Biodegradation Behavior of Acid-Containing Cellulose Acetate Film in Soil

Yoichiro Yamashita,[1] Takeshi Endo[2]

[1]Cigarette Materials R&D Division, Japan Tobacco, Incorporated, 3-2-34 Sakae-cho, Asaka, Saitama 351-0012, Japan
[2]Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

ABSTRACT: The biodegradation behavior of various cellulose acetate (CA; degree of substitution = 2.5) films that contain acids was examined by a laboratory soil burial test to clarify the effects of additives on the biodegradability of CA. The biodegradation rate of the CA films containing polyphosphoric acid, phosphoric acid, and *p*-toluenesulfonic acid increased compared to that of the nonadditive CA film. CA films containing mandelic acid and maleic acid showed a small tendency to increase. Conversely, CA films containing adipic acid did not affect the biodegradability of CA. A similar experiment was carried out with a sterilization system. The acid-containing CA film, which showed an accelerated biodegradation rate, was chemically deacetylated by contact with water in the environment and was consequently converted to a lower degree of acetyl group substitution matter that had higher biodegradability. An IR analysis suggested that this deacetylating ability of acids is correlated with the intensity of their interaction with the acetyl group of CA. In the biodegradation process, the contact efficiency of acids to CA was considerably lowered by the elution of internal acids with time. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 466–473, 2005

Key words: biodegradable; degradation; cellulose acetate; films; FTIR

INTRODUCTION

In recent years, the problem of solid waste disposal, such as compost, wastewater treatment plants, and landfill/litter in the natural environment, has reached a critical stage and is a matter of grave public concern. The plastics industry is currently engaged in the development of biodegradable materials, together with the recycling of general-purpose plastic, as countermeasures to aid the reduction of the environmental burden. Cellulose acetate (CA; see Fig. 1), which has a wide scope of applications such as textiles, moldings, and filters for cigarettes, is a biodegradable material, although its biodegradation rate is not as good as that of natural materials such as cellulose.[1–5] Therefore, the biodegradability of CA has to be further improved.

Extensive research on the biodegradability of CA has been conducted by several organizations.[1–5] The research shows that the biodegradation rate of CA depends on the degree of acetyl group substitution (DS) of CA. In other words, as the DS decreases, the biodegradation rate increases. The rate-determining step of its biodegradation rate is considered to be deacetylation.[4,6,7] In the biodegradation mechanism, deacetylation is accelerated by a hydrolase enzyme, which is supplied by microorganisms.[6–9] In contrast, it is conceivable that the acetyl group of CA can be "chemically" eliminated as acetic acid by acid or base catalysis without the participation of microorganisms.[10–14] It may also be that, under acidic or basic conditions, the CA composition as waste is easily changed into lower DS matter; and later, shifting to subsequent microbe metabolism would be conducive. This work was aimed at analyzing this hydrolysis. The results of the study on the influence of the hydrolysis behavior and biodegradation rate of CA in the presence of acids are reported.

EXPERIMENTAL

Preparation of CA film

The CA (DS = 2.5) was commercially available from Daicel Chemical Industries, Ltd. (Osaka, Japan). CA films were obtained from a 20% solution (w/v) of CA in acetone. The insoluble matter in the solution was removed beforehand by suction filtration. The films were cast by drawing a film on a glass plate using a 0.6-mm draw blade. After air-drying, the films were cut into circular pieces with a 5.0-cm diameter. The thickness of the films was approximately 0.1 mm after solvent removal.

Correspondence to: Y. Yamashita (yoichiro.yamashita@ims.jti.co.jp).
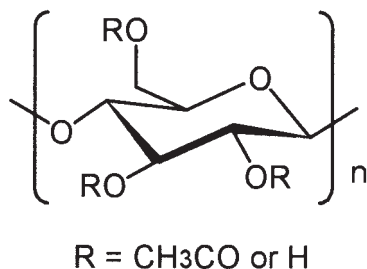
Figure 1 The molecular structure of CA.

When various compounds were added to a CA film, the indicated amounts of the corresponding chemical compounds were added to the solution of CA in acetone. All chemicals were of the highest commercially available purity. Thereafter, the films were prepared in the same way. Optical microscopy showed that all the acids used in this study were miscible with the CA.

Laboratory soil burial test

Soil was gathered from our company's premises. After removing pebbles and so forth with a sieve, it was used as the soil for the examination. Soil (10-cm thickness) was placed in 50-cm square trays. The water content of the soil was prepared to 60–70% of the maximum water-absorbing capacity (~50 wt %) of the soil. Then, the circular pieces of CA films (5-cm diameter) were buried in the soil and were left in a thermohygrostat at 30°C for a fixed period of time (see Fig. 2). During this period, the soil water content was adjusted daily to maintain a specified amount. The pieces, which were collected at predetermined dates, were extensively washed with distilled water and then dried at 60°C in a vacuum for 24 h before weighing. The percent weight loss was calculated from the weight difference before and after the examination.

