

Effect of UV Irradiation on Cellulase Degradation of Cellulose Acetate Containing TiO₂

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Abstract: Cellulose acetate (CA) films containing anatase type titanium dioxide (TiO₂) nanoparticles were prepared by solution casting. The film surface was modified by UV irradiation using a grid type UV irradiator. The UV irradiation caused slight increase in photodegradation of the CA films with TiO₂ compared to the CA film alone. However, CA films irrespective of TiO₂ content did not show a significant enzymatic degradation by a cellulase from *Aspergillus niger* without UV irradiation. Upon UV irradiation, the biodegradability remarkably improved even in the CA film without TiO₂. The irradiation of CA films decreased both the water contact angle and the degree of substitution (DS) implying the decrease in acetyl groups of the CA film surface due to the photo-scission of the acetyl group and photooxidation, resulting in more facile biodegradation of the surface film layer. The substantial enhancement in biodegradation of the UV irradiated CA film containing TiO₂ was attributed to the increased hydrophilicity, lowered DS and zeta potential due to the photoscission and the photooxidation effect of UV light. Also the increased surface area of the CA film due to the photocatalysis of TiO₂ particles may encourage the facile biodegradation.

Keywords: Cellulose acetate, Titanium dioxide, UV, Photodegradation, Biodegradability

Introduction

Cellulose acetate is one of the most important derivatives of cellulose and several fields of application have been found including modern coating, controlled release, optical film and membranes as well as the traditional textile field in the forms of fiber, film and plastic [1,2]. Biodegradability of cellulose acetate (CA) has been a main issue for the formation of environmentally sustainable polymer materials. It has been known that full hydrolysis of cellulose can be achieved by the concerted action of exoglucanases (cellobiohydrolases, CBH), endoglucanases (EG) and β -glucosidases [3]: Initially the EGs attack on cellulose by hydrolyzing randomly the internal cellulose bonds in amorphous regions providing the new chain ends accessible to the CBHs liberating cellobiose, and finally β -glucosidases hydrolyze cellobiose into glucose. However, the CA of a high DS has inhibited the cellulolytic degradation by cellulases due to the presence of acetyl groups [3,4]. Cellulose triacetate film was not biodegraded aerobically [5]. Biodegradation of cellulose esters is dependent on both DS and acyl chain length [6]. Recently it has been reported that enzymes capable of deacetylation promoted CA degradation by cellulases [7,8]. UV irradiation enhances the biodegradability of CA by increasing the surface area of the irradiated CA due to the dissolution of low molecular weight water-soluble compounds into liquid phase, possibly resulting in a higher enzyme accessibility [9]. The latter study actually reported that UV irradiation did not change DS significantly and the irradiation caused 23 % weight reduction in the sterilized acetate buffer solution without cellulases in the case of CA with 1.7 DS. Also patents reported that the photochemical sensitivity of CA improved when titanium

dioxide (anatase TiO₂) was incorporated into a CA matrix, which was verified by a tensile test only [10,11].

When titanium dioxide is irradiated with UV light, excited electron-hole pairs result in the chemical process to degrade organic compounds [12]. The photocatalytic reaction of TiO₂ can be ignited by irradiating with the UV light of 380 nm or less in order to surpass gap energy of 3.2 eV between valence and conduction bands. On UV irradiation, valence electrons (e⁻) of TiO₂ are excited to the conduction band producing holes (h⁺) in the valence bands. The electrons and holes migrate to the TiO₂ surface which can induce oxidation/reduction reaction, which can reduce oxidants such as oxygen (O₂ + H⁺ + e⁻ → H₂O[·]) in the conduction band, and the holes in the valence band can oxidize reductants such as water (H₂O + h⁺ → OH[·] + H⁺). Therefore the photocatalyst can degrade many organic materials because of its higher oxidation ability compared with the covalent bond energies of many organic materials. The promising application fields of photocatalysis can be selective organic synthesis, water purification, air cleaning, disinfection and photoactive materials, and hydrophilic surface generation, etc. [12,13]. UV irradiation alone can be an effective surface modification method for polymeric materials such as PET, PP and PTT via the photo-scission of main chain and the photo-oxidation of surface layer [14-16]. The UV irradiation on CA film containing nano-sized TiO₂ was carried out to improve the cellulase susceptibility of CA.

