

# Photodegradation of Cellulose Acetate Film in the Presence of Benzophenone as a Photosensitizer

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**ABSTRACT:** To study the effectiveness of photosensitizers to accelerate the degradation of cellulose acetate (CA) under ambient environment, CA (degree of substitution = 2.45) films containing benzophenone, which is one of the typical photosensitizers, were prepared and their degradative behavior by photoirradiation was examined. Decrease in molecular weight of CA and generation of carbon dioxide, carbon monoxide, and acetic acid from the CA films were observed by the irradiation of xenon arc lamp light, which was passed through a filter for cutting off the wavelength shorter than 275 nm. With increasing the con-

centration of benzophenone, the molecular weight of CA decreased and the generation of the degradation products from the CA films increased. These results may suggest that radical reactions of CA films proceed by photoirradiation and lead to oxidation and random cleavage of CA, and that benzophenone is an effective additive to accelerate the degradation of CA under ambient environment. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3235–3239, 2007

**Key words:** cellulose acetate; photosensitizer; benzophenone; photodegradation

## INTRODUCTION

Cellulose acetate (CA) (Fig. 1) is obtained by acetylation of cellulose, and has been used in various applications including photographic film, cigarette filter, base material for adhesive tape, and coating material. Although CA has good light stability, free radical generation in CA and photodegradation of CA under irradiation with ultraviolet have been reported in some literatures.<sup>1–3</sup> Hon has reported that ultraviolet exposure to CA fibers led to loss of sample weight and acetic acid content.<sup>2</sup> In our previous study using a xenon fadometer for light stability tests, however, CA films showed no detectable acetic acid generation or decrease in the molecular weight by photoirradiation for at least 28 days.<sup>4</sup> Therefore, photodegradation of CA under ambient environment seems to be very slow.

One of the effective ways to accelerate the degradation of polymer materials, which are carelessly discarded into the natural environment, is addition of photosensitizers to the polymers.<sup>5–7</sup> For example, some photosensitizers including derivatives of benzophenone and anthraquinone induce free radicals by photoirradiation and accelerate the degradation of polyethylene by radical reactions.<sup>5,8</sup>

Merlin and Fouassier reported the generation of free radicals by irradiation of ultraviolet to cellulosic materials including CA with or without photosensitizers, and assumed that the glycosidic scission and the hydrogen abstraction occurred.<sup>3,9</sup> However, the effectiveness of photosensitizers for the photodegradation of cellulose derivatives including CA under ambient environment has not been demonstrated since the previous studies intended to realize the degradation of cellulosic polymers during the photo-graft polymerization on the polymers using photosensitizers.

In this study, to investigate the effectiveness of photosensitizers to accelerate the degradation of CA under ambient environment, degradative behavior of CA films containing benzophenone has been examined under simulated solar exposure by means of a xenon fadometer.

## EXPERIMENTAL

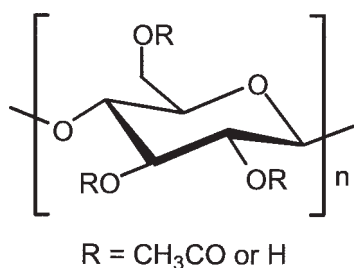
### Materials

CA (degree of substitution = 2.45) and benzophenone were purchased from Acros Organics (Geel, Belgium) and Sigma-Aldrich (St. Louis, MO), respectively, and used without further purification.

### Preparation of CA films

CA films containing up to 160 mg/g of benzophenone were prepared by a simple casting method. About 1 mL of acetone solution containing benzophenone and 5% of

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**Figure 1** Molecular structure of cellulose acetate.

CA (w/v) was spread on a glass petri dish (the inner diameter: 32.6 mm), and the acetone was evaporated under ambient atmosphere. Then, the films were dried under vacuum, punched into round shape with the diameter of 25 mm, and stored at 22 °C, 60% relative humidity, for at least 1 week. The thickness of the films was measured using a micrometer and the films of  $40 \pm 5 \mu\text{m}$  thickness were selected to be used for further investigation.

#### UV–vis absorption spectroscopy

The UV–vis spectra of the CA films were collected in a UV–visible spectrophotometer, UV-1700 (Shimadzu, Kyoto, Japan).

