

Preparation and physical properties of starch-based nanocomposite films with the addition of titanium oxide nanoparticles

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In this study, starch/polyvinyl alcohol (PVA)/titanium oxide (TiO₂) nanocomposite films were synthesized using a casting method. The characteristics of the starch/PVA nanocomposite films were evaluated by a scanning electron microscope (SEM), and X-ray diffraction (XRD). The physical properties such as tensile strength (TS), elongation at fracture (%E), degree of swelling (DS), solubility (S), and water vapor absorption of the prepared nanocomposite films were studied. The results of the investigation of the physical properties for the films indicated that compared with films without added TiO₂ nanoparticles, the mechanical properties and water resistance were enhanced up to 1.14–1.52 times by the addition of TiO₂ nanoparticles. In order to extend the application area of the nanocomposite films containing TiO₂ nanoparticles, the photocatalytic activity of films with/without TiO₂ nanoparticles was also examined by monitoring the degree of decomposition of BPA and 2,4-D. All the tested nanocomposite films revealed photocatalytic activity under UV and visible light irradiation although the rate of decomposition was slow compared to the use of UV light irradiation.

Key words: Starch/PVA nanocomposite films, Titanium oxide (TiO₂) nanoparticle, Physical properties, Photocatalytic degradability.

Introduction

Recently, large amounts of synthetic plastics have been produced from petroleum, and used throughout the world in the food industry, biomedical fields, and agriculture. With the increase of the number of applications, disposal of waste synthetic plastics has become a serious problem such as endocrine disruptor leaks with incineration or landfill of the various vinyl waste, styrofoam, and plastic containers and the generation of air pollution by an incomplete combustion of the waste of poisonous dioxin formation, etc. Therefore, the environmental pollutions from these plastic wastes have become a global issue [1–3]. One solution to solve this problem is to make plastics using biodegradable polymers, which are degraded in the soil, activated sludge, or compost after the service life is over. Thus, enhancing the biodegradability is an important issue for industrial applications of biodegradable polymers. Starch is one of the natural biopolymers most widely used to develop environmentally-friendly materials to substitute for petrochemical-based, non-biodegradable plastic materials. Being an inherently biodegradable, renewable, and low-

cost material, starch has a high potential in various applications. However, wide applications have been limited due to the lack of a water barrier property and poor mechanical properties, such as film brittleness caused by high intermolecular forces. Therefore, many attempts have been made to overcome these problems by blending starch with other biodegradable synthetic polymers for numerous applications [4–6].

Starch blended with polyvinyl alcohol (PVA) films is one of the most popular biodegradable polymers. However, the physical properties such as the mechanical properties and water resistance of the starch/PVA blended films are still lower than those of other polymers made from petroleum [7]. In recent studies, these problems were partially solved by irradiation with electron beam and ultraviolet [8], the addition of crosslinking agents [9], the use of chemically modified starch [10] and the preparation of biodegradable nanocomposites [11, 12].

Nanocomposites can be made with a variety of enhanced physical, thermal and other unique properties. They have properties that are superior to conventional microscale composites and can be synthesized using simple and inexpensive techniques. In many studies, starch-based nanocomposite polymers have been prepared using nanoclay, nano-SiO₂ or whiskers as nanofibrils and their mechanical properties, thermal properties, and water resistances have been investigated. Park *et al.* [13] and

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Dean *et al.* [14] have synthesized starch/clay nanocomposites with improved physical properties and water resistance using nanoclays. Tang *et al.* [15] have reported that the tensile strength and water barrier properties of starch/PVA blend films were improved by the addition of nano-SiO₂ particles. In addition, Anglès and Dufresne [16] have reported that biodegradable nanocomposite films were prepared using starch and whiskers as nanofibrils and the mechanical behavior of them was improved. Other advantages have been reported on the performance of biodegradable polymers to be resulting from using nanoclay, nano-SiO₂ or whiskers, including an increased thermal stability [17-19]. Thus, it can be found that the mechanical properties, thermal properties, and water barrier properties were improved by the addition of nanoparticles to biodegradable polymers. In this paper, we focus on TiO₂ nanoparticles as an inorganic filler in a biodegradable polymer matrix. TiO₂ is one of the most widely studied photocatalysts for the decomposition of hazardous organic materials because it has high photocatalytic activity, chemical stability, is an abundant resource, with low cost and nontoxicity [20].

