

Synthesis, Physical Properties, and Characterization of Starch-Based Blend Films by Adding Nano-Sized TiO₂/Poly(methyl methacrylate-co-acrylamide)

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ABSTRACT: The purpose of this study was to improve the physical properties and to expand the application range of starch-based blend films added nano-sized TiO₂/poly(methyl methacrylate-co-acrylamide) (PMMA-co-AM). Starch-based blend films were prepared by using corn starch, polyvinyl alcohol (PVA), nano-sized PMMA-co-AM, nano-sized TiO₂/PMMA-co-AM particles, and additives, i.e., glycerol (GL) and citric acid (CA). Nano-sized PMMA-co-AM was synthesized by emulsion polymerization and TiO₂ nanoparticles were also prepared by using sol-gel method. Nano-sized TiO₂/PMMA-co-AM particles were synthesized by wet milling for 48 h. The morphology and crystallinity of TiO₂, nano-sized PMMA-co-AM and TiO₂/PMMA-co-AM particles were investigated by using the scanning electron microscope (SEM) and X-ray diffractometer (XRD). In addition, the functional groups of the TiO₂/PMMA-co-AM particles were characterized by IR spectrophotometry (FTIR). The physical properties such as

tensile strength (TS), elongation at break (%E), degree of swelling (DS), and solubility (S) of starch-based films were evaluated. It was found that the adding of nano-sized particles can greatly improve the physical properties of the prepared films. The photocatalytic degradability of starch/PVA/nano-sized TiO₂/PMMA-co-AM composite films was evaluated using methylene blue (MB) and acetaldehyde (ATA) as photodegradation target under UV and visible light. The degree of decomposition (C/C₀) of MB and ATA for the films containing TiO₂ and CA was 0.506 and 0.088 under UV light irradiation and 0.586 (MB) and 0.631 (ATA) under visible light irradiation, respectively. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1850–1858, 2011

Key words: starch-based blend films; nano-sized TiO₂/poly(methyl methacrylate-co-acrylamide) composite; physical properties; photocatalytic degradability

INTRODUCTION

Synthetic plastics such as polyethylene (PE), polypropylene (PP), poly ethylene terephthalate (PET), polystyrene (PS), and polycarbonate (PC) have become important materials used in daily life, food packing or food service items, and agriculture because of their unique characteristics, i.e., easy availability, low cost, and long lasting among other properties.¹ Unfortunately, however, use of these synthetic plastics has brought an environmental pollution because they take hundreds of years to degrade. Thus, disposal of waste plastics has become a serious problem.^{2–5} Consequently, there is a growing interest in developing biodegradable polymers made from renewable and natural polymers such as starch, proteins, and cellulose

lose to replace synthetic nondegradable materials. Of these materials, starch is a natural polymer, inexpensive, and readily available resource, and it is often used as filler for the replacement of petroleum-derived synthetic polymers to decrease environmental pollution.^{6,7} However, starch has severe limitations because of its solubility and poor water-resistance, making starch products very sensitive to the relative humidity at which they are stored and used.⁸ Therefore, many attempts have been made to overcome these problems by blending starch with other biodegradable synthetic polymers for numerous applications, i.e., starch/polyvinyl alcohol (PVA), starch/poly(lactic acid) (PLA), and starch/polyester blend polymers.^{9–15}

Starch/PVA blended films are one of the most popular biodegradable polymers. However, the mechanical properties and water resistance of the starch/PVA blended films are still lower than those of other polymers made from petroleum. These problems were

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partially solved by irradiation of electron beam and ultraviolet,^{16,17} addition of crosslinking agents,¹⁸ use of chemically modified starch,^{19,20} and preparation of biodegradable polymer nanocomposites adding nano-sized particles.²¹

Of these methods, biodegradable polymer nanocomposites are a relatively new class of reinforced polymers containing nanometric-sized particles with dimensions typically in the range of 1–150 nm, i.e., nanoclay or silicate. In general, because of the ultra-fine phase dimensions involved, nanocomposites exhibit new and improved mechanical properties when compared to their micro- or macrocomposite counterparts.²² In many studies, biodegradable polymers nanocomposites have been synthesized using organic–inorganic nanoclay and investigated their physical properties. Park et al.²³ and Dean et al.²⁴ have generated starch/clay nanocomposites with improved mechanical properties and decreased water vapor permeability by using clays. Lee et al.²⁵ have reported that nanoclays are able to improve strength and modulus of a polylactic acid (PLA) matrix. Other benefits have also been reported on the performance of many polymers to be resulting from using clay nanoparticles, including increased glass transition^{26,27} and thermal degradation temperatures.^{28,29} Thus, addition of nano-sized clay-particles for biodegradable polymers improved the physical and thermal properties for their use. However, elongation of biodegradable nanocomposites polymers was drastically decreased by the addition of small quantities of nanoclay or silicate. In addition, the degree of biodegradation was relatively slow. Therefore, the development of new nano-sized particles is necessary to improve on these weak points such as the decrease of elongation and the degree of biodegradation.