#### Photoirradiation

CA films were placed in glass vials (20 mL,  $23 \times 75 \text{ mm}^2$ ) and the vials were sealed with aluminum caps attached by poly(tetrafluoroethylene)/silicon septum, and then they were exposed to light from a xenon arc lamp of 1.5 kW in a fadometer TS-2 (Suga Test Instruments, Tokyo, Japan). The light was filtered at the cut-off value of 275 nm so that the spectra were similar to those from the solar according to the spectra data in the user's manual of the fadometer. The intensity of illumination at the sample vials was  $107 \text{ W/m}^2$  (integrated from 300 to 700 nm). During the irradiation, the temperature in the instrument was kept at around 35 °C by air-cooling.

#### Size exclusion chromatography

Number-average molecular weight of degraded CA was estimated by size exclusion chromatography (SEC) by means of an HLC-8220GPC system (TOSOH, Tokyo, Japan) equipped with differential refractive index detector and four consecutive TSK<sub>gel</sub> columns ( $\alpha$ -M,  $\alpha$ -4000,  $\alpha$ -3000,  $\alpha$ -2500) produced by TOSOH. The system was operated at 40 °C and at a flow rate of 1.0 mL/min using *N,N*-dimethylformamide containing 0.01M lithium bromide as an eluent. Polystyrene standards were employed for calibration.

#### <sup>1</sup>H NMR spectra

<sup>1</sup>H NMR (400 MHz) spectra of the CA films were recorded with a JEOL ECX-400 (JEOL, Tokyo, Japan)

using dimethylsulfoxide-*d*<sub>6</sub> as a solvent and tetramethyl silane as an internal standard.

#### Gas chromatography

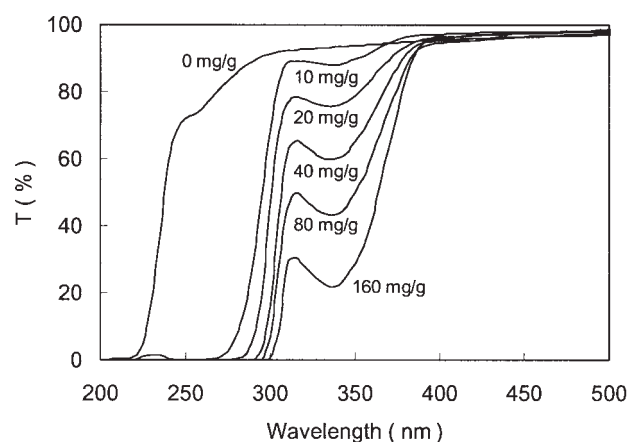
Carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), and acetic acid generated from the CA films were analyzed by gas chromatography. CO<sub>2</sub> and CO in the glass vials were detected by means of a thermal conductivity detector. Two-hundred microliters of the gas phase in the glass vials were obtained by an airtight syringe and injected into a gas chromatograph Agilent 6890 series (Agilent Technologies, DE). Helium gas was used as a mobile phase, and a packed column WG-100 (GL Sciences, Tokyo, Japan) was used for a solid immobile phase. The temperatures of the injector and the detector were set at 250 °C and the temperature in the oven was kept at 50 °C during the measurement.

Acetic acid was extracted from the CA film by shaking in the vial for 30 min with 3 mL of ethanol solution containing anethole as an internal standard. The extract was analyzed by means of the gas chromatograph equipped with flame ionization detector. Helium gas was used as a mobile phase, and a DB-WAX column (0.53 mm inner diameter, 1.0  $\mu\text{m}$  film thickness, 15.0 m length; Agilent Technologies) was used for a solid immobile phase. The temperatures of the injector and the detector were set at 250 °C. The oven temperature program had an initial temperature of 160 °C for 0 min, and then was programmed to reach 220 °C at the ratio of 20 °C/min, then held for 2 min. The injection volume was 1  $\mu\text{L}$  and the split ratio at the injector was 1 : 10.