Materials and Methods

Chemicals and Enzyme

Cellulose acetate powder was purchased from Aldrich (USA), and had a molecular weight of 30,000 and acetyl content of 39.8 %. The DS of the cellulose acetates was ca 2.5. Anatase type titanium dioxide (TiO₂) nano-particles of

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15 nm or less were also obtained from Aldrich. The cellulose (EC 3.2.1.4) from *Aspergillus niger* was supplied by TCI (Japan).

Film Preparation

The CA powder was dissolved with the mixed solvent system of methylene chloride and acetone (9:1) and the CA solution was cast on 10 × 10 cm stainless steel plate to obtain ten samples. The solvent in the cast solution was dried at 4 °C for 6 h. For the TiO₂-containing CA film, TiO₂ nanoparticles were mixed into the solvent and the suspension was subsequently agitated with a 40 kHz ultrasonicator (Daihan, Korea) at room temperature for 30 minutes before the powder addition. The thickness of the prepared CA films was ca. 150 μm.

UV Irradiation and Photodegradation

The UV irradiator (UVO cleaner, Jelight) of a maximum power of 24 mW/cm² was used to irradiate both sides of a CA film. The UV energy (J/cm²), calculated by multiplying UV irradiation time and UV intensity, was adjusted by prolonging UV irradiation time up to 30 min. The amount of photodegradation was determined by weight loss of the irradiated samples compared with the sample without irradiation after vacuum drying of the three irradiated CA films at 60 °C for 1 h to constant weight.

Biological Degradation by Cellulase

To one 250-ml Erlenmeyer flask were added 225 unit of cellulase, unless stated otherwise, suspended in 100 ml of 0.1 M acetate buffer (pH 4.8) and the CA films of 25 × 25 mm which were weighed to ca 0.189 ± 0.002 g for the CA film without TiO₂. The flasks were incubated at 28 °C with 120 rev/min in a rotary shaker. During the incubation and in triplicate experiments, the weight of the film was periodically measured up to 7 days. The CA film was taken from the test flask, washed with deionized water, dried for 60 min in a vacuum oven and its dry weight was measured. Degradation of CA films by the cellulase was determined gravimetrically based on % weight loss of the cellulase-treated CA samples when compared with the pristine CA film.

Evaluation of DS and Zeta Potential

CA film was dissolved in DMSO-d₆, and the DS was analyzed by a JNM-A500 high-resolution ¹³C nuclear magnetic resonance spectrometer (Varian unity inova 300, 300 MHz for ¹H NMR, B₀=7.05T) operated at 125.65 MHz for ¹³C at 120 °C with 5 mm diameter tubes containing 1 ml of sample. ¹³C NMR spectra were acquired with the proton broadband decoupling with following parameters: spectral width 33.9 kHz, scan 72000, repetition time 3.0-s, pulse width 4.75 ms, and data size 32 K. DS was calculated from the equation suggested by Ishiyaki *et al.* [9]. In addition the zeta potentials of three CA films were measured and averaged to show the photooxidation due to the UV irradiation using a ELS 300D electrophoretic light scattering spectrophotometer (Otsuka, Japan) with a NELS flat board cell.

Evaluation of Surface Energy

The contact angles of water and diiodomethane on the CA film were measured by the sessile drop method using a static goniometer (AhTech, Korea). Five measurements were averaged to calculate the surface energy of the CA film according to the method suggested by Owens and Wendt [17].