Deterioration test under a pseudo soil environment

The examination was conducted using sea sand (20–35 mesh), and the same laboratory soil burial test method was used. The sea sand and the distilled water were sterilized beforehand to prevent microbial influence in the examination.

Acidic solution immersion test

An acidic solution was obtained from analytical grade p-toluenesulfonic acid monohydrate (Wako Pure Chemical Industries, Ltd., Osaka, Japan). The circular pieces of CA film were immersed in 100 mL of p-toluenesulfonic acid aqueous solution (~4 wt %, pH 5.6) and left at 22°C for a predetermined time (1–8 days). The pieces were collected at predetermined

dates and extensively washed with distilled water. Subsequently, they were dried at 60°C in a vacuum for 24 h before analysis.

Analytical methods

DS measurements of CA

The acetyl content (weight percent of combined acetic acid) was determined titrimetrically according to ASTM D 871-63. The DS was calculated with the following formula: $DS = 0.02701E/(1 - 0.007E)$, where E is the acetyl content.

IR

The IR spectra of the CA films containing additives were recorded on a Jasco FTIR 420 spectrometer (Tokyo) to determine the interaction between CA and the additives. Absorption bands at 1735–1750, 1215–1235, and 1030–1050 cm^{-1} are attributable to the carbonyl groups, acetyl ester bonds, and ether bonds within the polymer chain of CA, respectively.

^{1}H-NMR

The ^{1}H-NMR spectra were recorded on a Jeol (Tokyo) Lambda 500 spectrometer to determine the deacetylation of CA by acids. The CA films to which predetermined acids had been added were immersed in D_2O and left for 10 days at room temperature. The detection of free acetic acid in D_2O was determined by ^{1}H-NMR.

Scanning electron microscopy (SEM)

SEM analyses of the residual and unexposed films was performed on a Jeol JSM-5310 SEM instrument (To-
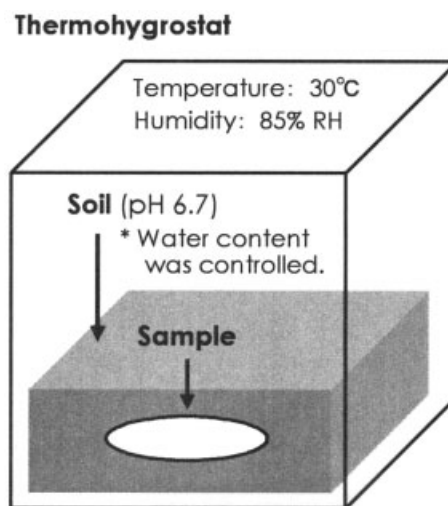
Figure 2 An illustration of a laboratory soil burial test.
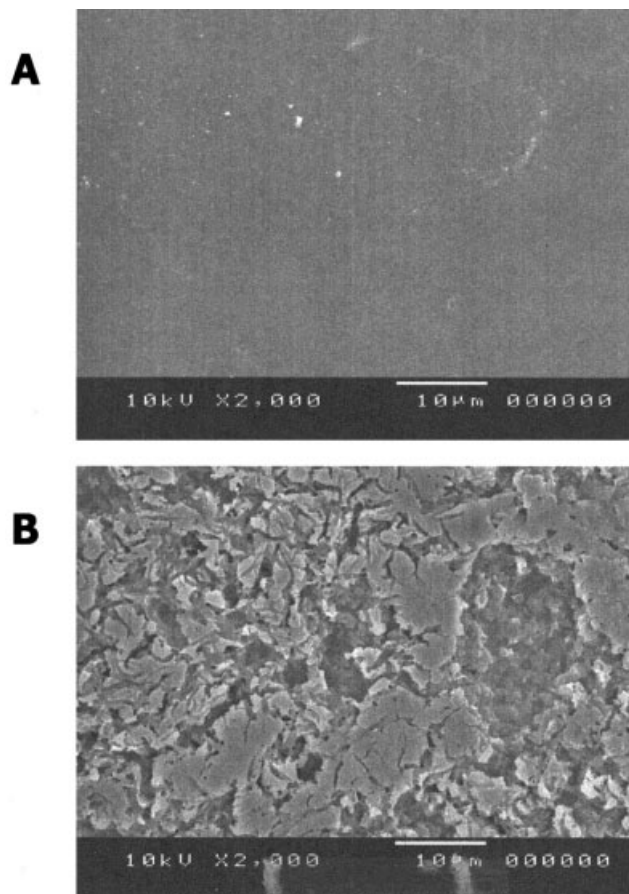
Figure 3 SEM photographs of (A) a control CA film and (B) a recovered CA film after a laboratory soil burial test for 29 days.

kyo). The films were sputter coated with a thin layer of gold to enhance conductivity for the SEM measurements.