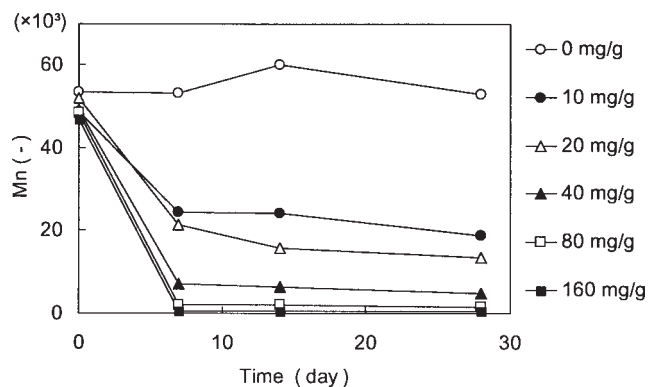
## RESULTS AND DISCUSSION

#### UV absorption of the CA films

To investigate the effect of the benzophenone concentration, we prepared CA films containing different amounts of benzophenone by casting. The transmittance of light of the CA films containing benzophe-



**Figure 2** UV–vis spectra of CA films containing different amount of benzophenone.



**Figure 3** Change in molecular weight of CA films containing benzophenone during photoirradiation. Number-average molecular weight ( $M_n$ ) was determined by size exclusion chromatography based on polystyrene standards (eluent: *N,N*-dimethylformamide containing 0.01M lithium bromide).

none is described in Figure 2. In the case of the CA film containing 10 mg/g of benzophenone, the slight absorbance was observed at 337 nm, and 0% transmittance was reached at  $\sim 265$  nm. The absorbance at 337 nm increased with increasing the benzophenone concentration. Furthermore, the wavelength, at which 0% transmittance reached, was changed from 265 to 295 nm as the benzophenone concentration increased from 10 to 160 mg/g.

Benzophenone appeared to have a good miscibility with CA, because all of the films prepared for this study were transparent and colorless by visual observation, regardless of the concentration of benzophe-

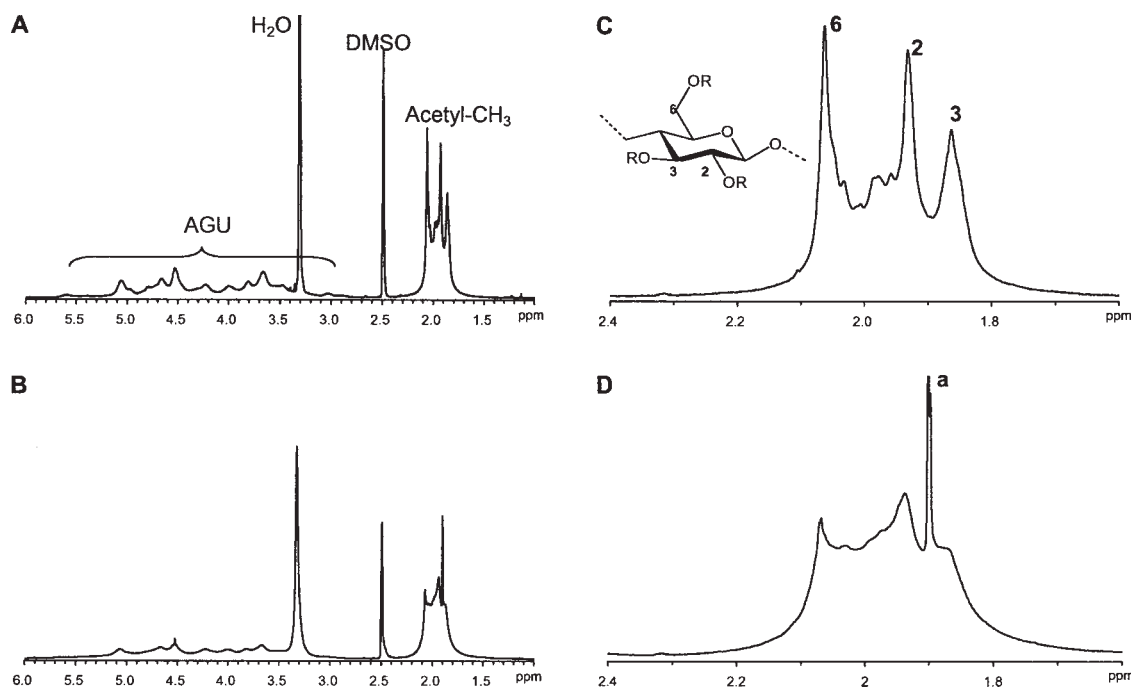
none. This suggests that benzophenone was homogeneously dispersed in the CA films, resulting in the uniform degradation described later.