The aim of this study is to prepare the eco-friendly nanocomposite films from biodegradable corn starch, PVA, and PMMA-*co*-AM, and to investigate the influence of PMMA-*co*-AM contents on the physical properties of starch/PVA/PMMA-*co*-AM blend films. In addition, the blend films of starch, PVA, and TiO₂/PMMA-*co*-AM were prepared and then its physical properties were measured. Here, TiO₂/MMA-*co*-AM nanoparticles were synthesized by using wet milling method. TiO₂/PMMA-*co*-AM composite were analyzed by using X-ray diffractometer (XRD), Fourier transform IR spectrophotometry (FTIR), and scanning electron microscopy (SEM). In this work, TiO₂/PMMA-*co*-AM nanocomposites were used to broaden the application range of biodegradable nanocomposite films as eco-friendly materials such as coating materials and wallpaper. TiO₂ photocatalysts are attractive and promising materials because they have high photocatalytic activity, stability, and nontoxicity. Especially, the high photocatalytic activity of TiO₂

has received much attention.³⁰ Thus, the photocatalytic degradability of methylene blue (MB) and acetaldehyde (ATA) of starch/PVA/TiO₂/PMMA-*co*-AM nanocomposite blend films were also investigated.

EXPERIMENTAL

Materials

Corn starch was obtained from Doosan Corn Products Korea. Methyl metacrylate (MMA), acrylamide (AM, > 99%+), potassium persulfate (K₂S₂O₈; KPS), sodium dodecylsulfate (SDS), polyvinyl alcohol (PVA), glycerol (GL), citric acid (CA) were purchased from Aldrich Chemical Company (Milwaukee, WI). Titanium-tetraisopropoxide (TTIP, > 98%), methylene blue (MB), hydrochloric acid, and ethanol were purchased from Junsei Chemical (Tokyo, Japan). Acetaldehyde (ATA) was obtained from Carlo Erba (Milan, Italy). PVA was 99% hydrolyzed with a molecular weight average of 89,000–98,000. MMA was distilled under vacuum to remove the inhibitors before polymerization. Distilled deionized (DDI) water was used in all experiments.

Preparation of nano-sized PMMA-*co*-AM and TiO₂/PMMA-*co*-AM particles

Nano-sized PMMA-*co*-AM latex was synthesized by emulsion copolymerization in a 500 mL reactor at a constant stirring rate of 300 rpm in a nitrogen atmosphere. DDI water (350 mL), surfactant SDS (0.45 g), initiator KPS (0.41 g), and monomers (MMA and AM) were added into the reaction bottle. MMA (16.72 g) and AM (5.94 g) were added at the mole ratio of 2 : 1, respectively. The reaction time and temperature for synthesizing latex were 20 h and 60°C. The latex was dialyzed in deionized water at room temperature for 3 days for characterization and preparation of TiO₂/PMMA-*co*-AM composite nanoparticles and starch/PVA blend films.

TiO₂ nanoparticles were prepared by sol-gel method based on the hydrolysis of TTIP.³¹ 20 mL of TTIP was slowly dropped in ethanol (200 mL) at room temperature for 5 min. Then, a drop-wise addition of hydrochloric acid solution (0.05 M) into the TTIP solution was conducted for 24 h under vigorous stirring condition. The suspension was then ultrasonicated at room temperature for 1 h and centrifuged at –4°C and 8000 rpm for 20 min. The white precipitate formed was filtered and dried at room temperature for 1 h. Finally, the dried TiO₂ particles were calcined at 450°C for 30 min in air gas flow (5 mL min⁻¹). TiO₂/PMMA-*co*-AM composites were synthesized by wet milling (8000M/Mixer/Mill/SPEX, NJ) for 48 h. TiO₂ nanoparticles (0.2, 0.5, 1.0, and 1.5 g) were added to PMMA-*co*-AM latex

TABLE I
Composition of Gel-Like Solutions Used to Prepare
Starch-Based Blend Films

Sample name	Starch (g)	PVA (g)	PMMA-co-AM (g)	TiO ₂ (g)	GL (g)	CA (g)	Water (g)
SPN0	5	5	0	–	–	–	100
SPN1	5	5	1	–	–	–	100
SPN2	5	5	2	–	–	–	100
SPN3	5	5	3	–	–	–	100
SPN4	5	5	4	–	–	–	100
SPN5	5	5	5	–	–	–	100
SPG4N0	5	5	0	–	4	–	100
SPG4N1	5	5	1	–	4	–	100
SPG4N2	5	5	2	–	4	–	100
SPG4N3	5	5	3	–	4	–	100
SPG4N4	5	5	4	–	4	–	100
SPG4N5	5	5	5	–	4	–	100
SPC4N0	5	5	0	–	–	4	100
SPC4N1	5	5	1	–	–	4	100
SPC4N2	5	5	2	–	–	4	100
SPC4N3	5	5	3	–	–	4	100
SPC4N4	5	5	4	–	–	4	100
SPC4N5	5	5	5	–	–	4	100
SPN3T0.2	5	5	3	0.2	–	–	100
SPN3T0.5	5	5	3	0.5	–	–	100
SPN3T1.0	5	5	3	1.0	–	–	100
SPN3T1.5	5	5	3	1.5	–	–	100
SPG4N3T0.2	5	5	3	0.2	4	–	100
SPG4N3T0.5	5	5	3	0.5	4	–	100
SPG4N3T1.0	5	5	3	1.0	4	–	100
SPG4N3T1.5	5	5	3	1.5	4	–	100
SPC4N3T0.2	5	5	3	0.2	–	4	100
SPC4N3T0.5	5	5	3	0.5	–	4	100
SPC4N3T1.0	5	5	3	1.0	–	4	100
SPC4N3T1.5	5	5	3	1.5	–	4	100

