

# Deterioration Behavior of Cellulose Acetate Films in Acidic or Basic Aqueous Solutions

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**ABSTRACT:** The deterioration behavior of cellulose acetate (CA) films (degree of substitution = 2.5) was examined in hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions of various concentrations to determine acid and base catalytic effects in heterogeneous systems at room temperature. With concentrations of 0.5N HCl and 0.01N NaOH and higher, the physical properties of the films changed. The films, recovered after 1–10 days of immersion, were slightly opaque and rubbery from swelling in the solutions before drying. They became brittle and shrank when they dried. For HCl immersion, the weight change of a film depended on the HCl concentration and the immersion time. With 6.0N HCl, the film shape was broken, and a fine powder was deposited in the solution with a recovery of 53.8 wt %. The

infrared spectrum of this deposit indicated that it was completely deacetylated cellulose. For NaOH immersion, although the weight change depended on the NaOH concentration, the weight loss reached 40–50% within the first 24 h, and it was constant with respect to the immersion time and base concentration in 0.5N NaOH or NaOH of a higher concentration. The infrared and gel permeation chromatography analyses showed that this deterioration mainly depended on the deacetylation of CA. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3354–3361, 2004

**Key words:** degradation; films; FT-IR; structure-property relations

## INTRODUCTION

Cellulose acetate (CA), which is made from wood pulp through the acetylation of cellulose, has been used in materials such as textiles, moldings, and filters for cigarettes. The physical properties of substituted cellulose derivatives (e.g., cellulose esters, ethers, and nitrates) have been investigated in detail. Cellulose chemistry has recognized the fundamental importance of the relationship between the observed physical properties of cellulose derivatives and the type of substituent, the degree of substitution (DS), and, especially in the range of lower DS values, the substituent distribution along the length of the cellulose chain.<sup>1–4</sup> In the manufacturing industry, the substituent factor is an essential problem with respect to the properties and manufacturing processes of factory products. The solubility and thermoplasticity of cellulose derivatives depend on DS, and they are influential in the manufacturing processes.<sup>5–7</sup> Biodegradability, which has recently attracted wide interest, also depends on DS. For CA, when DS is lower, the biodegradation rate increases.<sup>8–13</sup> Therefore, controlling

DS is very important for the functional design of products.

CA has ester bonds and glycosidic linkages in its structure, and it is conceivable that these bonds of CA react to hydrolysis by acid and base catalysis. In products manufactured from CA, if hydrolysis occurs during their use, it causes a change in the quality (i.e., deterioration) and is not desirable. In other words, hydrolysis (i.e., deacetylation) reduces DS, changes the physical properties, and emits an odor through the formation of acetic acid. It is well known that CA can be hydrolyzed by acid or base catalysis in a homogeneous system or at high temperatures.<sup>13,14</sup> For the deterioration of CA products, it is generally said that the CA composition has resistance to organic acid and has almost none to strong acids and bases [e.g., concentrated sulfuric acid, hydrochloric acid (HCl), and sodium hydroxide (NaOH)].<sup>15,16</sup> Furthermore, the hydrolysis behavior of cellulose, which is formed through the deacetylation of CA, has been actively investigated.<sup>17</sup> However, there is limited information available on the hydrolysis potential of CA under mild conditions (i.e., at room temperature) for a consideration of the deterioration of CA products through hydrolysis.

The purpose of this study was to improve our understanding of acid and base catalytic effects on CA hydrolysis in heterogeneous systems at room temperature. This article describes our initial results concern-

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ing the hydrolysis behavior of CA films in acidic and basic solutions of various concentrations.

## EXPERIMENTAL

### Preparation of the CA films

CA (DS = 2.5) was acquired from Daicel Chemical Industries, Ltd. (Osaka, Japan). The CA films were obtained from a 20% solution (w/v) of CA in acetone. The insoluble part of the solution was removed beforehand by suction filtration. The films were cast by being drawn on glass plates with a 0.6-mm draw blade. After being air-dried, the films were cut into circular pieces 5.0 cm in diameter and were dried at 60°C *in vacuo* for 24 h before being weighed. The thickness of the films was approximately 0.1 mm after the removal of the solvent.

### Acidic–basic solution immersion test

An acidic or basic solution was obtained from an HCl solution or an NaOH solution of standardized volumetric analysis grade (Wako Pure Chemical Industries, Ltd., Osaka, Japan). The circular pieces of CA films were immersed in 300 mL of an HCl or NaOH solution that was prepared to a predetermined normality ( $10^{-3}$ –6N), and they were left at 22°C for a determined time (1–10 days). The pieces, collected at predetermined dates, were washed extensively with distilled water and dried at 60°C *in vacuo* for 24 h before they were weighed. The weight-loss percentage was calculated from the difference in the weights before and after examination.

### Analytical methods

DS measurements of CA

The acetyl content (the weight percentage of combined acetic acid) was sought titrimetrically according to

ASTM D 871-63. DS was calculated with the following formula:  $DS = 0.02701E/(1 - 0.007E)$ , where  $E$  is the acetyl content.