RESULTS AND DISCUSSION

### Biodegradability of acid-containing CA films

The biodegradation behavior of acid-containing CA films was examined by the laboratory soil burial test to clarify the effects of internal acids that are known to cause chemical deterioration (hydrolysis) of CA[10–14] on the CA biodegradability.

Previous literature[1–5] shows that CA with a DS of 2.5 is essentially biodegradable. In order to consider the deterioration process, the film surface morphology on the buried films was examined by SEM. The SEM images of the buried films showed that they had surface erosion such as fissures and holes, which is postulated to be caused by biological attack (e.g., Fig. 3). Similar to previous studies, it was observed that the CA film with a DS of 2.5 biodegraded in our experimental system (Fig. 2). Figure 4 presents the changes in the weight of acid-containing CA films and the

nonadditive CA film as determined by the laboratory soil burial test. The weight loss of the nonadditive CA film increased slightly with the experimental time. By contrast, the weight loss of the acid-containing CA films was greater than that of the nonadditive CA film (Fig. 4). It is conceivable that the weight loss of acid-containing CA films in the early stage (i.e., 20-day burial) could be attributed to certain factors, such as the elution of acid, chemical deacetylation, and biodegradation of CA. This, in turn, made the verification of the biodegradation behavior more difficult. Each acid used in the experiment has high water solubility,[15] and the elution of acid to the periphery of the film is a factor that should not be ignored. The weight change of the CA film containing 25 wt % adipic acid under a pseudo (sterilized) soil environment is shown in Figure 5. In this experimental system, the behavior of the CA film is characterized by the behavior of the chemical (nonmicrobial) reaction, which occurs under the natural environment (left in the soil). The percent weight loss of the CA film reached approximately 20% within the first day and thereafter it was constant with respect to experimental time. If the adipic acid elutes to the periphery of the film completely, the weight loss is 20%. This experimental value was in good agreement with the theoretical value for the complete elution of the acid. That is, this phenomenon indicates the elution of an acid in this system. Undoubtedly, the same may be said of other acids. In fact, when each acid-containing CA film was immersed in water for 1 day, the IR spectrum of the recovered film had no absorption band, which indicated the presence of acid (e.g., Fig. 6). Because in most cases the elution of each acid took several days to complete, the weight loss
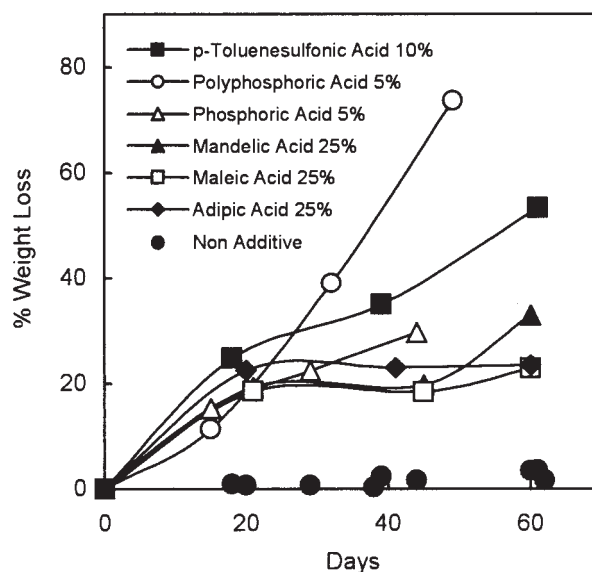
Figure 4 The changes in weight of CA films containing acids after a laboratory soil burial test.
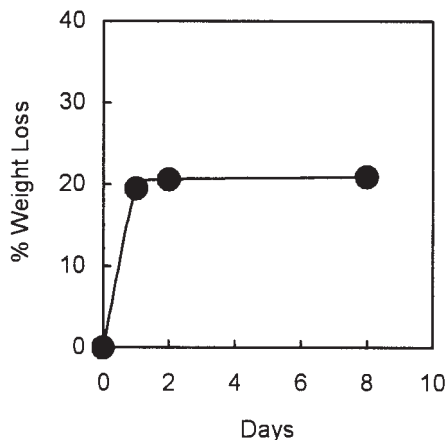
Figure 5 The changes in weight of a CA film containing 25 wt % adipic acid under a pseudo (sterilized) soil environment.
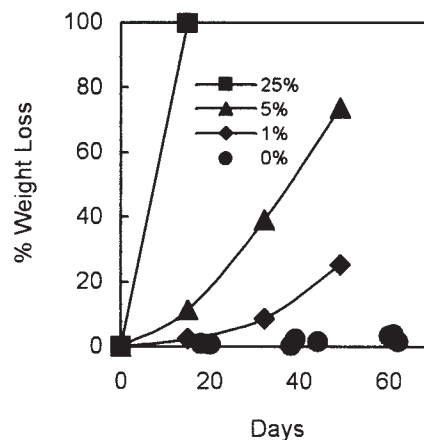
Figure 7 The changes in weight of CA films containing polyphosphoric acid of various concentrations after a laboratory soil burial test.