contained 3 g copolymer nanoparticles, respectively. The crystallinity of the nano-sized TiO₂, PMMA-co-AM and TiO₂/PMMA-co-AM particles were characterized using X-ray diffractometer (D/MAX Ultima III, Rigaku, Japan). Also, the size and the shape were observed using scanning electron microscopy (SEM, S-4700, Hitachi, Japan). Fourier transform IR spectrophotometry (FTIR, IRPrestige-21, Shimadzu, Japan) was used to characterize the functional groups of the TiO₂/PMMA-co-AM composite.

Preparation of starch/PVA blend films

Starch/PVA blend films were prepared using a casting method. The preparation of starch/PVA/PMMA-co-AM blend films was as follow. At first, PVA solution was prepared by dissolving PVA in hot water (95°C). Corn starch, PMMA-co-AM latex contained copolymers of 1, 2, 3, 4, and 5 g and additives (GL and CA) were mixed directly together with water using a Kitchen-aid mixer for 15 min. The PVA solution and mixed starch/PMMA-co-AM/additives were mixed at 90°C for 20 min. Then, the mixture was blended to form homogeneously gel-like solution with a mechanical stirrer (200 rpm) at room tempera-

ture for 80 min. Starch/PVA/TiO₂/PMMA-co-AM blend films were also prepared in the same method as above. The mixing composition is shown in Table I. Bubbles, the by-product of preparation, were removed by using an aspirator. The gel-like solution thus prepared was poured on to a prewarmed (60°C) teflon mold (200 × 200 × 1 mm). Water was evaporated from the molds in a ventilated oven at 40°C for 24 h. Dried films were put in open polyethylene bags and stored at 25°C and at relative humidity of (RH) 57% for one week before they were measured.

Physical properties of films

Tensile strength (TS) and elongation (%E) were evaluated for each film using the Instron 6012 testing machine. Three dumbbell shaped specimens (ASTM D-412) were cut from each film. Each specimen had a width of 12 mm. The average thickness of the specimen was about 0.12 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. Crosshead speed was 20 mm min⁻¹ and load cell was 250 kg_f. The tests were carried out at 25°C and 58% RH at a constant temperature and in a humid room.

The degree of swelling (DS) and solubility (S) of the films were measured applying the following method. Dried biodegradable starch/PVA blend films were immersed in distilled water at room temperature (25°C). After the equilibrium (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 the film at the adsorbing equilibrium, and W_0 is the first dry weight of the film.

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

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

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

Photocatalytic experiments

Photocatalytic activities of biodegradable films were evaluated using a decomposition test of methylene

blue (MB, C16H18N3Cl) 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 concentration of MB was determined by absorbance measurement with a UV-vis spectrometer (1601, Shimadzu).

Photocatalytic degradability of acetaldehyde (ATA) for the films was also analyzed by using GC/MS (Gas Chromatography Mass Spectrometer, QP-5050A, Shimadzu). Each film and 1 mL ATA were put into the reactor. Then, dark condition was maintained until ATA was adsorbed to the film surface for 3 h. When ATA changes no longer appeared on the specific peak of ATA on GC/MS, fluorescent (FL60, Shin-Kwang, Korea) and UV lamp (UV-A, F6T5BL, 6W, Sankyo Denki) were radiated. Then decomposition of ATA was measured every 1 h.

RESULTS AND DISCUSSION

Characterization of TiO_2 /PMMA-co-AM composite

The XRD patterns of TiO_2 , PMMA-co-AM, and TiO_2 /PMMA-co-AM composite particles are shown in Figure 1. The TiO_2 diffraction patterns revealed the main peaks with 2θ values of 25.4° , 30.7° , 37.8° , 48.0° , 53.9° , 55.0° , and 62.8° corresponding to anatase TiO_2 . The intensity of TiO_2 characteristic peaks increased with increasing amount of TiO_2 loaded on PMMA-co-AM. This indicates that TiO_2 is incorporated into the PMMA-co-AM. No clear changes were