In this study, we synthesized starch/PVA nanocomposite films from TiO₂ as nanoparticles using a casting method. The physical properties such as tensile strength (TS), elongation at fracture (%E), degree of swelling (DS), and solubility (S) and water vapor absorption for the films are investigated. The photocatalytic degradability of bisphenol A (BPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) of starch/PVA nanocomposite films with TiO₂ nanoparticles were also investigated.

Experimental

Materials

Corn starch (CS) was obtained from Doosan Corn Products Korea, Inc. Polyvinyl alcohol (PVA), reagent grade glycerol (GL), bisphenol A (BPA) 2,4-dichlorophenoxyacetic acid (2,4-D) were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI). PVA was 99% hydrolyzed with a molecular weight average of 89,000-98,000. Commercial titanium oxide (TiO₂) (P-25, Degussa Corporation, Germany) having a specific surface area of 50 m²g⁻¹ and an average particle diameter of 30 nm was dried at 100 °C for 4 h in a vacuum oven before use. Distilled deionized water (DW) was used in all experiments.

Preparation of starch/PVA nanocomposite films

Starch/PVA nanocomposite films were obtained by a casting method. First, PVA solution was prepared by dissolving PVA in hot water (95 °C). CS, 40 wt.% GL as an additive, and TiO₂ nanoparticles (5, 8, 12, and 15 wt.%) were mixed directly together with water using a kitchen-aid mixer (Anymix, Hyun-woo Star, Seoul, Korea) for 60 minutes. CS and PVA had the same mass ratio, and the content of TiO₂ nanoparticles and additives was expressed as a mass percent ratio to total CS and PVA weight,

Table 1. Composition of gel-like solutions used to prepare starch/PVA nanocomposite blend films

Sample name	CS (g)	PVA (g)	GL (wt.%)	TiO ₂ (wt.%)	DW (g)
CSP	5	5	-	-	100
CSPG4	5	5	40	-	100
CSPG4T5	5	5	40	5	100
CSPG4T8	5	5	40	8	100
CSPG4T12	5	5	40	12	100
CSPG4T15	5	5	40	15	100

respectively. The PVA solution and mixed starch/TiO₂/additives were mixed at 90 °C for 30 minutes. Then, the mixture was blended to form a homogeneous gel-like solution with a mechanical stirrer (1200 rpm) at room temperature for 90 minutes. The mixing composition is shown in Table 1. Bubbles, the by-product of preparation, were removed using an aspirator. Thus, the gel-like solution prepared was poured on to a pre-warmed (50 °C) teflon mold (200 × 200 × 1 mm). Water was evaporated from the molds in a ventilated oven at 50 °C for 24 h. Dried films were put in open polyethylene bags and stored at 25 °C and at a relative humidity (RH) of 55% for one week before they were measured.

X-ray diffraction analysis for starch/PVA nanocomposite films using Cu K_α radiation was performed by scanning at a rate of 2 degrees/minute with a diffractometer (XRD, Rigaku D/MAX Ultima III) and the scan range of the diffraction angle (2θ) was 52 ≤ θ ≤ 80. The surface morphology of the nanocomposite films were also observed by scanning electron microscopy (SEM, Hitachi, S-4700, Japan).

Physical properties of films

Tensile strength (TS) and elongation (%E) were evaluated for each film using an Instron 6012 testing machine. Three dumbbell shaped specimens (ASTM D-412) were cut from each film. Each specimen had a width of 15 mm. The average thickness of the specimen was about 0.125 mm. The thickness of the films was measured on a mechanical scanner (digital thickness gauge 'Mitutoyo', Tokyo, Japan) at 15 random positions around the film. The mean standard deviation within the film was about 5% of the average thickness. The gauge length and grip distance were both 50.0 mm. The crosshead speed was 20 mm/minute and the load cell was 250 kg_f. The tests were carried out at 25 °C and 55% RH in a constant temperature and humidity room.