### Change in molecular weight of CA

The degradative behavior was evaluated by the change in the molecular weights of the CA films, which were estimated by SEC using polystyrene standards. The changes in the number average molecular weights of the specimens during the photoirradiation are described in Figure 3. The molecular weights of the CA films containing benzophenone decreased with the photoirradiation time, while no significant change was observed in the film without benzophenone even after 28 days. Furthermore, higher concentration of benzophenone led to remarkable decrease in the number-average molecular weight. The number-average molecular weight of the CA film containing 160 mg/g of benzophenone decreased from  $\sim 50,000$  to less than 1000 within 7 days.

### $^1\text{H}$ NMR investigation

Figure 4 shows  $^1\text{H}$  NMR spectra of the CA film containing 160 mg/g of benzophenone before [Fig. 4(A,C)] and after [Fig. 4(B,D)] 28-day photoirradiation. The consecutive small peaks between 2.9 and 5.7 ppm, which are assigned to anhydroglucose units (AGU),<sup>10,11</sup> are visible before irradiation [Fig. 4(A)], while these peaks change into broader spectrum after irradiation [Fig. 4(B)]. This observation may suggest that carbon-carbon single bond cleavages occurred inside the six-membered rings as



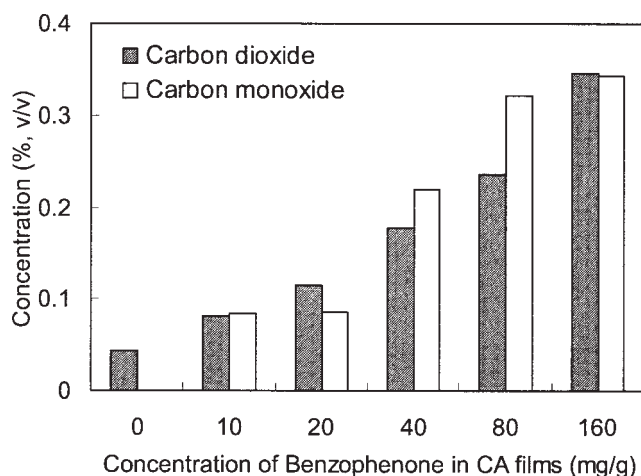
**Figure 4**  $^1\text{H}$  NMR spectra of the CA films containing 160 mg/g of benzophenone before (A, C) and after (B, D) photoirradiation for 28 days. AGU: anhydroglucose unit; DMSO: dimethylsulfoxide. a: new peak appeared after photoirradiation.

well as glycosidic scissions. Before the irradiation, the sample shows clear three peaks at 1.6–2.3 ppm, which correspond to the 2, 3, 6 positions for acetyl substitution in AGU of CA [Fig. 4(C)].<sup>10–12</sup> After the irradiation for 28 days, these three peaks reduced significantly [Fig. 4(D)] and one peak [a in Fig. 4(D)] appeared at 1.91 ppm, after photoirradiation. Since the increasing acetic acid with the concentration of benzophenone was detected from CA films after the photoirradiation, as described later (Fig. 6), the new peak at 1.91 ppm could be assigned to acetic acid. These data support strongly that the side chain cleavage (i.e., deacetylation) occurred as well as the main chain scission.