ATR and SEM Analysis

A Jasco FT-IR 300E spectrophotometer with a KRS5 crystal was used to analyze the surface functional change of the irradiated CA film. The absorbance difference between the irradiated samples and the untreated standard was obtained by subtracting the standardized absorbance of the former from that of the latter. A Jeol 6380 scanning electron microscope (Japan) was used to detect microscopic the surface change of the irradiated and enzyme-treated samples.

Results and Discussion

Photolytic Degradation of CA Film Containing TiO₂

The UV irradiation alone on both sides of CA film did not cause a significant photodegradation on CA films with or without TiO₂ particles with increase in UV energy as shown in Figure 1. The UV energy was calculated by multiplying UV irradiation time and UV intensity. However, the sample containing 0.5 % TiO₂ showed a slightly higher weight loss compared with the pure CA film. The weight loss of the irradiated CA surface can be explained by ATR and ¹³C-NMR analysis. In Figure 2 the surface ester groups of CA vibrates at 1743, 1215 and 1047 cm⁻¹ which correspond the stretching of C=O, C-C-O and O-C-C bonds, respectively and the methyl of acetate also has a bending peak at 1369 cm⁻¹. The vibration of acetate linkage lost their intensity with increasing UV irradiation, which strongly suggests the cleavage of acetyl groups, resulting in the deacetylation of the CA in the surface layer. The TiO₂-incorporated sample showed the same behavior although not shown. As expected in ATR analysis, the DS values of the irradiated samples, calculated by ¹³C-NMR, decreased from 2.45 to 2.21 with

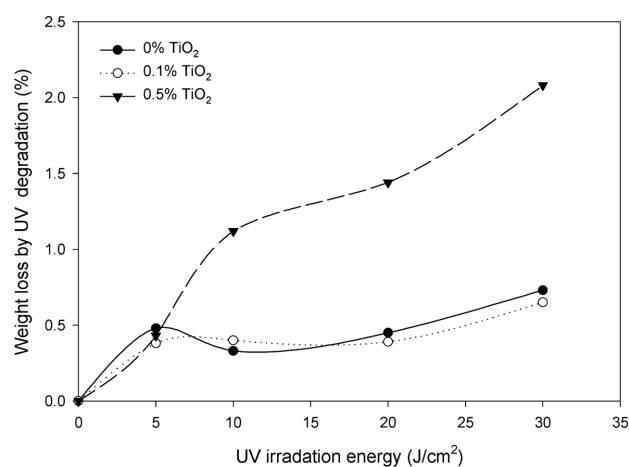


Figure 1. Photodegradation of CA films.

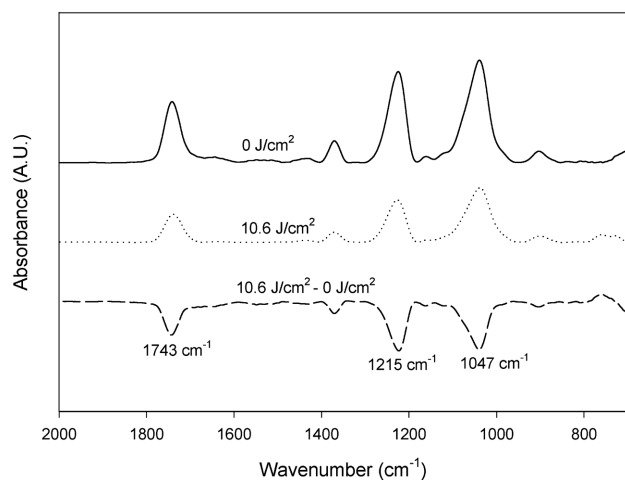


Figure 2. ATR spectra of UV-irradiated CA films.