from day 20 onward can be regarded as being dependent on the biodegradation of CA films. In other words, a weight loss that is greater than the acid content directly indicates the biodegradation of CA. In this laboratory soil burial test, the experimental results vary with the soil conditions (especially microorganisms), even if the same soil is used. Specifically, the
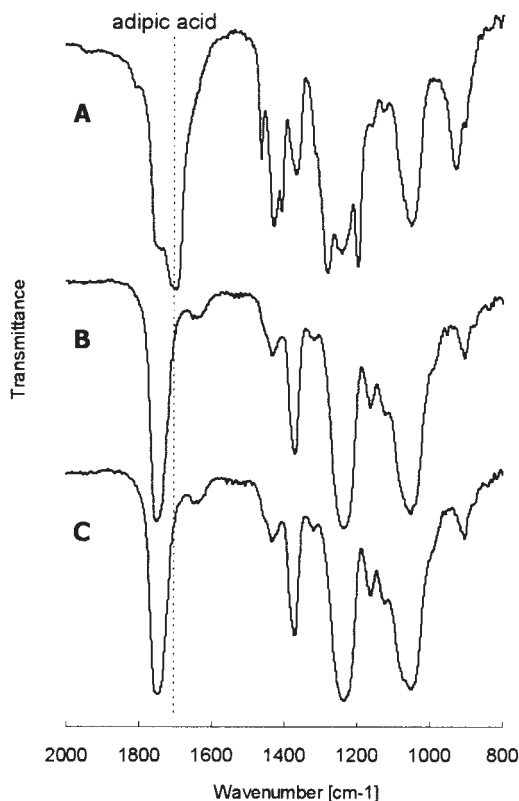

Figure 6 IR spectra of (A) a CA film containing adipic acid, (B) a CA film containing adipic acid immersed in water for 1 day, and (C) a nonadditive CA film.

acclimation period has a large variation (i.e., time lag of results). This point should be constantly kept in mind as we discuss the biodegradation rate [e.g., weight loss of DS 2.5 CA films after 60-day burial = 1.7–3.7%, weight loss of CA films containing 5 wt % phosphoric acid (as more biodegradable samples) after 45-day burial = 12.4–29.6%]. Our aim is to consider the effect of acids on the CA biodegradability. Even if the universality (reproducibility) of the kinetics remains to be proved, it is clear that a weight loss (minus the elution of acid) that exceeds that of the control CA suggests an improvement in the biodegradability of CA. (The universality of our results needs to be confirmed by further research on environmental factors such as microorganisms, soil properties, and water and temperature conditions.) When Figure 4 is seen from the above viewpoint, it is clear that the biodegradation rate of the CA films containing polyphosphoric acid, phosphoric acid, and p-toluenesulfonic acid increased compared to that of the nonadditive CA film. CA films containing mandelic acid and maleic acid showed a small tendency to increase. Conversely, the biodegradability of CA in CA films containing adipic acid was not affected. Thus, the acid-containing CA film showed that the biodegradability of the CA improved, and the degree of this tendency depended on the nature of the acid. Moreover, as shown in Figure 7, a correlation between the acid content and the biodegradation rate of CA was observed.