The degree of swelling (DS) and solubility (S) of the films were measured applying the following method. Dried biodegradable starch/PVA nanocomposite films were immersed in distilled water at room temperature (25 °C). After equilibration (24 h), moisture on the surface

of the film was removed, and the weight of the films was measured. DS in films was calculated as (1) :

$$DS = \frac{(W_e - W_0)}{W_0} \quad (1)$$

where W_e is the weight of film at the adsorption equilibrium, and W_0 is the first dry weight of film.

The swelled films were dried again for 24 h at 60 °C, and thier solubility (S) was calculated with the following equation (2) :

$$S = \frac{(W_0 - W_d)}{W_d} \quad (2)$$

where W_0 is the first dry weight of film, and W_d is the dry weight of swelled film.

Water vapor absorption

The pieces of prepared nanocomposite films were cut into small pieces (5×5 cm) and the weight of pieces was measured immediately. Then, they were dried in an oven at 60 °C overnight and weighed. The water content (k) of starch/PVA nanocomposite films was calculated as (3):

$$k = \frac{(W_f - W_0)}{W_0} \quad (3)$$

where W_0 is the mass of the dried sample and W_f is the mass of the sample before drying. Water vapor adsorption of the films was evaluated after storage in desiccator chambers over salt solutions at a constant 53% RH for 10 days at 25 °C. The constant 53% RH was obtained with a saturated salt solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (~53% relative humidity).

Photocatalytic experiments

Photocatalytic activities of starch/PVA nanocomposite films were evaluated using a decomposition test of BPA and 2,4-D in an aqueous solution under UV and visible light. UV illumination was carried out with two UV-A lamps (F10T8BLB, Sankyo Denki) and the light intensity of the bulbs was 5 W/m^2 . To obtain visible light rays, ordinary fluorescent lights were used. The initial concentration of the BPA solution was 10 ppm. The prepared nanocomposite films of 0.2 g was added into 1 l BPA solution. Similar to BPA, the photodecomposition was also carried out for 2,4-D. The pH value of the BPA and 2,4-D solution was kept around 6.5-7. With an appropriate time interval, a 5 ml sample solution was collected, and the concentrations of BPA and 2,4-D remaining in solutions were determined by a UV-Visible spectrometer (1601, Shimadzu, Japan).

Result and Discussion

The XRD patterns of TiO_2 (P-25) and starch/PVA films with/without added TiO_2 nanoparticles are shown in Fig. 1. The TiO_2 diffraction patterns revealed the main

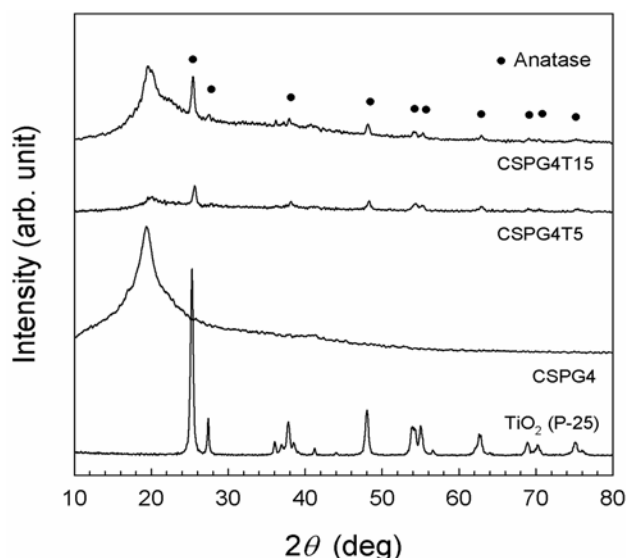


Fig. 1. XRD patterns of TiO_2 (P-25) nanoparticles, GL-added film without TiO_2 nanoparticles (CSPG4), GL-added nanocomposite film with 5 wt.% TiO_2 nanoparticles (CSPG4T5), and GL-added nanocomposite film with 15 wt.% TiO_2 nanoparticles (CSPG4T15). (See Table 1 for an explanation of codes)

peaks with 2 theta values in degrees of 25.31, 27.45, 37.92, 48.14, 54.34, 55.18, 62.94, and 69.12 corresponding to anatase TiO_2 . The intensity of TiO_2 characteristic peaks increased with an increasing amount of TiO_2 loading in the starch/PVA blend film. This indicates that TiO_2 is incorporated into the films. No clear changes were observed in the TiO_2 phase by the blending of the starch/PVA films. This is advantageous because the anatase phase TiO_2 is known to have a relatively higher photocatalytic activity.