Molecular weight measurements of CA

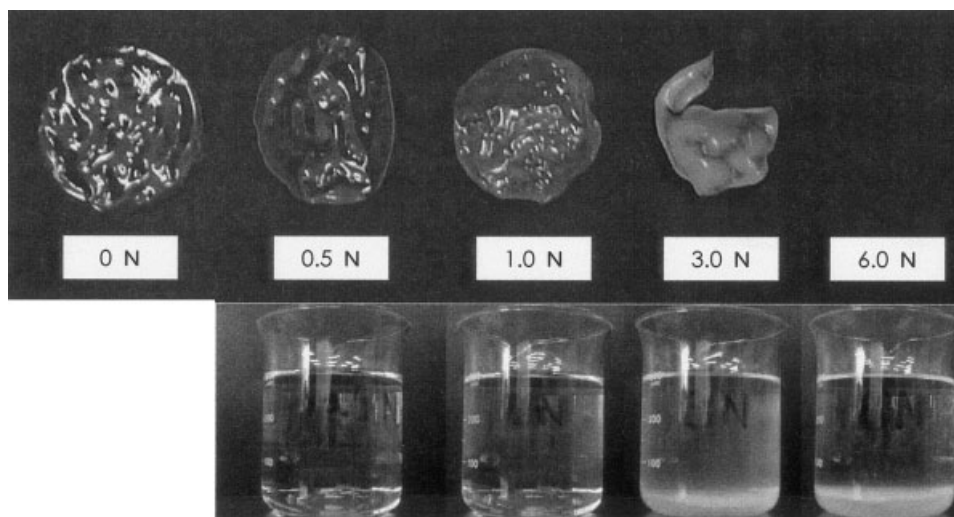
The molecular weights of CA films before and after immersion testing were measured by gel permeation chromatography (GPC) on a Tosoh HLC-8020 chromatographic system consisting of a liquid chromatograph, a refractive-index detector, and a Tosoh SC-8010 system controller. Three Tosoh TSKgel columns (7.8-mm inside diameter  $\times$  300 mm/column; G2000HXL, G3000HXL, and G4000HXL) were placed in series and operated at a flow rate of 1.0 mL/min. The sample concentration was 10 mg/mL, and the injection volume was 50  $\mu$ L. The analysis was performed with dimethylformamide (DMF; Wako Pure Chemical Industries) containing 0.1% (w/v) LiBr as the eluent. The molecular weights were calculated with respect to polystyrene standards without further corrections.

Infrared (IR) spectroscopy

The IR spectra of residual and unexposed samples were recorded on a Jasco FTIR 420 spectrometer to determine the elimination of acetyl groups of CA. Absorption bands at 1735–1750, 1215–1235, and 1030–1050  $\text{cm}^{-1}$  were attributable to carbonyl groups, acetyl ester bonds, and ether bonds, respectively, within the polymer chain.

Scanning electron microscopy (SEM)

SEM of residual and unexposed films was performed without the coating of the films or any other surface treatment with a JEOL JSM-5310 SEM instrument.



**Figure 1** External appearance of CA films immersed in HCl solutions of various concentrations for 10 days.

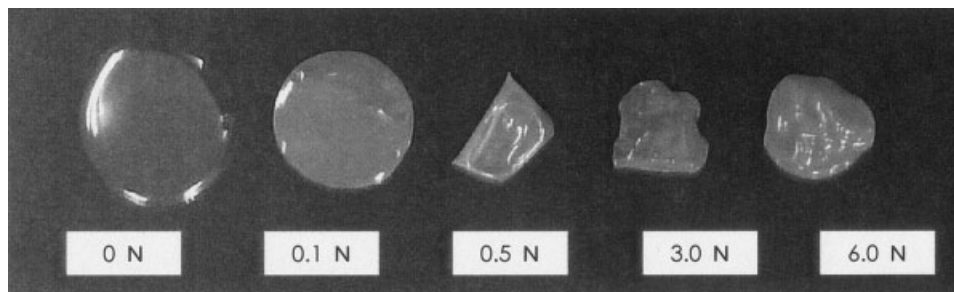


Figure 2 External appearance of CA films immersed in NaOH solutions of various concentrations for 10 days.

## RESULTS AND DISCUSSION

### Deterioration behavior of CA films immersed in HCl and NaOH solutions

The deterioration behavior of CA films ( $DS = 2.5$ ) in HCl solutions of various concentrations was examined to determine the acid catalytic effect in a heterogeneous system at room temperature. The external appearance of the CA films immersed in 0.5, 1.0, 3.0, or 6.0N HCl for 10 days is shown in Figure 1 along with the solution. As shown in Figure 1, the CA film deteriorated with the immersion of the HCl solution. In the case of 6.0N HCl, the film shape was broken completely (i.e., it disappeared; there was no fragment of the broken film), and a fine white powder was deposited in the solution. As reported previously,<sup>16</sup> the CA composition had no resistance to a strong acid at room temperature. In 3.0N HCl or HCl of a lower concentration, the recovered films showed changes in the physical properties. Before drying, a film recovered after a 10-day immersion in 3.0N HCl was slightly

opaque (white), and its rubbery state from swelling in the solution indicated the hydrophilization of the film (the control film was transparent and did not swell in neutral water). It became brittle and shrank when it dried. This tendency gradually became unremarkable as the HCl concentration was reduced (the effect of the HCl concentration on deterioration is discussed in detail in a later section).