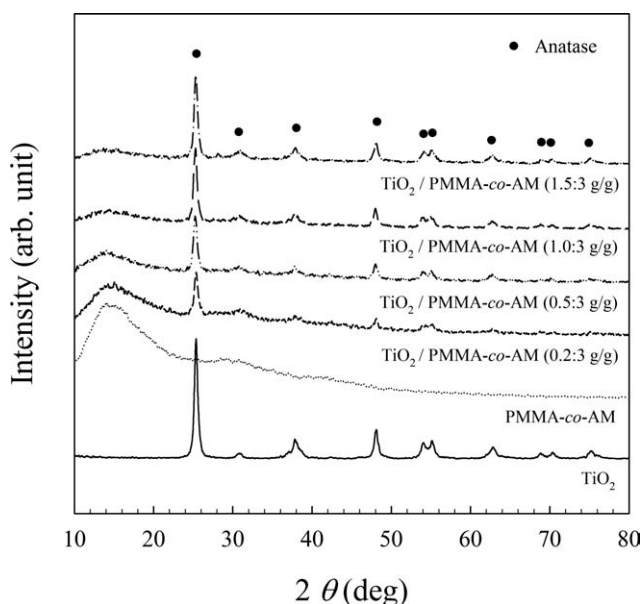


Figure 1 XRD patterns of TiO_2 , PMMA-co-AM, TiO_2 /PMMA-co-AM ($0.2 : 3 \text{ g g}^{-1}$), TiO_2 /PMMA-co-AM ($0.5 : 3 \text{ g g}^{-1}$), TiO_2 /PMMA-co-AM ($1.0 : 3 \text{ g g}^{-1}$), and TiO_2 /PMMA-co-AM ($1.5 : 3 \text{ g g}^{-1}$).

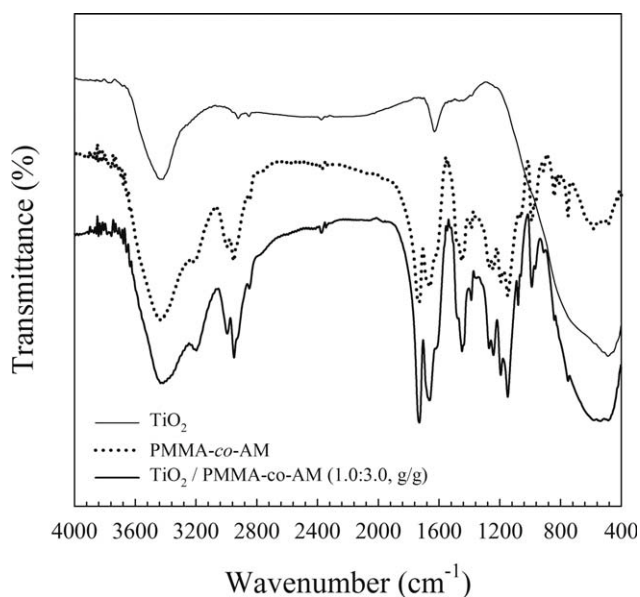


Figure 2 FTIR spectrum of TiO_2 , PMMA-co-AM, TiO_2 /PMMA-co-AM composite.

observed in the TiO_2 phase by the mixing of PMMA-co-AM. This is advantageous because the anatase phase TiO_2 is known to have relatively higher photocatalytic activity.

Figure 2 represents the FTIR transmittance spectra of TiO_2 , PMMA-co-AM, and TiO_2 /PMMA-co-AM composite particles. In general, the Ti-O stretching peaks appear near 500 cm^{-1} . In the PMMA-co-AM spectrum, the peaks at 3435 and 3197 cm^{-1} are attributed to the bend of O-H and N-H stretching vibration. The peaks at 2950 and 2951 cm^{-1} can be assigned to the C-H and $-\text{CH}_2-$ stretching vibration. The spectrum shows the C=O stretching vibration at around 1650 cm^{-1} . The peaks around 1200 cm^{-1} originate from the C-O stretching of the ester group. The characteristic peaks were observed with the C-N stretching vibration and $-\text{NH}_2$ bending vibration near 1447 and 1173 cm^{-1} , respectively. In TiO_2 /PMMA-co-AM composites spectrum, the absorption peaks at 1580 , 1267 , and 1086 cm^{-1} are induced by Ti-N-H deformation vibration, C-O-H vibration, and Ti-O-C vibration, respectively. This indicates that TiO_2 nanoparticles reacted with hydroxyl and with amino group of PMMA-co-AM.

Figure 3(a-c) show the SEM images of TiO_2 , PMMA-co-AM, and TiO_2 /PMMA-co-AM composite nanoparticles. SEM images showed that the average size of raw TiO_2 nanoparticles was about 20 nm [Fig. 3(a)]. Figure 3(b) shows SEM images of the PMMA-co-AM particles prepared by emulsion polymerization. The images show that copolymer nanoparticles are successfully synthesized. The surface of the copolymer nanoparticles was smooth and had a regular spherical shape. The average size of spherical