Fig. 2(a), (b), (c), (d), and (e) show the SEM images of raw TiO_2 and films to which 40 wt.% GL as additive and 5 wt.% and 15 wt.% TiO_2 nanoparticles are added, respectively. The average size of raw TiO_2 nanoparticles was indicated as about 50 nm via using the SEM image (Fig. 2(a)). It is possible to see a very good dispersion of TiO_2 nanoparticles for films, as there is not a rough area or large agglomeration.

Fig. 3. represents the results of mechanical properties i.e., tensile strength (TS) and elongation at fracture (%E) of the films with 40 wt.% GL added and with the addition of TiO_2 nanoparticles (5, 8, 12, and 15 wt.%). With an increase in the TiO_2 nanoparticle content, TS values increased whereas %E values decreased compared with that of a film without added TiO_2 nanoparticles. That is, TS increased about 1.52 times; conversely %E decreased 1.60 times when the TiO_2 nanoparticle content increased from 0 to 15 wt.%.

An investigation of the degree of swelling (DS) and solubility (S) for the films plays a key role in determining the degree of combination between the components of films as well as their resistance to water [21]. DS and S of starch/PVA nanocomposite films with TiO_2 nanoparticle content are shown Table 2. It can be seen that DS of

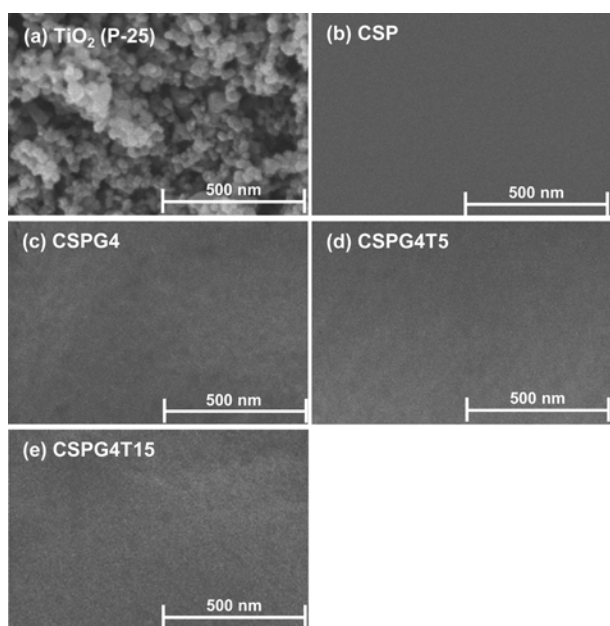


Fig. 2. SEM image of TiO_2 (P-25) nanoparticle and starch/PVA nanocomposite films with/without added TiO_2 nanoparticles. (a) Raw TiO_2 (P-25) nanoparticles, (b) starch/PVA blend films without GL and TiO_2 nanoparticles, (c) GL-added film without TiO_2 nanoparticles (CSPG4), (d) GL-added nanocomposite film with 5 wt.% TiO_2 nanoparticles (CSPG4T5), (e) GL-added nanocomposite film with 15 wt.% TiO_2 nanoparticles (CSPG4T15).

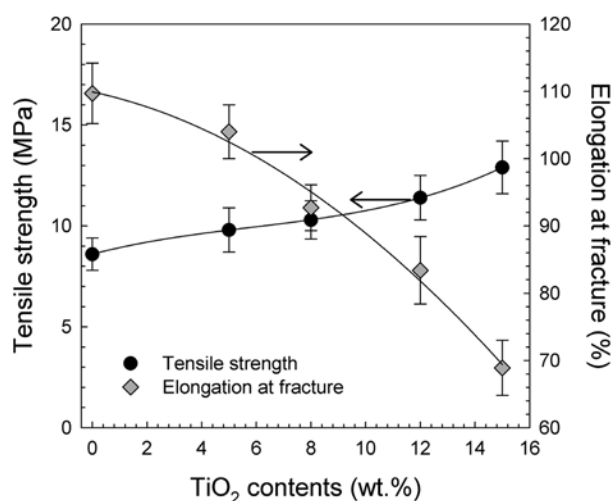


Fig. 3. Tensile strength (TS) and elongation at fracture (%E) as a function of the TiO_2 nanoparticle content of the starch/PVA nanocomposite films.