Biodegradation process

In order to consider the biodegradation process of the acid-containing CA films, the changes in the DS and weight were examined in the CA film containing 10 wt % p-toluenesulfonic acid via the laboratory soil burial test. These results, along with those of the nonadditive
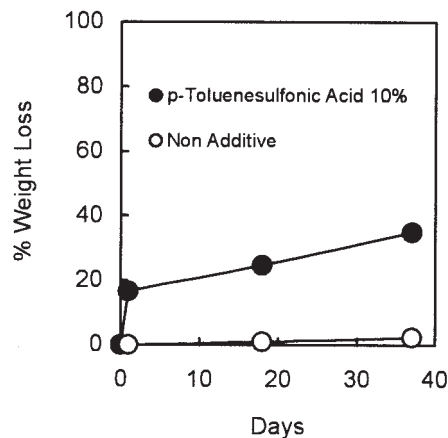
(A)
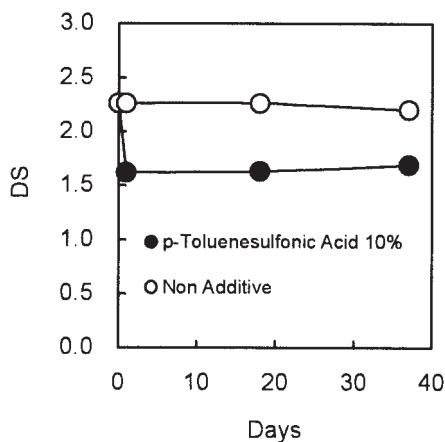
(B)

Figure 8 The changes in (A) weight and (B) DS of CA films containing 10 wt % *p*-toluenesulfonic acid after a laboratory soil burial test.

CA film, are shown in Figure 8. We observed that the DS of the CA film containing 10 wt % *p*-toluenesulfonic acid decreased to approximately 1.6 within the first day and it was constant with respect to experimental time. The percent weight loss after 1-day burial was approximately 17% and it clearly exceeded the *p*-toluenesulfonic acid content. If the *p*-toluenesulfonic acid elutes to the periphery of the film completely, 19% of the weight is lost including the reduction in the DS (i.e., elimination of acetyl groups) from 2.5 to 1.6. The experimental value was in good agreement with this theoretical value. From the first day onward, the percent weight loss of the CA film containing 10 wt % *p*-toluenesulfonic acid increased with time and reached approximately 35% after 37 days. This weight loss is considered to be dependent on the biodegradability of CA, which was characterized by a lower DS. It is well known that, as the DS decreases, the biodegradation rate increases.[1–5]

It is interesting that the DS of the CA film containing 10 wt % *p*-toluenesulfonic acid decreased within the
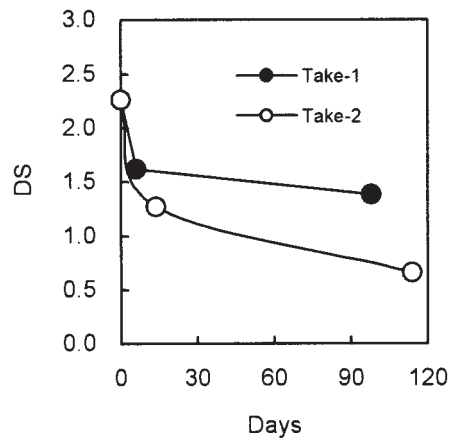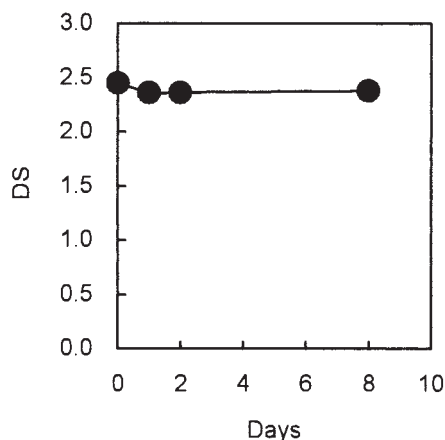

Figure 9 The changes in DS of a CA film containing 10 wt % *p*-toluenesulfonic acid under a pseudo (sterilized) soil environment.

first day, although the rate-determining step of its biodegradation rate may be considered to be the deacetylation step.[4,6,7] This reduction in the DS could not to be attributed to the deacetylation by "microorganisms." That is, it is satisfactory to consider this DS reduction as "chemical" deacetylation by *p*-toluenesulfonic acid. In order to verify this proposed process (i.e., chemical deacetylation), a similar experiment was carried out with a sterilization system (see Experimental section). As is evident from Figure 9, the CA film containing 10 wt % *p*-toluenesulfonic acid was capable of deacetylating without the participation of microorganisms. In order to consider the deacetylation behavior further, a water immersion test was carried out with a sterilization system, and the detection of free acetic acid in water was examined by ^{1}H-NMR to verify the chemical deacetylation of acid-containing CA films. These results are shown in Table I. Chemical deacetylation was observed in the case of CA films

TABLE I
Deacetylation of CA Films Containing Acids Immersed in D_2O after 10 Days

Acids	Content (wt %)	pK_a	Deacetylation[a]
Adipic	25	4.26	ND
Benzoic	25	4.00	ND
Lactic	25	3.66	ND
	50		D
Formic	25	3.55	ND
	50		ND
Mandelic	25	3.19	D
Phenylphosphonic	25	1.82	D
Maleic	25	1.75	D
Benzenesulfonic	25	0.04	D