A similar immersion test was carried out in an NaOH solution as a basic solution for comparison with the deterioration behavior in an acidic solution. The external appearance of CA films immersed in 0.1, 0.5, 3.0, or 6.0N NaOH for 10 days is shown in Figure 2. At all of these NaOH concentrations, no deposit, such as the fine white powder obtained by immersion in 3.0 and 6.0N HCl solutions, was observed. The CA films were recovered with their initial shape, but they showed changes in their physical properties. The films recovered after 1–10-day immersions were slightly opaque (white) and rubbery from swelling in the so-

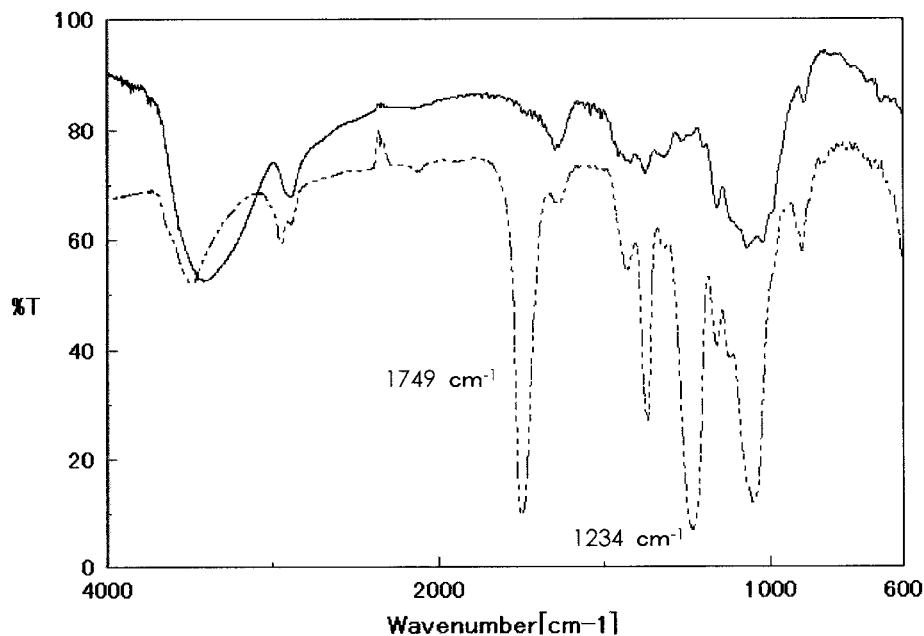
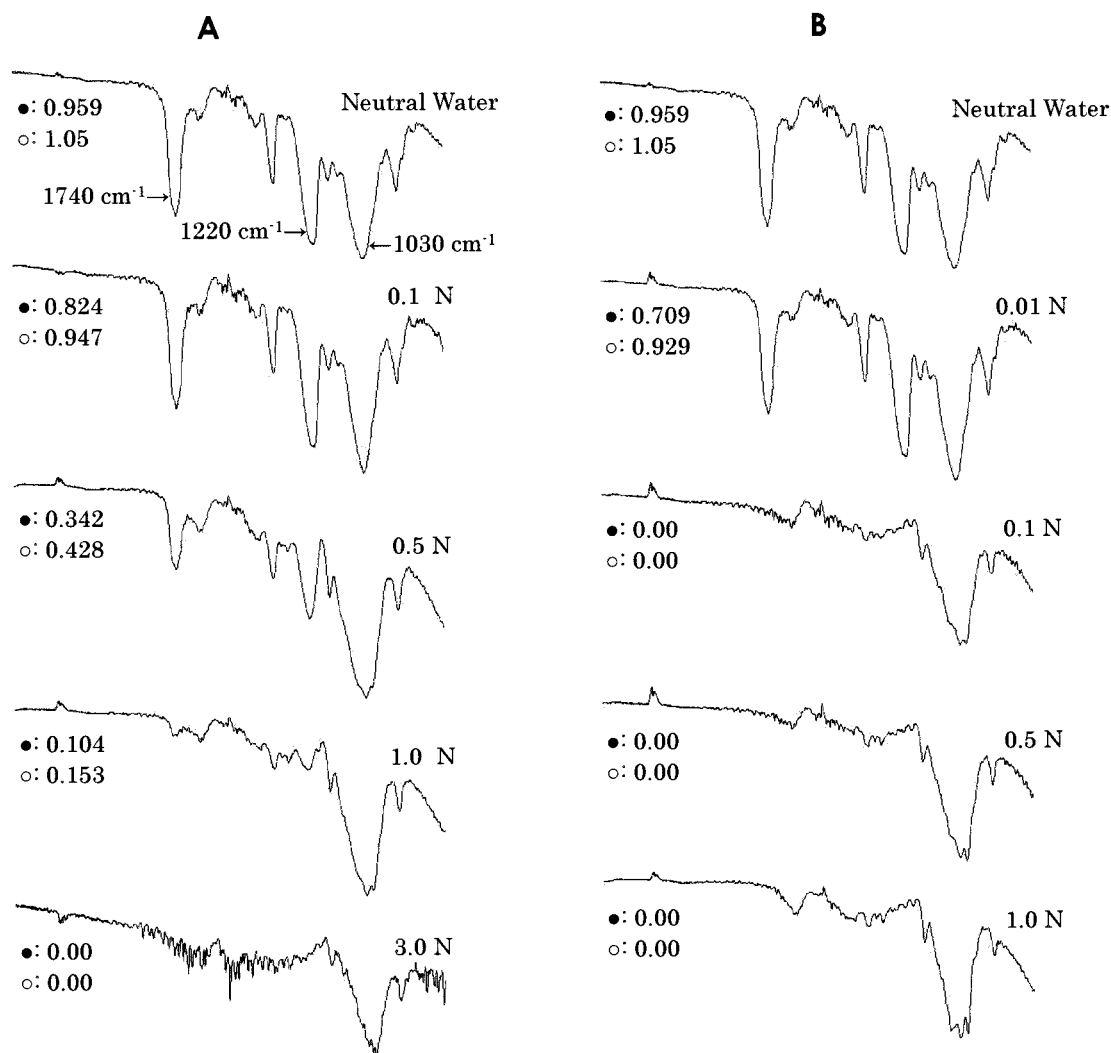