Table 2. Degree of swelling (DS) and solubility (S) of starch/PVA nanocomposite films in terms of TiO_2 nanoparticle contents

Sample name	Degree of swelling (DS)	solubility (S)
CSPG4	0.618 ± 0.025	0.334 ± 0.018
CSPG4T5	0.605 ± 0.021	0.321 ± 0.015
CSPG4T8	0.589 ± 0.030	0.310 ± 0.019
CSPG4T12	0.575 ± 0.026	0.301 ± 0.014
CSPG4T15	0.543 ± 0.030	0.289 ± 0.021

the nanocomposite film decreased with an increase in the TiO_2 nanoparticle content. The DS value of the CSPG4 film was 0.618 ± 0.025 , while the CSPG4T15 had the lowest DS at about 0.541 ± 0.030 . Table 2 also shows the solubility of the nanocomposite films, and as can be seen from the table, the films have low S values when compared with the film without added TiO_2 nanoparticles, and the solubility for water of the nanocomposite film decreased with an increase in the TiO_2 nanoparticle content. From these results, it can be explained that the inter-intramolecular combination is improved by the presence of interactions between the added TiO_2 nanoparticle and the starch/PVA/additives mixture.

Water absorption is an important factor to evaluate the use and application of starch-based composite plastics. Thus, the water contents of the nanocomposite films synthesized with TiO_2 nanoparticle contents stored at 51% RH up to 10 days were investigated, and the results are shown in Fig. 4. A steady-state of the water contents for all the films was reached within about 70 h. The figure indicates that the water content of the nanocomposite films prepared decreased with an increase of the TiO_2 nanoparticle content. This results indicated that the water resistance of nanocomposite films was better than for a film without added TiO_2 nanoparticles. The reason is that a specific matrix-reinforcement combination is formed by the addition TiO_2 nanoparticle between the components of the films.

In order to extend the application area of starch/PVA nanocomposite films with added TiO_2 nanoparticles, the photocatalytic activity of starch/PVA nanocomposite films with/without TiO_2 nanoparticles was examined by monitoring the degree of decomposition of a BPA solution as an endocrine disruptor and 2,4-D as a herbicide. The nanocomposite films were illuminated with a UV lamp that had a broad emission spectrum of 315-400 nm. The

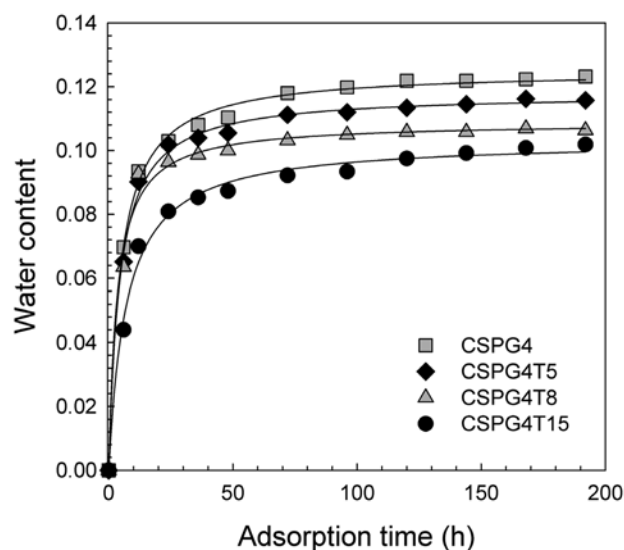


Fig. 4. Water contents of prepared starch/PVA nanocomposite films in terms of the TiO_2 nanoparticle content.