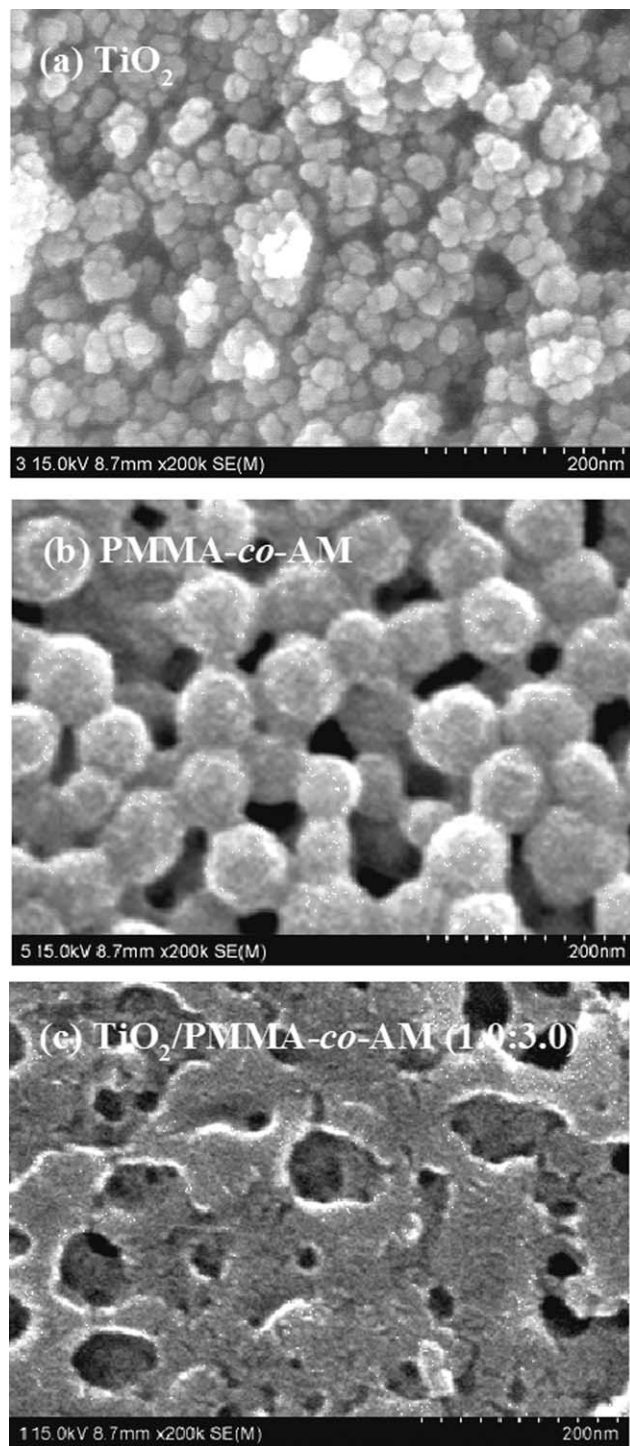


Figure 3 Scanning electron microscope (SEM) images of (a) TiO_2 , (b) PMMA-co-AM , and (c) $\text{TiO}_2/\text{PMMA-co-AM}$ composite.

copolymer particles was about 90 nm. SEM images of $\text{TiO}_2/\text{PMMA-co-AM}$ composite particles are shown in Figure 3(c). These findings verify that TiO_2 particles and nano-sized copolymer particles were dispersed by the wet milling. However, the copolymer particles of spherical shape were destroyed because of the increasing temperature by the milling.

Physical properties of starch/PVA blend films

Table II show the results of the physical properties i.e., tensile strength (TS), elongation at break (%E), degree of swelling (DS), and solubility (S) with PMMA-co-AM nanoparticles contents of the films to which 4 g glycerol (GL) and citric acid (CA) as additives are added, respectively. With increasing PMMA-co-AM nanoparticles contents, TS and S values increased whereas %E and DS decreased. Although each film has different additives, the mechanical properties of each film were improved by adding PMMA-co-AM nanoparticles. Especially, the low S values indicate that water resistance of films has improved. In addition, it was observed that the physical properties of the films synthesized were superior to that of the other films prepared using added nanoclay (Park et al.,²³ Dean et al.,²⁴ and Tang et al.³²) or nano- SiO_2 particles (Xiong et al.³³ and Tang et al.³⁴). As mentioned above, the mechanical properties and water resistance of biodegradable films made from starch, PVA, and additives are lower than those of other films made from polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and polycarbonate (PC). These problems were partially solved by changing the preparation method, the addition of additives or the third materials such as nano-sized particles and the chemical change of a composition element. This study improved on the defect of biodegradable films by adding nano-sized PMMA-co-AM particles.

To extend the application range of biodegradable films added PMMA-co-AM nanoparticles, instead of PMMA-co-AM nanoparticles, starch/PVA blend films were prepared by using $\text{TiO}_2/\text{PMMA-co-AM}$ composite. TiO_2 was used for photocatalyst to examine the photocatalytic degradability of two toxic organic compounds; methylene blue (MB) and acetaldehyde (ATA). TiO_2 and PMMA-co-AM composite were synthesized by using wet milling (SPEX). In many studies, composites of TiO_2 and copolymers nanoparticles were prepared by encapsulation emulsion polymerization.^{35–37} However, encapsulated TiO_2 composites in copolymers nanoparticles reduced the photocatalytic degradability due to structural hindrance of copolymers networks. Therefore, in this work, the wet milling method was used to increase the degree of dispersion of TiO_2 on the surface of PMMA-co-AM nanoparticles.

Table III show the results of the physical properties of the TiO_2 added of films. TS, DS, and S slightly increased while %E decreased. There were few changes in the physical properties of films with/without TiO_2 except for S. The S values of films increased because TiO_2 combined with films were easily dispersed in water.