Figure 3 IR spectra of (—) a fine white powder collected from a 6.0N HCl solution and (---) a control CA film.



**Figure 4** ATR-IR spectra of CA films immersed in (A) HCl and (B) NaOH solutions of various concentrations for 10 days along with absorbance ratios of (●)  $A_{1740 \text{ cm}^{-1}}/A_{1030 \text{ cm}^{-1}}$  and (○)  $A_{1220 \text{ cm}^{-1}}/A_{1030 \text{ cm}^{-1}}$ .

lution before they were dried. They became and shrank when they dried; this was similar to the case of HCl immersion.

### Deterioration process

#### Hydrolysis behavior

In the case of 6.0N HCl, the film shape was broken completely, and a fine white powder was deposited in the solution. The identification of this deposit was carried out to determine the deterioration process. The IR spectra of this deposit (i.e., the fine white powder) and the control CA film are shown in Figure 3. For the fine white powder, the absorbances at 1749 and 1234  $\text{cm}^{-1}$ , attributed to acetyl groups, disappeared completely. These IR spectra clearly show that the fine white powder that deposited in the solution was formed from the CA film by deacetylation. The recovery of the fine white powder was 53.8 wt % of the initial film. If CA (DS = 2.5) deacetylated completely,

a weight of 39.3% was lost by the elimination of acetic acid. This experimental recovery agreed well with the theoretical value obtained by deacetylation. CA has

**TABLE I**  
Changes in the Weight and Molecular Weight of CA Films (DS = 2.5) Immersed in HCl Solutions of Various Concentrations After 1 Day