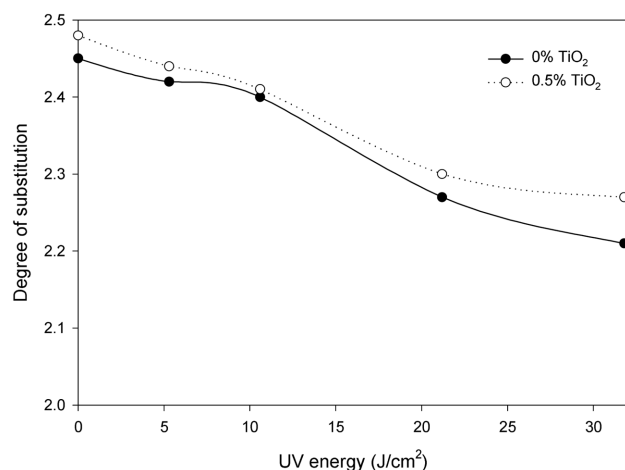


Figure 3. Effects of UV energy on the DS of CA films.

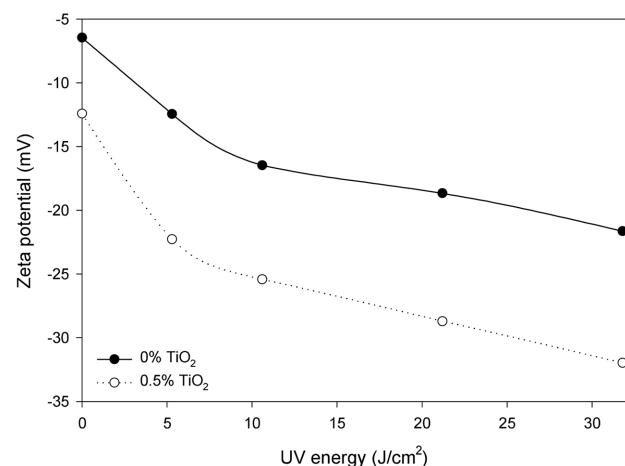


Figure 4. Effects of UV energy on the zeta potentials of CA films.

increasing UV energy as indicated in Figure 3. Unsurprisingly the zeta potential of CA films changed from -6.5 mV to

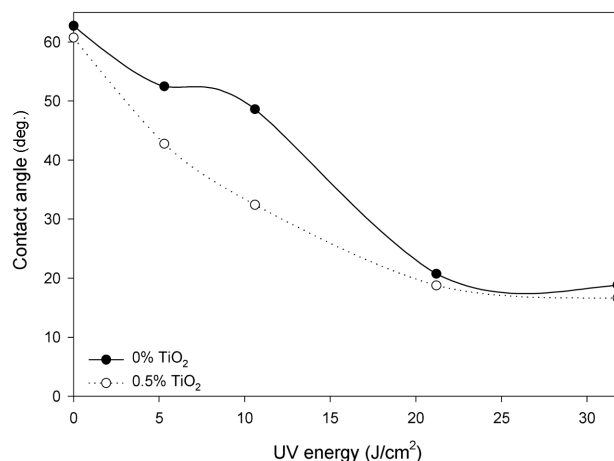


Figure 5. Water contact angles of UV-irradiated CA films.

Table 1. Surface energy (mN/m) of UV-irradiated CA films containing TiO₂

UV energy (J/cm ²)	TiO ₂ concentration (%)					
	0			0.5		
	γ^p	γ^d	γ^{total}	γ^p	γ^d	γ^{total}
0	21.8	40.1	61.8	23.0	37.7	60.7
5.3	27.4	36.0	63.4	32.7	31.0	63.8
10.6	29.6	33.9	63.4	37.7	27.5	65.2
21.2	42.0	26.2	68.2	42.6	25.1	67.7
31.8	42.5	25.7	68.3	43.3	24.6	67.8

γ^{total} , γ^d , γ^p indicate total surface energy, nonpolar and polar components, respectively.

-21.6 mV with increase in UV energy, suggesting more negative surface produced resulting from the photodegradation of CA molecules as shown in Figure 4. However, the TiO₂ particle did not seem to accelerate the DS and zeta potential change significantly indicating the negligible contribution of photocatalytic degradation considering 0.5 % TiO₂ content.