maximum illumination was at 352 nm. In addition, the nanocomposite films were exposed to ordinary fluorescent light for visible light irradiation. The degree of photocatalyst degradability of BPA and 2,4-D was calculated as the ratio of the initial (C_0) and the final concentrations (C). Fig. 5(a) and (b) represent the degree of photocatalyst degradability of BPA and 2,4-D in the nanocomposite films as a function of the UV irradiation time. The initial concentration of BPA and 2,4-D was 10 ppm, respectively. With an increase of the TiO_2 nanoparticle content, the decomposition of BPA and 2,4-D increased. The degree of photocatalyst degradability of BPA and 2,4-D in nanocomposite films with 15 wt.% TiO_2 nanoparticle added was about 0.534 and 0.396, respectively. The decomposition of 2,4-D was better than BPA, probably because the molecular size of BPA is bigger than that of 2,4-D, thus

the degree of contact of TiO_2 nanoparticles into the nanocomposite film was low, the degree of the decomposition of 2,4-D was higher than that of BPA.

Fig. 6(a) and (b) show the degree of photocatalyst degradability of BPA and 2,4-D with visible light irradiation time for each film. Although the degree of photocatalyst degradability of BPA and 2,4-D for visible light irradiation in the nanocomposite films is lower than that for UV irradiation, the decomposition of BPA and 2,4-D increased with an increase of the TiO_2 nanoparticle content. When visible light was irradiated on the nanocomposite films with 15 wt.% TiO_2 nanoparticles added for 240 min, the degree of photocatalyst degradability of BPA and 2,4-D was about 0.825 and 0.597, respectively. All the tested nanocomposite films revealed photocatalytic activity under visible light, although the rate of decomposition was slow

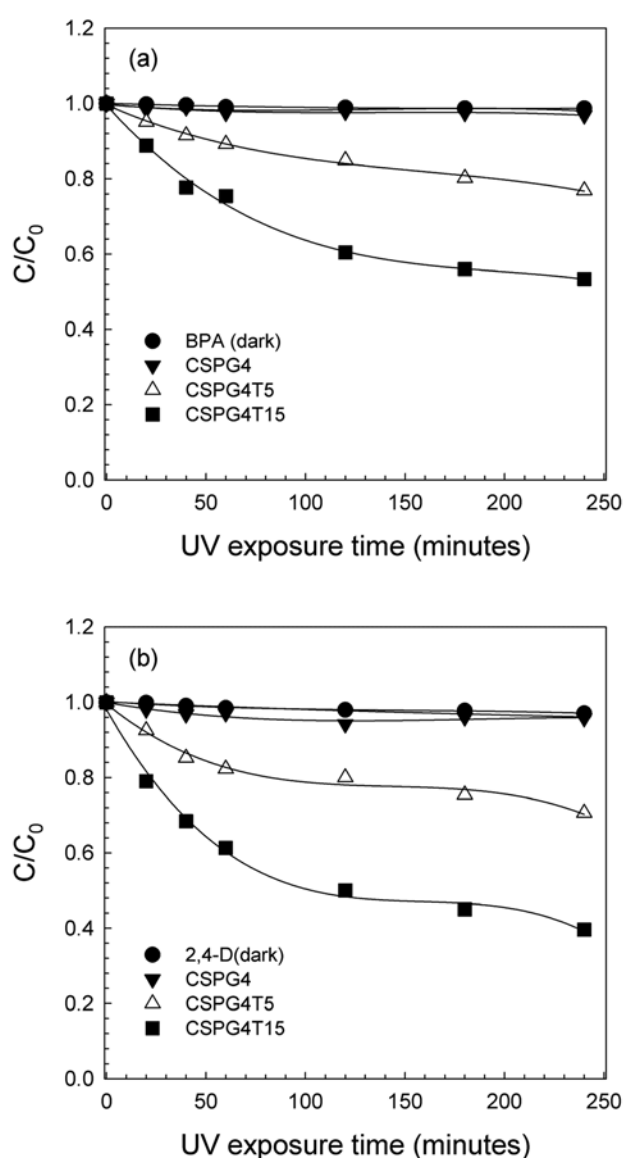


Fig. 5. Photocatalytic degradability of bisphenol A (BPA) (a) and 2,4-dichlorophenoxyacetic acid (2,4-D) (b) on starch/PVA/ TiO_2 nanocomposite films as a function of irradiation time with UV light.