TABLE II
Tensile Strength, Elongation at Break, Degree of Swelling, and Solubility of Starch/PVA Blend Films in Terms of PMMA-co-AM Contents

Sample name	Tensile strength (MPa)	Elongation at break (%)	Degree of swelling	Solubility
SPN0	55.58 ± 3.6	20.27 ± 4.0	2.51 ± 0.10	0.210 ± 0.02
SPN1	60.81 ± 3.9	16.37 ± 3.5	2.64 ± 0.09	0.184 ± 0.02
SPN2	64.24 ± 4.1	12.76 ± 2.1	2.75 ± 0.08	0.173 ± 0.01
SPN3	69.83 ± 3.9	10.18 ± 3.0	2.90 ± 0.09	0.169 ± 0.02
SPN4	79.55 ± 5.1	7.67 ± 2.3	2.96 ± 0.08	0.161 ± 0.02
SPN5	91.41 ± 4.5	4.92 ± 3.1	3.06 ± 0.11	0.151 ± 0.03
SPG4N0	4.98 ± 1.1	154.10 ± 6.9	0.97 ± 0.09	0.558 ± 0.01
SPG4N1	10.62 ± 1.9	132.06 ± 7.0	0.99 ± 0.12	0.538 ± 0.02
SPG4N2	15.44 ± 3.0	104.11 ± 6.2	1.15 ± 0.10	0.519 ± 0.02
SPG4N3	18.02 ± 2.2	81.98 ± 5.2	1.21 ± 0.09	0.514 ± 0.02
SPG4N4	23.42 ± 3.1	63.45 ± 5.5	1.35 ± 0.10	0.467 ± 0.03
SPG4N5	32.11 ± 3.6	51.01 ± 6.0	1.41 ± 0.15	0.402 ± 0.02
SPC4N0	22.41 ± 2.5	201.31 ± 13.0	2.10 ± 0.10	0.404 ± 0.02
SPC4N1	28.73 ± 2.9	151.94 ± 10.2	2.13 ± 0.09	0.388 ± 0.03
SPC4N2	34.22 ± 2.8	119.56 ± 8.0	2.26 ± 0.09	0.370 ± 0.01
SPC4N3	41.26 ± 3.1	97.35 ± 8.6	2.29 ± 0.08	0.373 ± 0.02
SPC4N4	50.71 ± 3.0	71.54 ± 7.5	2.36 ± 0.10	0.342 ± 0.02
SPC4N5	43.79 ± 4.1	65.46 ± 6.4	2.48 ± 0.11	0.321 ± 0.04

Photocatalytic activity of biodegradable films

The photocatalytic activity of biodegradable films with/without PMMA-co-AM and TiO₂/PMMA-co-AM was examined by monitoring the degree of decomposition of MB solution and a typical indoor air pollutant, ATA. Prepared films were illuminated with a UV lamp that has a broad emission spectrum of 315–400 nm. The maximum illumination was yielded at 352 nm. In addition, films were exposed to ordinary fluorescent lights for visible light irradiation. The degree of photocatalyst degradability of MB and ATA was calculated as the ratio of initial (C₀) and final concentration (C).

Figure 4(a,b) show the degree of the decomposition of MB in the films as a function of the UV and

visible light irradiation time. The initial concentration of MB was 5 ppm. Figure 4(a) shows the photocatalyst degradability of MB with UV irradiation time for each film. Noticeable differences of the photocatalyst degradability of MB were observed with the addition with/without TiO₂ and additives (GL and CA) in the films. Especially, the photocatalyst degradability of MB for the film (CSPGNT3), which was prepared by corn starch, PVA, TiO₂/PMMA-co-AM, and GL as additive was superior to those of the other films because of the physical properties of the film added GL. In previous our work,³⁸ we reported the physical properties of biodegradable films according to the kinds of additives used. The GL added films, in general, have low the physical

TABLE III
Tensile Strength, Elongation at Break, Degree of Swelling, and Solubility of Starch/PVA/PMMA-co-AM Blend Films in Terms of TiO₂ Contents

Sample name	Tensile strength (MPa)	Elongation at break (%)	Degree of swelling	Solubility
SPN3T0	69.83 ± 3.9	10.18 ± 3.0	2.90 ± 0.10	0.169 ± 0.02
SPN3T0.2	76.03 ± 3.2	9.25 ± 2.1	2.94 ± 0.09	0.186 ± 0.02
SPN3T0.5	77.05 ± 3.4	8.09 ± 2.6	2.98 ± 0.08	0.198 ± 0.03
SPN3T1.0	85.80 ± 3.1	7.14 ± 3.1	3.01 ± 0.07	0.231 ± 0.02
SPN3T1.5	92.91 ± 3.9	6.10 ± 2.2	3.06 ± 0.08	0.260 ± 0.02
SPG4N3T0	18.02 ± 2.2	81.98 ± 5.2	1.21 ± 0.09	0.514 ± 0.02
SPG4N3T0.2	18.64 ± 1.5	81.10 ± 2.4	1.26 ± 0.12	0.533 ± 0.02
SPG4N3T0.5	20.67 ± 2.1	76.05 ± 5.5	1.33 ± 0.10	0.545 ± 0.02
SPG4N3T1.0	27.72 ± 2.0	69.72 ± 4.0	1.38 ± 0.09	0.576 ± 0.03
SPG4N3T1.5	33.65 ± 2.1	64.46 ± 3.0	1.43 ± 0.07	0.595 ± 0.03
SPC4N3T0	41.26 ± 3.1	97.35 ± 8.6	2.29 ± 0.08	0.373 ± 0.02
SPC4N3T0.2	43.15 ± 2.6	94.21 ± 7.0	2.31 ± 0.09	0.399 ± 0.03
SPC4N3T0.5	44.05 ± 3.0	91.09 ± 4.5	2.34 ± 0.11	0.434 ± 0.01
SPC4N3T1.0	48.44 ± 2.1	82.54 ± 6.0	2.39 ± 0.09	0.448 ± 0.02
SPC4N3T1.5	57.89 ± 2.6	74.52 ± 8.0	2.48 ± 0.07	0.458 ± 0.03