Hydrophilicity and Microscopic Change of UV-irradiated CA Films

It has been reported that the UV irradiation can change the hydrophobic surface of TiO₂ layer to a completely wettable surface [13]. Water contact angle decreased to 20° for the UV-irradiated CA film with UV energy of 31.8 J/cm^2 when compared with 60° for the pristine CA film in Figure 5. And the CA with TiO₂ particles showed slightly more rapid surface change when compared to the pure CA. The reason for the observed phenomenon may be found from the surface energy calculation (Table 1). The total surface energy of CA increased from 61.8 mN/m for the unirradiated CA, comparable to the reported surface energy of 58 ± 3 [18], upto 68.3 mN/m for the UV-irradiated CA with 31.8 J/cm^2 due to the photo-oxidation, where the polar surface energy component increased and the nonpolar component decreased concomitantly. The

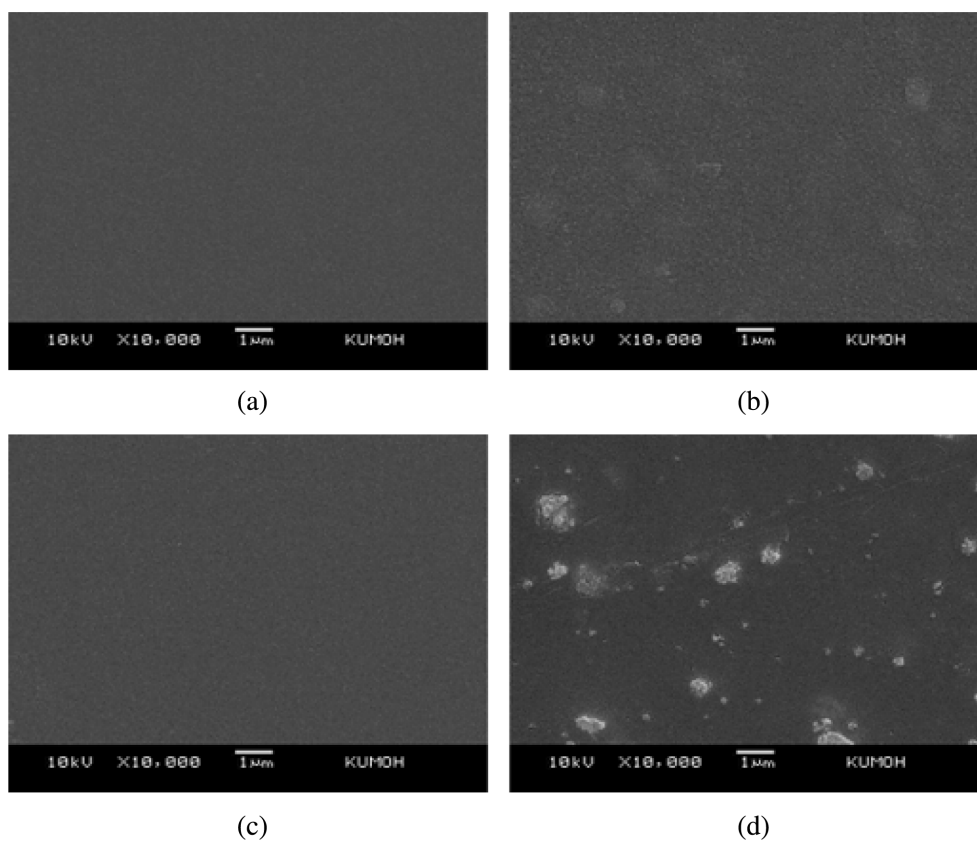


Figure 6. SEM photographs of CA films, unirradiated with (a) 0 % TiO₂, (b) 0.5 % TiO₂, UV-irradiated (31.8 J/cm²) with (c) 0 % TiO₂, and (d) 0.5 % TiO₂.