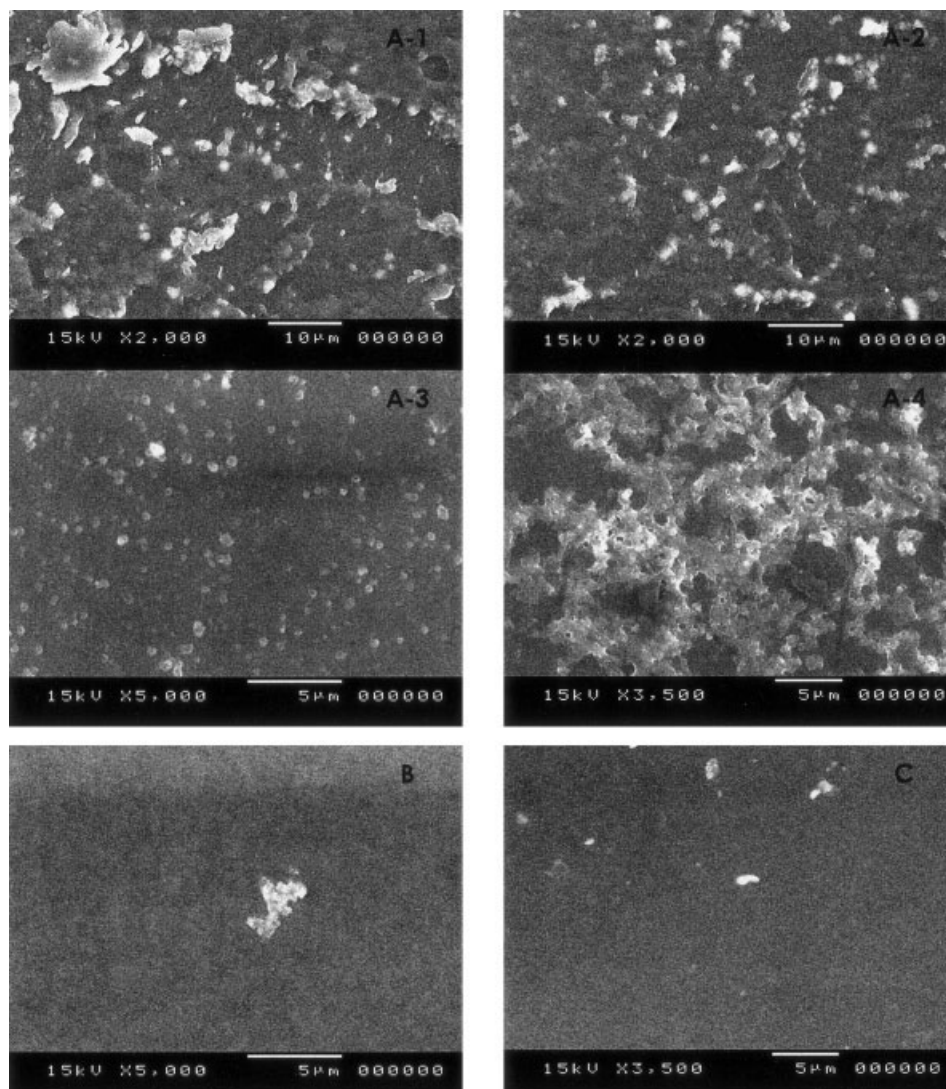
Condition	Weight loss (%)	$M_n$ ( $10^5$ ) <sup>a</sup>	$M_w/M_n$ <sup>a</sup>
Control <sup>b</sup>	—	1.40	2.60
1.0N HCl	8.0	1.30	2.64
3.0N HCl	12.5	1.20	2.63
6.0N HCl	92.0 (40.0) <sup>c</sup>	— <sup>d</sup>	— <sup>d</sup>

<sup>a</sup> Determined by GPC measurements (see the Experimental section).

<sup>b</sup> Not immersed.

<sup>c</sup> The fragments eliminated from the CA film, such as a fine white powder deposited in the solution, are included and are not included in the weight loss.

<sup>d</sup> Measurement was impossible because the recovered film was insoluble in DMF.



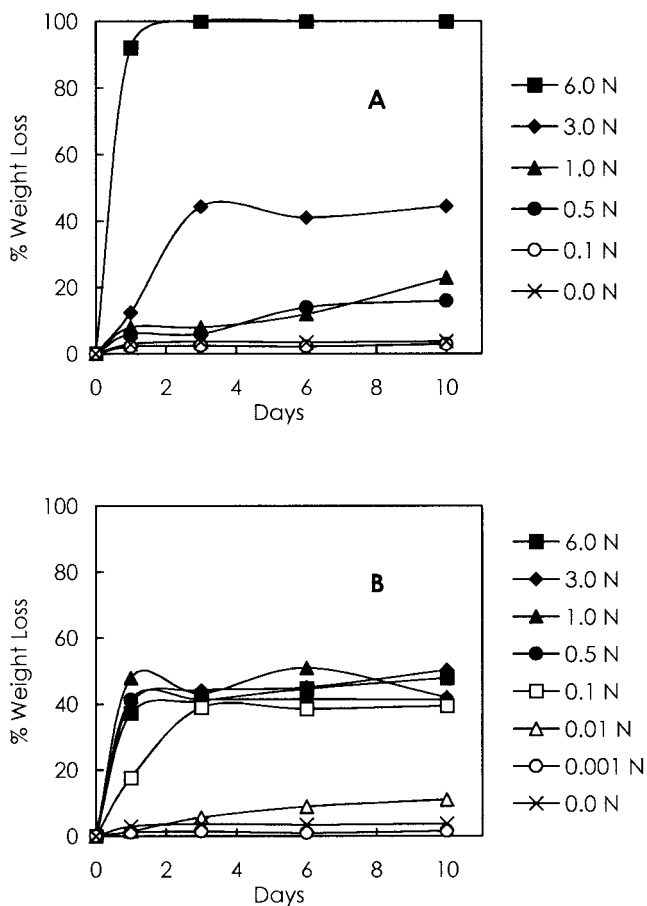
**Figure 5** SEM photographs of films immersed in (A) 3.0N HCl, (B), 3.0N NaOH, and (C) neutral water for 10 days.

ester bonds and glycosidic linkages in its structure, and it is conceivable that these bonds can react to hydrolysis by acid catalysis. These results indicate that the CA film immersed in a 6.0N HCl solution was hydrolyzed by acid catalysis, and this hydrolysis occurred mainly at acetyl groups (although it seems that there was a small amount of soluble matter formed by depolymerization and/or deacetylation of CA in solution indicated by the 6.9 wt % loss of experimental recovery in comparison with the theoretical value for the solid state, the identification of the soluble matter was not carried out).