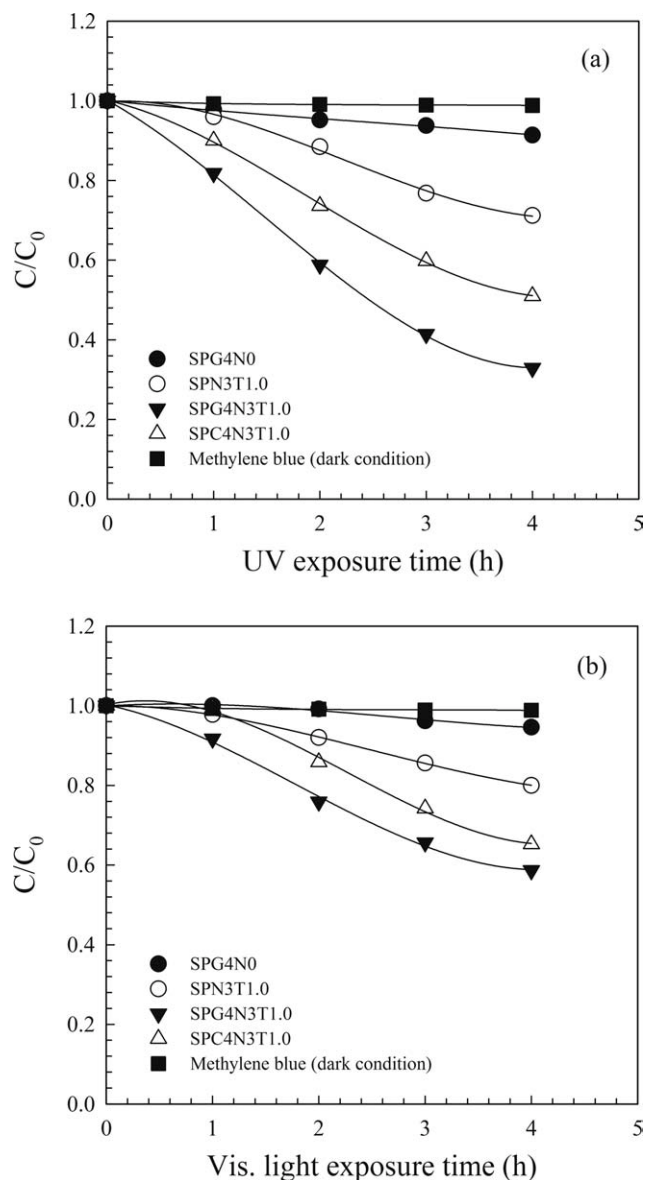


Figure 4 Photocatalytic degradability of methylene blue on starch/PVA/TiO₂/PMMA-co-AM blend films as a function of irradiation time with UV (a) and visible light (b).

properties, that is, low tensile strength and low water resistance because of the weak combination between composition materials. However, in this study, these properties provide information that the photocatalyst degradability of MB for CSPGNT3 film is better than the others. This means that pores which can adsorb other materials as well as H₂O molecules exist owing to the weak combination of composition materials. For this reason, the photocatalyst degradability of MB for CSPGNT3 film with many pores which can adsorb MB was better than other films. Figure 4(b) shows the photocatalyst degradability of MB with visible light irradiation time for each film. It is well known that the photocatalytic activity of pure TiO₂ is good only under UV

light irradiation, and thus, great efforts have been devoted to activating its photocatalytic activity under visible light. Therefore, the photocatalytic degradability of MB for the biodegradable films was investigated by visible light irradiation. All the tested films revealed photocatalytic activity under visible light, although the rate of decomposition was slow compared to the use of UV irradiation except for the film without TiO₂.

Figure 5(a,b) show the degree of ATA decomposition in the films as a function of the UV and visible light irradiation time. The initial concentration of ATA was 1 ppm. Figure 5(a) shows the photocatalyst degradability of ATA with UV irradiation time