TiO₂-containing CA film has a lower γ^{total} , lower γ^{d} and higher γ^{p} when compared with the unfilled CA and the former film showed the stronger sensitivity of surface energy to the UV energy indicating that the photocatalysis of TiO₂ contributed to increase the photodegradation (Figure 1). After UV-irradiation the CA films containing TiO₂ revealed several large aggregated particles indicating the degradation of CA molecules on the film surface as well as the inhomogeneous distribution of TiO₂ particles in the film as shown in Figure 6.

Cellulase Degradation of CA Film Containing TiO₂

The decreased DS in both CA films suggested much faster and larger biodegradation by the endoglucanase (EC 3.2.1.4). Figure 7 shows the biodegradation results of the CA films after 7 day incubation. While both unirradiated samples DS of 2.5 did not show significant biodegradation of less than 1.4 % while the irradiated samples showed a remarkably increased biodegradation. Particularly the samples of 0.5 % TiO₂ content were readily hydrolyzed by the cellulase compared with CA film without TiO₂, which corresponded to approximately 50 % increase. Also the effect of cellulase concentration was shown in Table 2. The same biodegradational behavior was observed at a lower cellulase concentration. The SEM micrographs of enzyme-treated CA films were presented in

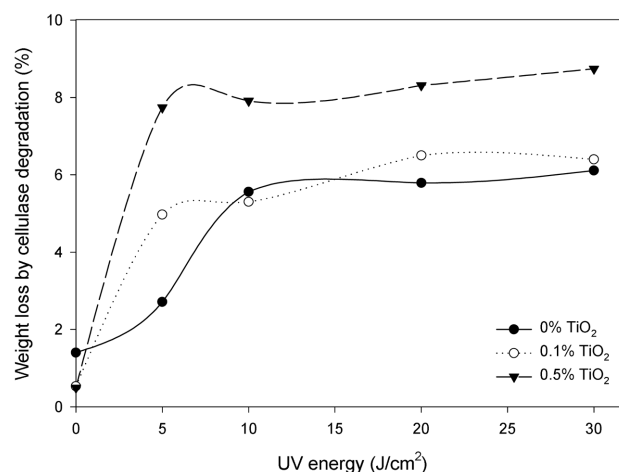


Figure 7. Cellulase degradation of UV-irradiated CA films of different TiO₂ content (225 unit/100 ml, 7 days).

Figure 8. The cellulase treatment did not make a significant difference in the surface morphology of unirradiated samples (Figure 8(a) and (b)) irrespective of the presence of TiO₂ particles both producing a spongy-like surface with many pinholes. However, the UV irradiation caused a remarkable

Table 2. Biodegradation of UV-irradiated CA films depending on cellulase concentration and UV energy (28 °C, pH 4.8, 7 days)

