. Photodegradation testing

The photodegradation of polymer nanocomposites was investigated in air, using UV-A (365 nm, 20 W) and UV-C (253.7 nm, 18 W) lamp unit (FIRST and FERN Co., Thailand), and solar radiation (150 W, ozone-free xenon short arc lamp, Oriel Solar Simulator). Samples were irradiated at ambient temperature for prescribed times up to 30 days for UV and 1 day for solar radiation in a chamber, providing shielding from external irradiations. Materials were placed at right angles to the direction of irradiation. After UV irradiation, the samples were measured for changes in weight.

2.4.3. Thermal testing

Differential scanning calorimetry (DSC) equipment Perkin Elmer Model: Pyris 1 (USA) was used to study the crystallization and melting behaviors of the samples. DSC scanning program was set as follows: firstly, the sample was heated from 50 to 160 °C at the heating rate of 10 °C/min and maintained at 160 °C for 1 min to erase the thermal history; secondly, the sample was cooled down to 50 °C at the cooling rate of 10 °C/min. For the annealed specimens, the sample was directly heated from 50 to 160 °C at the heating rate of 10 °C/min. Thermogravimetric analysis (TGA) equipment Perkin Elmer Model: TGA 7 HT (USA) was employed to examine the thermal stability of the samples. The weight of each sample was about 7 mg. Experiments were carried out from 50 to 600 °C with a heating rate of 10 °C/min in a nitrogen (N_2) atmosphere.

3. Results and discussion

3.1 Surface morphology

SEM micrographs of the PBS/modified TiO_2 nanocomposites with 0, 1, 5 and 10 wt% of TiO_2 before UV and solar radiation are shown in Fig. 2. The PBS sample containing no TiO_2 nanoparticles has a smooth surface with no evidence of surface topography observed at the magnification used during SEM observations. An increase in TiO_2 loading induces the agglomeration of the nanoparticles [16]. The nanocomposites containing 1 and 5 wt% of TiO_2 exhibit an even distribution of TiO_2 nanoparticles with few agglomerates. Similarly, the nanocomposite filled with 10 wt% of TiO_2 had an even distribution of nanoparticles but there are also some large agglomerates of TiO_2 present. It can be observed that an increasing concentration of modified TiO_2 nanoparticles in the composites results in rougher surfaces, which should lead to a greater surface area [17,23].

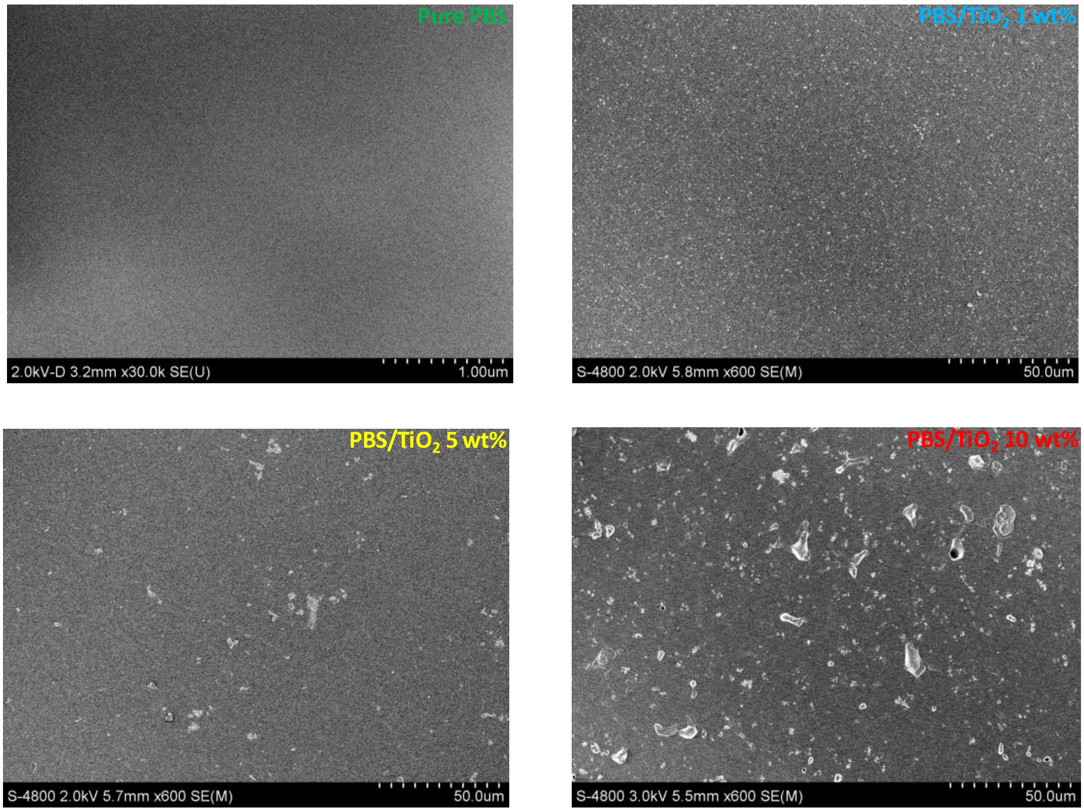


Fig. 2. SEM micrographs of pure PBS and biopolymer.