Further IR analyses were carried out on the recovered films immersed in HCl and NaOH solutions of various concentrations to determine the effects on DS. With this technique, we can estimate quantitatively DS of CA by measuring absorbances at 1740/1220 and 1030  $\text{cm}^{-1}$  of the films and comparing the calculated ratios of the absorbances ( $A_{1740/1220 \text{ cm}^{-1}}/A_{1030 \text{ cm}^{-1}}$ ) against known values correlated with measured acetyl

contents.<sup>18,19</sup> In these analyses, attenuated total reflection (ATR)-IR spectroscopy was used to measure the acetyl contents on the film surface. The ATR-IR spectra of the recovered films are shown in Figure 4 along with the calculated ratios of the absorbances. The absorbance of the acetyl groups clearly decreased with HCl and NaOH immersion as the HCl and NaOH concentration increased. These results suggest that the CA composition is capable of deacetylation by immersion in acidic and basic solutions at room temperature.

To consider the hydrolysis behavior further, we examined the molecular weights of the recovered films by GPC. The changes in the molecular weight of the recovered films in HCl solutions of various concentrations are shown in Table I. The recovered films had almost the same molecular weight distribution [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ )] as that of the control. Moreover, low-molecular-weight fragments in the recovered films were not detected by GPC analyses. The



**Figure 6** Changes in the weights of CA films (DS = 2.5) immersed in (A) HCl and (B) NaOH solutions of various concentrations.

GPC results indicated that there was no measurable main-chain cleavage. Therefore, it seems that the glycosidic linkages of CA have good stability to hydrolysis. In other words, the hydrolysis of CA films immersed in acidic and basic solutions occurs mainly at acetyl groups.

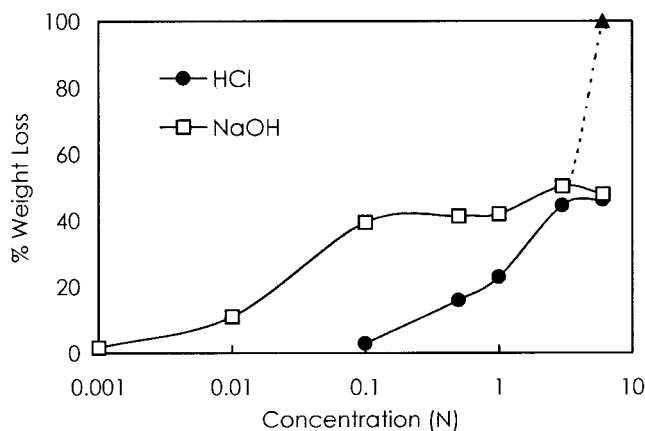
As mentioned previously, the immersed films showed changes in their physical properties. In HCl and NaOH solutions, the immersed films were slightly opaque, and the rubbery state from swelling in the solutions indicated the hydrophilization of the films. They became brittle and shrank when they dried. This phenomenon is explained by the characteristics of the cellulose structure formed by the deacetylation of CA.<sup>17,20–23</sup>

#### Disintegration process

In the case of HCl solutions, the film shape was broken, and a fine white powder was deposited in the solutions as the HCl concentration increased. To consider the deterioration process further, we examined the film surface morphology of the immersed films by SEM. SEM photographs of films immersed in 3.0N

HCl, 3.0N NaOH, and neutral water for 10 days are shown in Figure 5. The SEM photograph of the film immersed in neutral water [Fig. 5(C)] shows that it had no surface erosion, such as traces of exfoliation and fissures caused by an external force. In the case of NaOH immersion, the SEM photograph [Fig. 5(B)] shows that the film had no surface erosion, just like the film immersed in neutral water. In contrast, in the case of HCl immersion, a large change in the surface morphology can be observed. Figure 5(A) shows that the film was eroded extensively, and fine fragments formed on its surface. It was difficult to attribute this surface erosion to disintegration by an external force. Therefore, it is satisfactory to consider the surface erosion of CA films a chemical phenomenon.

In the case of HCl solutions, it seems possible that the disintegration process, that is, the deposition process of a fine white powder, involves the elution (i.e., solubilization in water) of CA molecules deacetylated by acid catalysis. Generally, for cellulose derivatives, the water solubility changes with the type and number of the substituent. Cellulose, which is insoluble in water because of the intermolecular hydrogen bonds of hydroxyl groups, becomes soluble in water through the moderate substitution of hydroxyl groups. It is known that CA (DS = 0.6–0.8) is soluble in water.<sup>5–7</sup> Therefore, it is likely that CA molecules elute into water once this critical degree of deacetylation is reached. Then, the CA molecules that have eluted into water are deposited as a fine white powder by further deacetylation. A recovered film immersed in NaOH, which had deacetylated completely, showed no change in an HCl solution. This indicates that the disintegration process of the film depended on the deacetylation and supports this hypothesis. In contrast, in the case of an NaOH solution, no surface