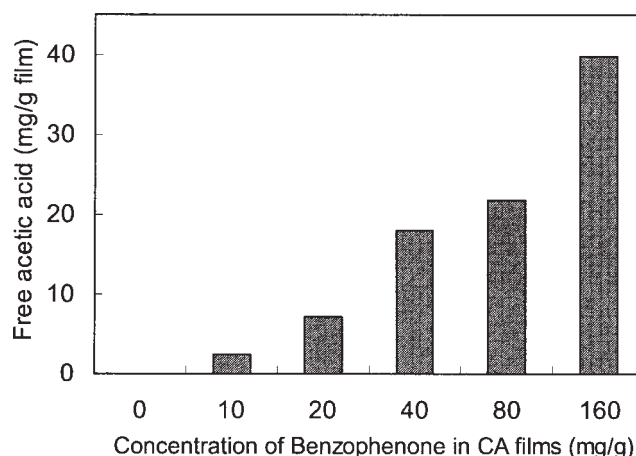
### Generation of degradation products from CA films

Some degradation products including CO<sub>2</sub>, CO, and acetic acid were generated by photodegradation of CA in a previous study.<sup>2</sup> In this current study, larger amounts of these three compounds were also detected in the vials along with increasing the concentration of benzophenone in the films (Figs. 5 and 6). Neither CO nor acetic acid, but only the ambient air level of CO<sub>2</sub>, was detected in the vial for the specimen without benzophenone, even after 28 days.

As described earlier, substantial decrease in the molecular weight and generation of CO<sub>2</sub>, CO, and acetic acid were observed by photoirradiation to the CA films containing benzophenone. On the other hand, any change in the molecular weight and any generation of the three compounds were not detected even after 28 days, when a vial containing a film with 160 mg/g of benzophenone was covered with aluminum foil to prevent light exposure to the film and placed in the xenon fadometer. These results indicated that both benzophenone and the photoirradiation are necessary for the degradation of the CA films observed in this study. While CO<sub>2</sub>, CO, and acetic acid were detected from the



**Figure 5** Generation of carbon dioxide (CO<sub>2</sub>) and carbon monoxide (CO) from the CA films containing benzophenone after photoirradiation for 28 days. The concentrations of CO<sub>2</sub> and CO in the glass vials are plotted.

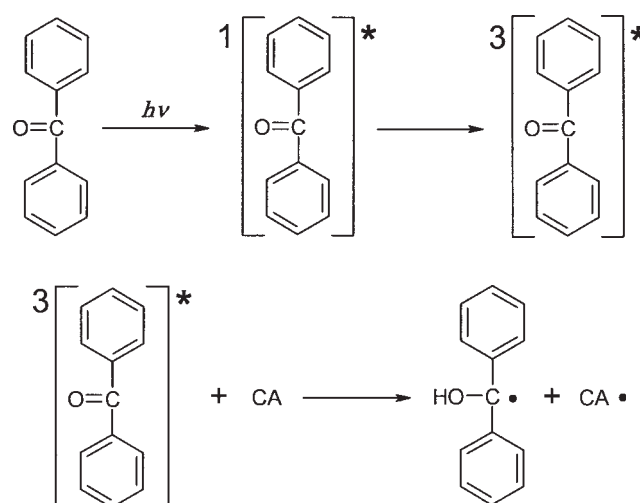


**Figure 6** Generation of acetic acid from the CA films containing benzophenone after photoirradiation for 28 days. The amounts of liberated acetic acid per initial film weight are plotted.

degraded films, other compounds might be generated. Hon observed the generation of several compounds including acetic acid, acetone, CO<sub>2</sub>, CO, methane, ethane, H<sub>2</sub>O, and H<sub>2</sub> by the irradiation of ultraviolet to CA fibers.<sup>2</sup> Since the irradiation spectrum is similar to those from the solar, CA can be degraded effectively under ambient environment in the presence of photosensitizers.

### Postulated mechanisms of the degradation

The absorption of ultraviolet under 380 nm increased by the presence of benzophenone (Fig. 2) and the light exposure to films led to the degradation of the CA molecules. A benzophenone molecule is generally considered to be raised to the triplet state via excited singlet state by light absorption and then abstract a hydrogen from a substrate, which leads to the oxidative degradation of the substrate.<sup>5,9,13–16</sup> Therefore it seems reasonable to suppose the following postulated mechanism of the degradation of CA with benzophenone.