[a] Deacetylation was determined by detection of free acetic acid (see Experimental section). ND, not detected, D, detected

Figure 10 The changes in DS of a CA film immersed in aqueous *p*-toluenesulfonic acid.

containing mandelic acid and maleic acid, which showed acceleration in the biodegradation rate of the CA film by the laboratory soil burial test. In contrast, in the case of CA films containing adipic acid, which did not show an acceleration in the biodegradation rate of CA film, chemical deacetylation was not observed. (Considering the above results, in the case of benzoic acid and formic acid in which the chemical deacetylation was not observed, acceleration in the biodegradation rate of CA film is not expected.)

The deacetylation behavior was examined on the nonadditive CA film in an acidic solution to consider the effect of external acid. That is, this experiment was carried out in order to verify the possibility of whether the CA deacetylates by the acid that eluted to the periphery of the film. The *p*-toluenesulfonic acid, equivalent to the amount of the addition to the CA film containing 10 wt % *p*-toluenesulfonic acid, was dissolved in 100 mL of water, assuming that the internal acid was diffused near the CA film and the nonadditive CA film was immersed in it. The change in the DS is shown in Figure 10. We observed that the CA film was hardly deacetylated by the external *p*-toluenesulfonic acid. This suggests that the contact efficiency of acid to CA is considerably lowered by the elution of internal acid.

From the above results, the biodegradation process of the acid-containing CA films can be proposed as follows. The CA is chemically deacetylated by contact with water as an external factor and the acids as additives and subsequently converted into a lower DS matter. This reaction is remarkable in the early stage because the contact efficiency of acid to CA is considerably lowered by the elution of internal acid. Because lower DS matter has higher biodegradability, the biodegradation rate of the acid-containing CA films increases compared to that of the nonadditive CA film.

Effect of acids on biodegradation process

As mentioned above, the addition of some acids to the CA film improved the biodegradability of the CA, because the CA is chemically deacetylated by acids. It has been established that there is a correlation between the reaction rate and the acid dissociation constant (K_a) for the acid catalytic reaction.[16,17] That is, as the acid dissociation constant in terms of pK_a decreases, the reaction rate increases. As shown in Table I, a correlation between the reactivity and pK_a of acids for the deacetylation of CA was observed. When the pK_a was less than ~3, the deacetylation of CA proceeded under this experimental condition (see Table I). Thus, it is observed that acids with a larger K_a have a greater influence on the acceleration of the biodegradation rate of CA. It is noteworthy that mandelic acid ($pK_a = 3.19$) showed the ability to deacetylate the CA but formic acid ($pK_a = 3.55$) did not. Acid catalysis can be roughly divided into two types.[16–18] One type is "specific acid catalysis," defined as the catalytic action in which only the strongest acid (i.e., the hydronium ion in this system as in Fig. 11 [I]) participates. Another type is "general acid catalysis," defined as the catalytic action in which the nondissociated acid as in Figure 11 [II] also participates. (Note: Because types [I] and [II] are mutually related and their contribution changes continuously, it is difficult to distinctly divide the acid catalysis into these types.) Considering these aspects, it seems reasonable to assume that the participation of type [II] enhances the ability to deacetylate the CA. Then, in order to consider the deacetylating ability of acids, the interaction behavior between various acids and CA was examined in the IR analyses. From the wavenumber shift of the absorption at 1748 and 1234 cm^{-1}, which is attributed to acetyl groups of the nonadditive CA film by adding acid, the existence of the interaction between the acid and CA was evaluated (Fig. 12, Table II). As shown in Table II, strong interactions with the acetyl groups of CA were observed in some acids (i.e., polyphosphoric acid, phosphoric acid, *p*-toluenesulfonic acid, mandelic acid, maleic acid, and benzenesulfonic acid). It seems that this interaction is due to the formation of a
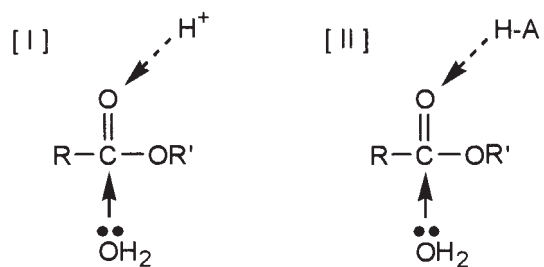
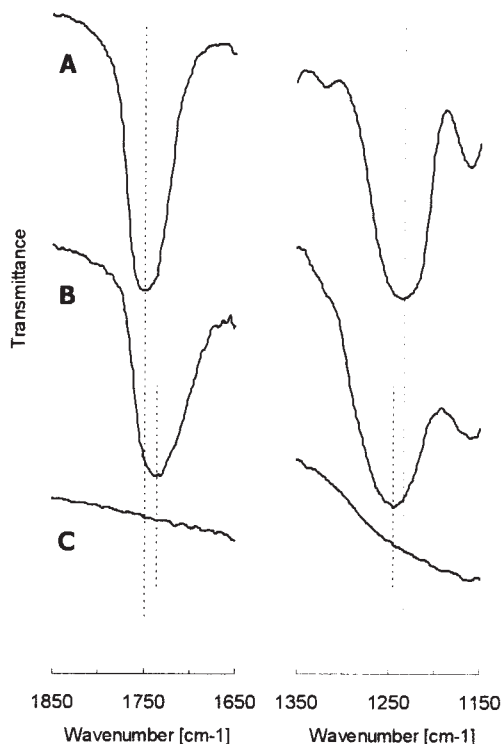**Figure 11** The reaction of acid catalysis for ester hydrolysis.