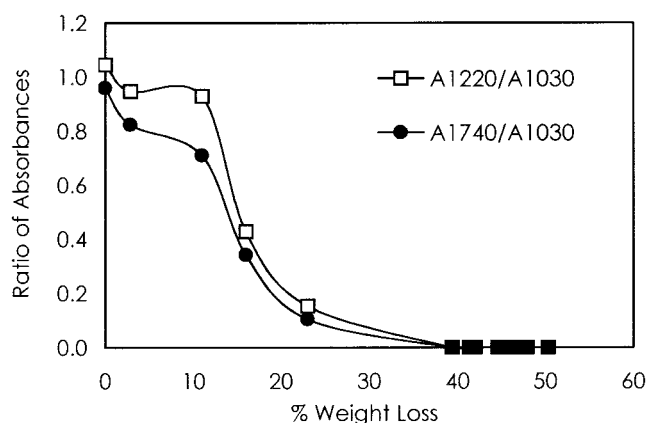


**Figure 7** Relationship between the concentration of HCl or NaOH and the weight loss of CA films (DS = 2.5) after 10 days of immersion. For 6.0N HCl immersion, the film shape was broken completely, and a fine white powder was deposited in the solution. These deposits (▲) were included and (●) were not included in the weight loss.

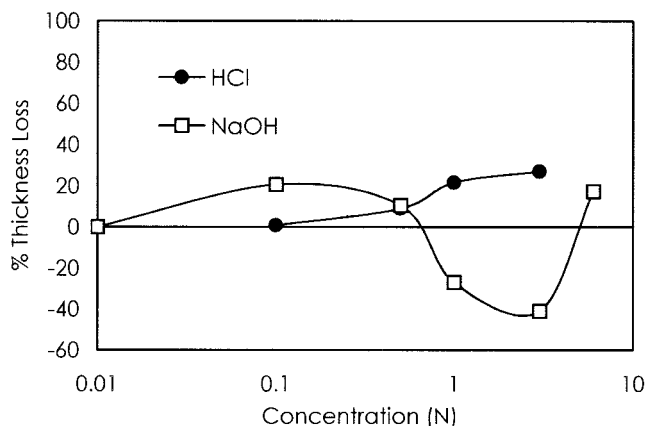
erosion and no deposits, such as the fine white powder obtained by HCl immersion, were observed, although the CA film deacetylated completely. It is known that cellulose becomes alkali cellulose swollen with water (i.e., insoluble matter in water) through an NaOH treatment.<sup>17,20</sup> It seems that CA deacetylated by NaOH becomes alkali cellulose, which is insoluble in water, so that the CA molecules (DS = 0.6–0.8), which are soluble in water, are not able to eliminate from the film in this system. The reactivity over deacetylation is different in HCl and NaOH. Our results show that the reaction rate of deacetylation by NaOH is relatively fast compared to the rate by HCl (see Figs. 6 and 7; we discuss this in detail later). It seems that the difference in the reactivity over deacetylation between HCl and NaOH also depends on this phenomenon. This hypothesis is explained more by further research regarding the reactive sites of deacetylation in consideration of other phenomena such as the permeation and diffusion of acid and base catalysts inside a film, the substituent distribution along the length of the cellulose chain, and, in the case of NaOH, the characteristic of alkali cellulose being required.

#### Effect of the HCl and NaOH concentrations on deterioration

Weight changes in CA films immersed in HCl and NaOH solutions are shown in Figure 6 with respect to time and in Figure 7 with respect to concentration. CA (DS = 2.5) is insoluble in water, and this experimental system is heterogeneous at the start of the immersion test. Therefore, the weight changes in the CA films indicate acid and base catalysis due to the extent of the dissolution of free acetic acid formed by deacetylation and/or low-molecular-weight matter formed by the main chain being cut off.



**Figure 8** Relationship between the absorbance ratios of  $A_{1740\text{ cm}^{-1}}/A_{1030\text{ cm}^{-1}}$  and  $A_{1220\text{ cm}^{-1}}/A_{1030\text{ cm}^{-1}}$ , which indicates the acetyl contents, and weight loss of CA films (DS = 2.5) immersed in HCl and NaOH solutions of various concentrations for 10 days. The absorbance ratio of a control film is plotted at the point of 0% weight loss.



**Figure 9** Relationship between the concentration of HCl or NaOH and the thickness loss of CA films (DS = 2.5) after 10 days of immersion.