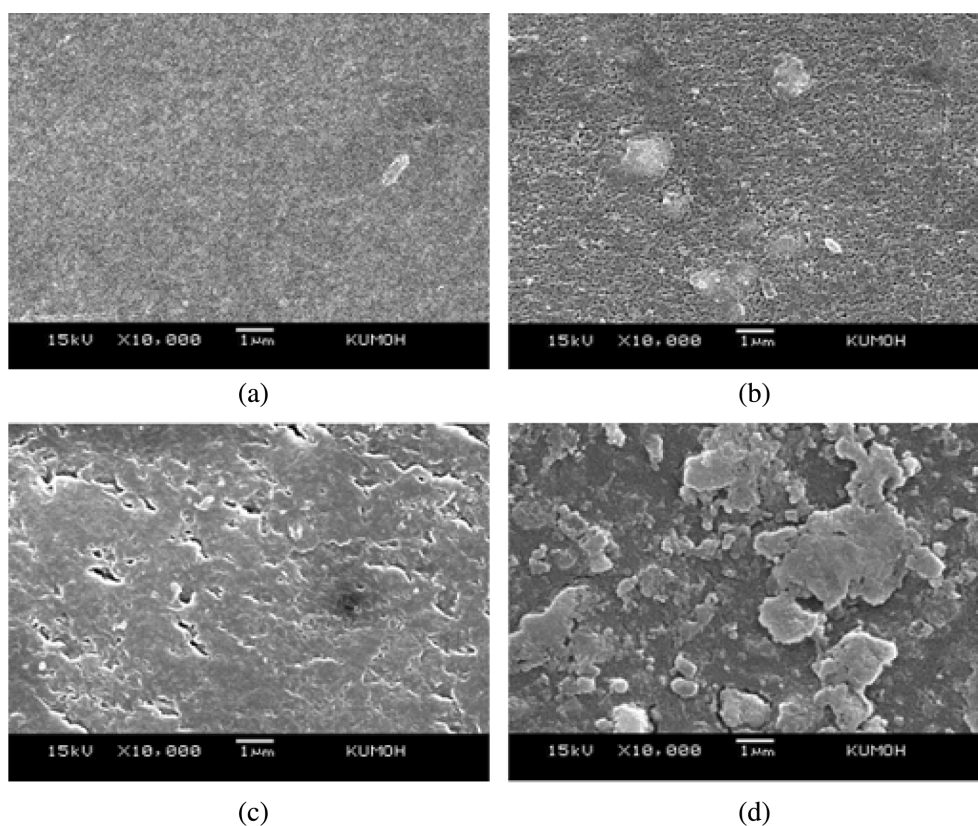
TiO ₂ concentration (%)	UV energy (J/cm ²)	Cellulase concentration (unit/100 ml)		
		45	135	225
0	0	0.6	0.5	1.4
	5.3	2.2	2.2	2.7
	10.6	2.5	3.9	5.6
	21.2	3.8	5.4	5.8
	31.8	4.7	6.0	6.1
0.5	0	0.6	0.4	0.5
	5.3	5.1	6.2	7.7
	10.6	5.4	6.4	7.9
	21.2	6.9	7.2	8.3
	31.8	6.7	7.0	8.7

difference in the biodegraded patterns by cellulase between the samples (Figure 8(c) and (d)), even though the weight loss was slightly larger in the case of the sample with TiO₂. While the sample without TiO₂ (Figure 8(c)) showed a very localized and inhomogeneous enzyme degradation, the CA sample with 0.5% TiO₂ (Figure 8(d)) suggested a rather uniform biodegradation except the TiO₂ particles and more

severe degradation was found in around TiO₂ particles due to the more pronounced photocatalysis of CA by the particles. The more uniform degradation and higher biodegradability of the UV-irradiated CA with the photocatalyst particles may be resulted from the higher accessibility of the glycosidic bonds in CA to cellulases after the UV irradiation because of the lower DS and increased hydrophilicity as well as the increased surface area, which is beneficially improved by the photocatalysis of CA by the particles.

Conclusion

Upon UV irradiation the biodegradability of CA film by cellulase was remarkably improved when compared with that of the unirradiated CA. The irradiated CA films decreased both water contact angle and DS implying the decrease in the acetyl groups of the CA film surface due to the photo-scission of the acetyl group and the photooxidation, resulting in more facile biodegradation of the surface film layer. However, when CA films without TiO₂ were irradiated with the UV light, only a slight weight loss occurred due to surface photodegradation. The substantial enhancement in cellulase degradation of the UV irradiated CA film containing TiO₂ attributed to the increased hydrophilicity and the lowered DS and zeta potential due to the photoscission and photooxidation effect of UV light, coupled with the increased surface area

**Figure 8.** SEM photographs of cellulase-treated CA films, unirradiated with (a) 0 % TiO₂, (b) 0.5 % TiO₂, UV-irradiated (31.8 J/cm²) with (c) 0 % TiO₂, and (d) 0.5 % TiO₂.

due to the photocatalysis of the CA film particularly surrounding the regions of TiO₂ particles.

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