Figure 12 IR spectra of (A) a nonadditive CA film, (B) a CA film containing phosphoric acid, and (C) phosphoric acid.
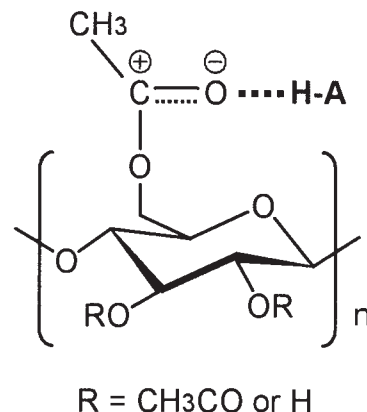

Figure 13 The interaction state between CA and acid.

sity of this interaction is a factor in the biodegradability of acid-containing CA films. In fact, acceleration in the biodegradation rate of CA was observed in the hydrogen bond between the hydroxyl group of the acid and the carbonyl group of CA, and the acetyl group is more activated to hydrolysis (Fig. 13). Accordingly, it is appropriate to consider that the inten-

TABLE II
Absorption Shift of Acetyl Group of CA Films Containing Acids in IR Spectra

Acids[a]	Absorption of acetyl group of CA[b] (cm^{-1})			Shift volume of X[c]
	[X]	[Y]	[X–Y]	
None	1748.2	1234.2	514.0	—
Polyphosphoric	1734.7	1234.2	500.5	−13.5
Phosphoric	1738.5	1244.8	493.7	−9.7
p-Toluenesulfonic	1736.6	—[d]	—[d]	−11.6
Mandelic	1733.7	1242.9	490.8	−14.5
Maleic	1736.6	—[d]	—[d]	−11.6
Lactic	1743.3	1234.2	509.1	−4.9
Formic	1745.3	1233.3	512.0	−2.9
Adipic	1745.3	1235.2	510.1	−2.9
Benzoic	1751.1	1235.2	515.9	2.9
Phenylphosphonic	1746.2	1239.0	507.2	−2.0
Benzenesulfonic	1733.7	1240.0	493.7	−14.5

[a] The acid content was an equimolecular amount against the acetyl groups of CA.
[b] Wavenumber.
[c] [Shift volume] = [X (film containing acid)] − [X (non-added film)]
[d] Because it overlapped with the absorption of acid, attribution was difficult.
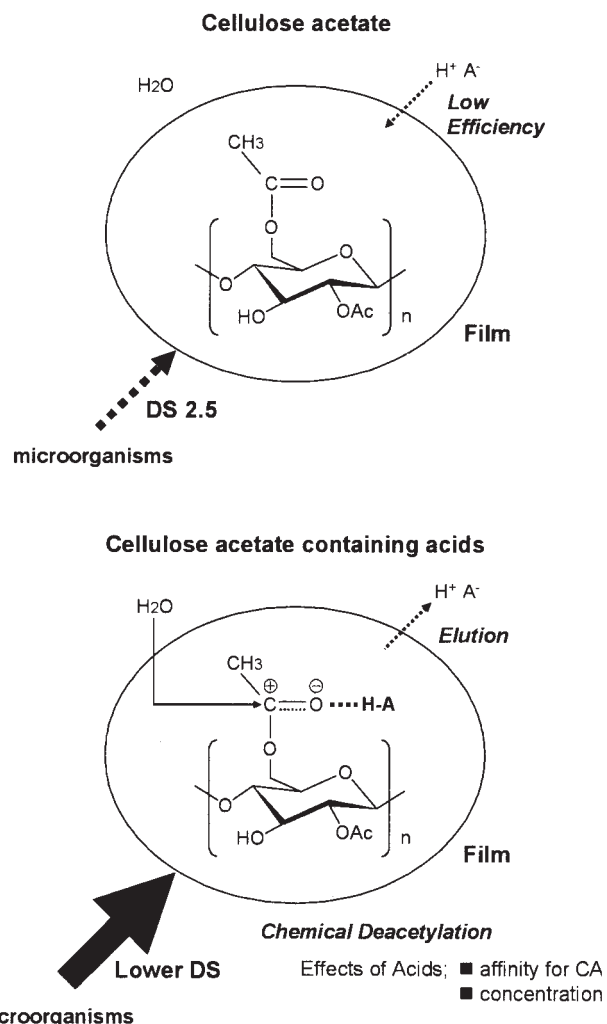