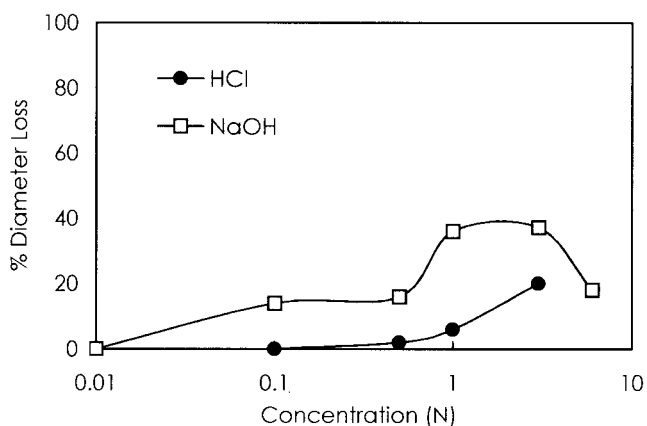
In the case of HCl solutions, the weight changes depended on the HCl concentration. The weight loss increased as the immersion time became longer, and the rate of weight loss gradually slowed as the HCl concentration was reduced. In 6.0N HCl, the weight loss increased to approximately 90% after 24 h and finally reached 100% (the fragments eliminated from CA films, such as the fine white powder deposited in the solution, are included in the weight change). In 0.5N or 1.0N HCl, the weight loss remained 15–25% even after 10 days, and this showed that the deterioration was advancing slowly. However, the films showed no change in weight in 0.1N HCl or HCl of a lower concentration. These observations indicate that the CA composition is resistant to acidic conditions of 0.1N HCl or less at room temperature.

In the case of NaOH solutions, the weight change also depended on the NaOH concentration. In  $10^{-3}$ N NaOH or NaOH of a lower concentration, the films showed no change in weight; that is, the CA composition is resistant to these base concentrations at room temperature. In 0.01N NaOH, the weight loss increased slightly with time and reached approximately 10% after 10 days. However, the weight loss reached 40–50% within the first 24 h, and then it was constant with respect to the immersion time and NaOH concentration in 0.5N NaOH or NaOH of a greater concentration. These experimental results of 40–50% loss agreed well with the theoretical value of 39.3 wt % loss obtained by deacetylation (it seems that a small amount of soluble matter formed by depolymerization and/or deacetylation of CA caused the difference in the recovery for the solid state between the experimental and theoretical values). This suggests that the weight loss of the CA composition is under the control of deacetylation. As previously stated, in the case of HCl solutions, there was good agreement with the theoretical value if the fragments eliminated from the CA film, such as the fine white powder, were not

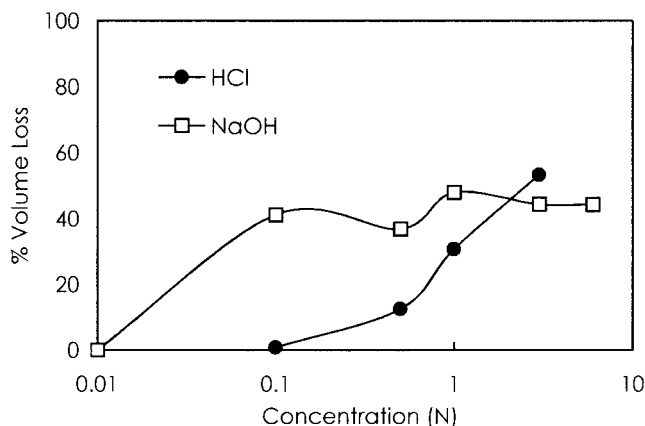
included in the weight loss, and this suggests similarly that the weight loss of the CA composition is under the control of deacetylation.

The monitoring of the deacetylation of CA was carried out by the IR analyses of immersed films (see Fig. 4). The relationship between the absorbances ratios of  $A_{1740\text{ cm}^{-1}}/A_{1030\text{ cm}^{-1}}$  and  $A_{1220\text{ cm}^{-1}}/A_{1030\text{ cm}^{-1}}$  indicated the acetyl contents, and the weight loss of CA films after a 10-day immersion is shown in Figure 8. There is a correlation between the reduction of the acetyl contents and the film weight loss. The weight loss increased as the acetyl contents became lower, and when the acetyl groups disappeared completely, the weight loss reached approximately 40%; this agreed well with the theoretical value of 39.3% weight loss obtained by the deacetylation of CA (DS = 2.5). It would be appropriate to consider that the film weight loss originates mainly in deacetylation.

A similar evaluation of the changes in the film shape was carried out to correlate the deterioration behavior (shown in Figs. 1 and 2) with the deacetylation, which is indicated by the film weight loss. The thickness and diameter changes of the CA films immersed in HCl and NaOH solutions are shown in Figures 9 and 10 with respect to the concentration. Like the appearance changes shown in Figures 1 and 2, the sizes of the films depended on the HCl and NaOH concentrations. Figure 11 shows the relationship between the HCl and NaOH concentrations and the changes in the film volume, which was calculated with the experimental values of the thickness and diameter under the assumption that the sizes of the films changed uniformly. The changes in the volume, depending on the HCl and NaOH concentrations, corresponded to the weight changes (i.e., the degree of deacetylation). This suggests that the deterioration of the CA films depended on deacetylation.



**Figure 10** Relationship between the concentration of HCl or NaOH and the diameter loss of CA films (DS = 2.5) after 10 days of immersion.



**Figure 11** Relationship between the concentration of HCl or NaOH and the volume loss of CA films (DS = 2.5) after 10 days of immersion. The film volume was calculated with the experimental values of the thickness and diameter under the assumption that the size of the films changed uniformly.

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