3.2 Photodegradation properties

The Fig. 3 illustrates the weight loss curves of the pure PBS and the biopolymer nanocomposites owing to UV-A, UV-C and solar radiation, respectively. As expected, the percentage of weight loss of the nanocomposite materials was higher than the pure PBS owing to UV-A, UV-C and solar radiation. This indicates that modified TiO_2 nanoparticles greatly enhanced the photocatalytic degradation of the PBS materials. Chemical bonds in biopolymer were oxidized to volatile compounds in the photodegradation that was catalyzed by TiO_2. Cavities were left on the surface of the nanocomposites [24]. Functionalized TiO_2 nanoparticles existing on the surface area suppressed photodegradation of the inner and backside of the specimens [22]. The degrees of the weight loss depend on the amount of added TiO_2 nanoparticles. Initially, the film was translucent and flexible. After 6 days UV irradiation, the film appeared rigid and turned slightly yellow. The sample caused cracks and breaks naturally after 6 days [19].

In previous report, the photolysis mechanism of polyesters has been suggested as proceeding via the “Norrish type photo cleavage”, especially the Norrish II type reaction, which was proposed based on increases in absorptions of hydroxyl and acrylic groups [25]. Very few characterization results of photolysis products and little information on the racemization have been given except for details of the changes in molecular weights of residual polymers [16,26].

The initiation in the photocatalytic degradation of biopolymer nanocomposites is quite different. The degradation of PBS/TiO_2 nanocomposites is caused by both the direct photolytic reaction of PBS and the photocatalytic reactions of PBS on the surface of modified TiO_2. The TiO_2 is stimulated by absorbing UV light to generate various active oxygen species such as O_2^{*-}, HOO^* and HO^*. These active oxygen species attack the biopolymer chains, which lead to the irregular bond scission. The reaction of O_2 with conduction band electrons is the key step in this solid-phase system according to the experimental result in air, nitrogen and argon atmosphere [27].

Lots of researches reported [27-29] the catalytic mechanism of TiO_2 and the main process as follows:

$$\boxed{TiO_2} \xrightarrow{hv} \boxed{TiO_2} \rightarrow e^-,\ h^+$$

$$H_2O + h^+ \longrightarrow HO^* + H^+$$

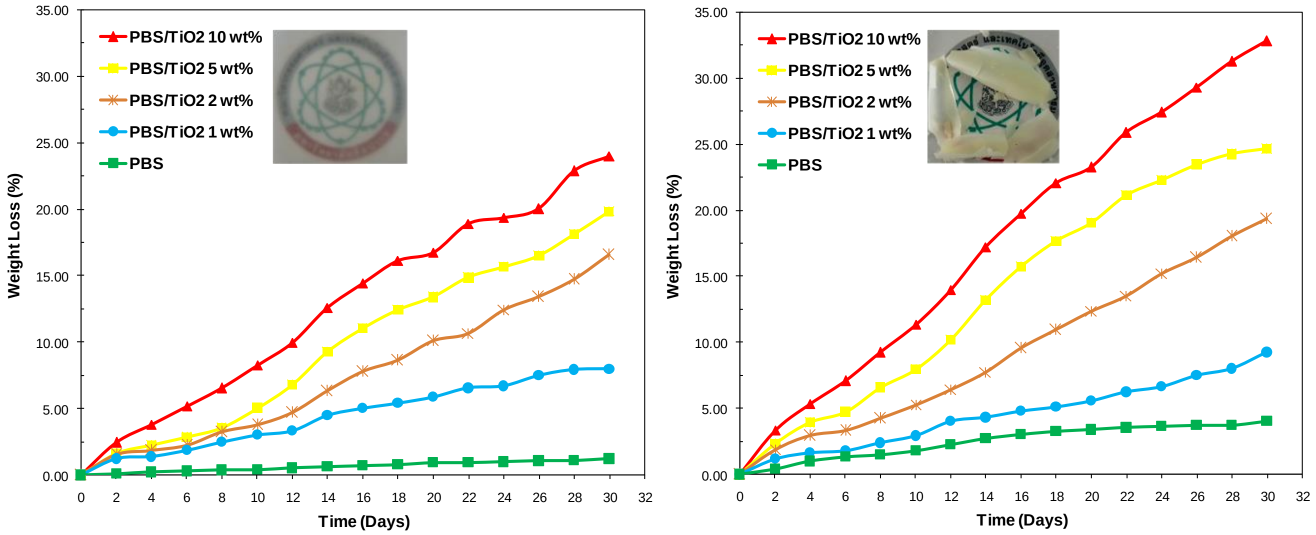
$$O_2 + e^- \longrightarrow O_2^{*-}$$

$$O_2^{*-} + H_2O \longrightarrow HOO^* + OH^-$$

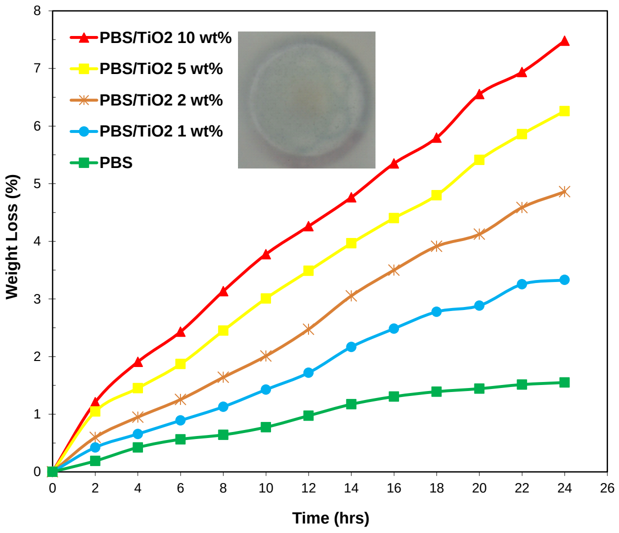
$$2\,HOO^* \longrightarrow O_2 + H_2O_2$$

$$h^+ + OH^- \longrightarrow HO^*$$

Once the carbon-centered radicals are introduced in the biopolymer chain, their successive reactions with O_2^{*-}, HOO^* and HO^* cause hydroxyl derivatives and carbonyl intermediates, resulting in chain cleavage. Finally, volatile species, such as carbon dioxide, are evolved [24].



(a) UV-A *(b) UV-C*



(c) solar

Fig. 3. Photodegradation properties of PBS/TiO_2 nanocomposites under UV-A, UV-C and solar radiation.

3.3 Thermal properties of biocomposites

The effect of modified TiO_2 content on the crystallization and melting behavior of biopolymer nanocomposite materials was studied in DSC experiments. Table 1 provides a summary of the DSC results, including of the cold crystallization temperature (T_{cc}), melting temperature (T_m), melting enthalpy (ΔH_m) and degree of crystallinity (X_c). For the case of biopolymer nanocomposites, the width of crystallization peaks becomes a little narrower, indicative of an increase in crystallization rate. The effect is not significant as observed from the small changes of the crystallization properties when compared to pure PBS [30]. For all samples, T_m decreased with increasing filler content. This may be due to in the nanocomposites, modified TiO_2 will expand PBS, hence causing slack polymer structure and reduced T_m [31]. The values of ΔH_m and X_c increased in the presence of fillers. These results suggest that TiO_2 plays the role of a nucleating agent for PBS leading to the formation of increased transcrystallinity [32]. Previous research works have demonstrated that the addition of inorganic fillers may affect the crystallinity of the biopolymer, thus affecting the mechanical properties of the materials [9].

The thermal degradation of pure PBS and biopolymer nanocomposite materials was investigated in terms of weight loss by TGA. The decomposition data are summarized in Table 1. Decreased initial degradation temperatures (T_d) was obtained for bulk nanocomposites, which might be caused by the accelerated decomposition of PBS chains with the aid of extra hydroxyl groups from functionalized TiO_2 [17,33]. The char residues (wt_R) of pure PBS at 600 °C are 1.30%, whilst those of the nanocomposite samples at 600 °C are in the range of 1.88-12.28%, and they increase with an increase of TiO_2 nanoparticles content in the materials.

Table 1. Thermal properties of pure PBS and biopolymer nanocomposites from DSC and TGA experiments.

Type of sample	**T_{cc} (°C)**	**T_m (°C)**	**ΔH_m (J/g)**	**X_c (%)**	**T_d (°C)**	**wt_R (%)**
Pure PBS	75.1	111.1	61.0	30.2	397	1.30
PBS/TiO_2 1 wt%	74.7	110.2	67.2	33.8	396	1.88
PBS/TiO_2 2 wt%	74.3	108.4	68.1	34.9	394	2.13
PBS/TiO_2 5 wt%	73.9	107.9	75.9	37.2	392	5.57
PBS/TiO_2 10 wt%	74.0	105.8	80.8	39.8	391	12.28

4. Conclusions

Biopolymer nanocomposite materials with different modified TiO_2 content in PBS matrix have been developed. Effect of functionalization on the photodegradation and thermal properties of nanocomposites has been studied. The surface morphology indicated that a uniform dispersion of filler in the PBS matrix existed when the TiO_2 nanoparticles content was less than 5 wt%. The photodegradation rate of materials can be controlled by TiO_2 nanoparticles content. The ΔH_m, X_c and wt_R of bulk composites increased, whereas the T_m and T_d decreased. The development of PBS/TiO_2 materials can lead to an eco-friendly disposal of polymer waste.

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Conflict of interest

The authors declare that there is no conflict of interest.

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