Figure 14 The proposed scheme of the biodegradation process for CA.

case of acids that showed this interaction (see Fig. 4). The effect of acids on the biodegradation process can be further explained by future research on the characteristics of acids that influence the intensity of the interaction between acids and CA.

To summarize our interpretation of the results, we propose the biodegradation process shown in Figure 14. CA is more activated to hydrolysis by the interaction with the internal acid. Consequently, CA is chemically deacetylated by contact with water in the environment and then converted into a lower DS matter. Because the lower DS CA has higher biodegradability, the biodegradation rate of acid-containing CA films increases compared to that of the nonadditive CA film. In addition, this chemical deacetylation by acids is remarkable in the early stage because the contact efficiency of acid to CA is considerably lowered by the elution of acids to the periphery of the film. Moreover, the deacetylating ability of acids is correlated to their concentration and the intensity of the interaction with the CA.

The results presented in this article indicate that, when lower DS matter, which is likely to be influenced by microbe metabolism, is forced into conversion using acids, the process of deacetylation by enzyme, which serves as a control of the biodegradation rate, can be supplemented in the biodegradation process of CA. The addition of acids to the CA is useful in improving the biodegradability of CA. However, the internal acids can elute to the environment by contact with water. As the internal acids elute, the acids do not work effectively for the deacetylation of CA. In addition, there are many points that are uncertain for the effect of leached acids on soil (i.e., contamination, pollution, etc.). Therefore, more research regarding the inhibition of acid elution and the effect of leached acids on soil is required.

References

1. Buchanan, C. M.; Gardner, R. M.; Komarek, R. J. J Appl Polym Sci 1993, 47, 1709.
2. Komarek, R. J.; Gardner, R. M.; Buchanan, C. M.; Gedon, S. J Appl Polym Sci 1993, 50, 1739.
3. Gu, J.-D.; Eberiel, D. T.; McCarthy, S. P.; Gross, R. A. J Environ Polym Degrad 1993, 1, 143.
4. Gu, J.-D.; Eberiel, D. T.; McCarthy, S. P.; Gross, R. A. J Environ Polym Degrad 1993, 1, 281.
5. Rivard, C. J.; Adney, W. S.; Himmel, M. E.; Mitchell, D. J.; Vinzant, T. B.; Grohmann, K.; Moens, L.; Chum, H. Appl Biochem Biotechnol 1992, 34, 725.
6. Sakai, K.; Yamauchi, T.; Nakasu, F.; Ohe, T. Biosci Biotechnol Biochem 1996, 60, 1617.
7. Moriyoshi, K.; Ohmoto, T.; Ohe, T.; Sakai, K. Biosci Biotechnol Biochem 2002, 66, 508.
8. Moriyoshi, K.; Ohmoto, T.; Ohe, T.; Sakai, K. Biosci Biotechnol Biochem 1999, 63, 1708.
9. Altaner, C.; Saake, B.; Puls, J. Cellulose 2001, 8, 259.
10. Yamashita, Y.; Endo, T. J Appl Polym Sci 2004, 91, 3354.
11. Reese, E. T. Ind Eng Chem 1957, 49, 89.
12. Miles, G. W. U.S. Pat. 835,350, 1906.
13. de Bordenave, J. F.; Bringardner, D. J. Textile World 1956, 106, 112.
14. Marusawa, H.; Uda, K. Sen-isokei Jyushi; Nikkan Kogyo Shimbun: Tokyo, 1970.
15. Budavari, S., Ed. The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals, 12th ed.; Merck & Co.: Trenton, NJ, 1996.
16. Leffler, J. E.; Grnwald, E. Rates and Equilibria of Organic Reactions; Wiley: New York, 1963.
17. Hammett, L. P. Physical Organic Chemistry, 2nd ed.; McGraw–Hill: New York, 1970.
18. Bronsted, J. N.; Wynne-Jones, W. F. K. Trans Faraday Soc 1929, 25, 59.