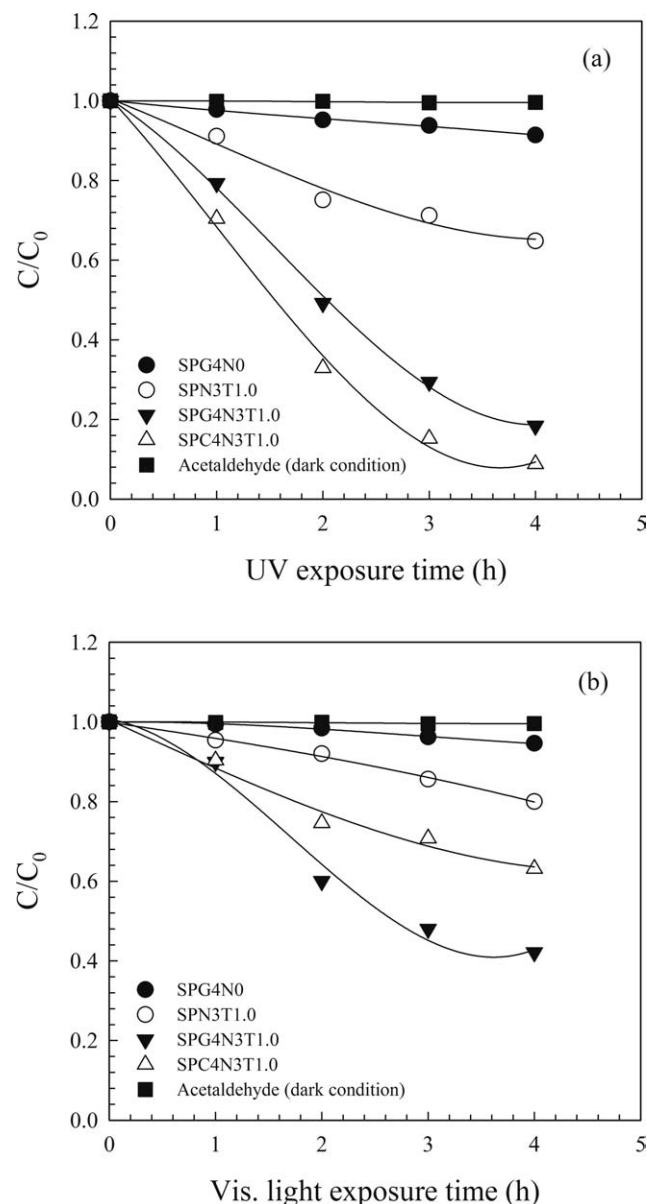


Figure 5 Photocatalytic degradability of acetaldehyde on starch/PVA/TiO₂/PMMA-co-AM blend films as a function of irradiation time with UV (a) and visible light (b).

for each film. With UV irradiation time, the photocatalytic degradation of ATA occurred relatively rapidly compared to the photocatalytic degradation of MB for each film. The photocatalytic degradability of MB and ATA for the films with/without TiO₂ and without additives was almost similar. However, clear differences in the photocatalyst degradability of MB and ATA were observed with the addition with TiO₂ and additives (GL and CA) in the films (CSPGNT3 and CSPCNT3). Furthermore, with the sort of additives, we discovered that the results of the photocatalytic degradability represented a reversible phenomenon. In other words, the photocatalyst degradability of ATA for CSPCNT3 film was better than CSPGNT3 film because CA with -COOH as functional group and ATA generally interact well with -COH as functional group and then the reactivity was improved by UV irradiation. Figure 5(b) shows the photocatalyst degradability of ATA with visible light irradiation time for each film. It is interesting to note that each and every film revealed photocatalytic activity under visible light. Compared to the photocatalyst degradability of MB, the rate of degradability occurred rapidly because of the increase of the slope in each point. The initial photocatalytic activity in CSPCNT3 film was increased because of the existence of interactions between -COOH and -COH as functional groups capable of hydrogen bonding.

CONCLUSIONS

Starch/PVA blend films were successfully prepared by using corn starch, polyvinyl alcohol (PVA), nano-sized poly(methyl methacrylate-co-acrylamide) (PMMA-co-AM), nano-sized TiO₂/PMMA-co-AM composites, and additives, i.e., glycerol (GL) and citric acid (CA). Nano-sized PMAA-co-AM particles were synthesized by the method of emulsion polymerization. In addition, nano-sized TiO₂/PMMA-co-AM composites were prepared by using wet milling (SPEX) for 48 h. These nano-sized particles were characterized using X-ray diffractometer (XRD), Fourier transform IR spectrophotometry (FTIR), and scanning electron microscopy (SEM). The physical properties such as tensile strength (TS), elongation (%E), degree of swelling (DS) and solubility (S) of the films contained nano-sized particles were investigated. From the results, with increasing PMMA-co-AM nanoparticles contents, TS and S values increased, whereas, %E and DS decreased. Although each film has different additives, the physical properties of each film were improved by adding PMMA-co-AM nanoparticles. In the results of the physical properties of the TiO₂ added of films, TS, DS, and S slightly increased while %E decreased. The photocatalytic degradability of the films added PMMA-co-AM and TiO₂/PMMA-co-AM composite was evaluated

using methylene blue (MB) and acetaldehyde (ATA) as photodegradation target under UV and visible light. The degree of decomposition (C/C_0) of MB for the film (CSPGNT3), which was prepared by corn starch, PVA, TiO₂/PMMA-co-AM, and GL as additive was 0.329 (UV light irradiation) and 0.586 (visible light irradiation). In addition, the degree of decomposition (C/C_0) of ATA for the films containing TiO₂ and CA was 0.088 (UV light irradiation) and 0.631 (visible light irradiation), respectively.

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