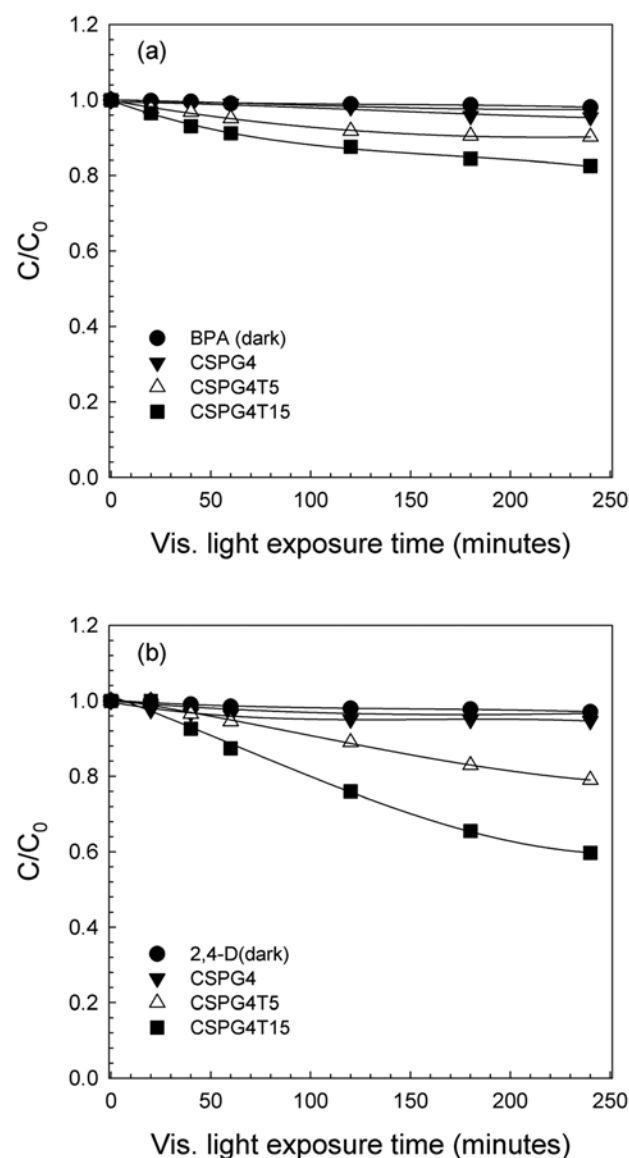


Fig. 6. Photocatalytic degradability of bisphenol A (BPA) (a) and 2,4-dichlorophenoxyacetic acid (2,4-D) (b) on starch/PVA/ TiO_2 nanocomposite films as a function of irradiation time with visible light.

compared to the use of UV irradiation except for the film without TiO₂ nanoparticles.

Conclusions

Starch/PVA nanocomposite films were successfully prepared using corn starch, polyvinyl alcohol (PVA), titanium oxide (TiO₂) nanoparticles, and glycerol (GL) as an additive. The physical properties i.e., tensile strength (TS), elongation at fracture (%E), degree of swelling (DS), solubility (S), and water vapor absorption of the nanocomposite films with added TiO₂ nanoparticles were evaluated. The results of the investigation show that the physical properties of the nanocomposite films were improved by the addition of TiO₂ nanoparticles. The TS increased about 1.52 times whereas %E decreased 1.60 times when the TiO₂ nanoparticles content was increased from 0 to 15 wt.%. In addition, DS and S decreased 1.14 and 1.15 times, respectively. With an increase in the TiO₂ nanoparticle content, the water resistance of the nanocomposite films was also enhanced because a specific matrix-reinforcement combination is formed by the addition of TiO₂ nanoparticles between the components of the films. The photocatalytic degradability of the nanocomposite films containing TiO₂ nanoparticles was examined using bisphenol A (BPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) as photodegradation materials under UV and visible light irradiation. All the tested nanocomposite films revealed photocatalytic activity under UV and visible light irradiation. The degree of decomposition (C/C₀) of BPA and 2,4-D for the nanocomposite film (CSPG4T15) with 15 wt.% TiO₂ nanoparticles added under UV light irradiation was about 0.534 and 0.396, respectively. In addition, the degree of decomposition (C/C₀) under visible irradiation was about 0.825 and 0.597, respectively.

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