CA-OOH  $\longrightarrow$  chain scission, generation of degradation products

CA has recently been drawing attention as a biodegradable polymer and it is well known that the lower degrees of substitution by acetyl group provide the higher biodegradability.<sup>17-22</sup> Yamashita and Endo reported that the presence of phosphoric acid as a catalyst for hydrolysis in CA films led to deacetylation of the CA molecules and increasing degradation of the films in soil.<sup>23</sup> The results in the current article indicate that the deacetylation of CA proceeds by photoirradiation, as mentioned earlier. Furthermore, Ishigaki et al. reported an increased enzymatic degradation of CA by irradiation of ultraviolet as well as a decrease in the molecular weight.<sup>24</sup> Therefore, the acceleration of photodegradation of CA may have some effectiveness in the acceleration of biodegradation.

### CONCLUSIONS

To study the effectiveness of photosensitizers to accelerate the degradation of CA under ambient environment, the degradative behavior of CA films containing benzophenone was evaluated under simulated solar exposure by means of a xenon fadometer. With increasing the concentration of benzophenone, decrease in the molecular weight of CA and increasing generation of CO<sub>2</sub>, CO, and acetic acid from the CA films were observed. These results suggest that benzophenone is an effective additive to accelerate the degradation of CA under ambient environment.

### References

- Jortner, J. *J Polym Sci* 1959, 37, 199.
- Hon, N.-S. *J Polym Sci Polym Chem Ed* 1977, 15, 725.
- Merlin, A.; Fouassier, J.-P. *Angew Makromol Chem* 1982, 108, 185.
- Hosono, K.; Kanazawa, A.; Mori, H.; Endo, T. *J Adhes Soc Jpn* 2006, 42, 350.
- Taylor, L. J.; Tobias, J. W. *J Appl Polym Sci* 1977, 21, 1273.
- Tsunooka, M. *Polym Appl (Jpn)* 1990, 39, 106.
- Tsunooka, M. *Chem Ind (Jpn)* 1990, 41, 751.
- Kubota, H.; Takahashi, K.; Ogiwara, Y. *Polym Degrad Stab* 1989, 24, 201.
- Merlin, A.; Fouassier, J.-P. *Angew Makromol Chem* 1980, 86, 109.
- Heinze, T.; Liebert, T. *Macromol Symp* 2004, 208, 167.
- Deus, C.; Friebolin, H.; Siefert, E. *Makromol Chem* 1991, 192, 75.
- Goodlett, V. W. J.; Dougherty, T.; Patton, H. W. *J Polym Sci Part A-1: Polym Chem* 1971, 9, 155.
- Torikai, A.; Takeuchi, T.; Fueki, K. *Polym Photochem* 1983, 3, 307.
- Lin, C. S.; Liu, W. L.; Chiu, Y. S.; Ho, S.-Y. *Polym Degrad Stab* 1992, 38, 125.
- Kaczmarek, H.; Kaminska, A.; Swiatek, M.; Sanyal, S. *Eur Polym J* 2000, 36, 1167.
- Millan, M. D.; Locklin, J.; Fulghum, T.; Baba, A.; Advincula, R. *C. Polymer* 2005, 46, 5556.
- Puls, J.; Altaner, C.; Saake, B. *Macromol Symp* 2004, 208, 239.
- Buchanan, C. M.; Gardner, R. M.; Komarek, R. J. *J Appl Polym Sci* 1993, 47, 1709.
- Komarek, R. J.; Gardner, R. M.; Buchanan, C. M.; Gedon, S. *J Appl Polym Sci* 1993, 50, 1739.
- Gu, J.-D.; Eberiel, D. T.; McCarthy, S. P.; Gross, R. A. *J Environ Polym Degrad* 1993, 1, 143.
- Gu, J.-D.; Eberiel, D. T.; McCarthy, S. P.; Gross, R. A. *J Environ Polym Degrad* 1993, 1, 281.
- Sakai, K.; Moriyoshi, K. *Kagaku Kogyo (Tokyo, Jpn)* 1997, 71, 490.
- Yamashita, Y.; Endo, T. *J Adhes Soc Jpn* 2004, 40, 368.
- Ishigaki, T.; Sugano, W.; Ike, M.; Taniguchi, H.; Goto, T.; Fujita, M. *Polym Degrad Stab* 2002, 78, 505.