

# Cellulose Triacetate Prepared from Low-Grade Hardwood Dissolving Pulp and Its Insoluble Residues in Acetylation Mediums

SHIRO SAKA, KEIKO TAKANASHI

Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Kyoto 606-01, Japan

Received 20 February 1997; accepted 16 June 1997

**ABSTRACT:** As cellulose triacetate is prepared from low-grade hardwood dissolving pulp, a considerable amount of the insoluble residue was present in the acetylation medium of the acetic acid/acetic anhydride/sulfuric acid system. The characterization of this residue indicated that the insoluble residue is composed of cellulose triacetate and xylan diacetate, retaining a fiber structure of swollen form. To reduce the insoluble residues, reaction conditions for acetylation were investigated. As one of the remedies of reducing the insoluble residues, 17 different solvents were selected to add to the acetylation medium, and among these, dichloroacetic acid was found to be very effective for its reduction. The obtained cellulose triacetate could then reveal good thermal properties similar to that from high-grade dissolving pulps. Therefore, acetylation systems with an addition of an appropriate solvent can have a potential to industrially manufacture a high-quality cellulose triacetate from even low-grade hardwood-dissolving pulps, as observed in low-grade softwood-dissolving pulps. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 289–297, 1998

**Key words:** cellulose triacetate; hardwood dissolving pulp; acetylation; insoluble residue; thermal properties

## INTRODUCTION

Cellulose acetate is one of the most important cellulose derivatives in the fiber and textile industries and is usually manufactured from cotton linters or high-quality wood dissolving pulps.<sup>1</sup> This is because low-grade dissolving pulps contain hemicelluloses; and hemicellulose acetates behave differently in the solution, resulting in industrial problems such as filterability, turbidity, and false viscosity.<sup>2–10</sup>

In spite of these problems, it is still beneficial

economically and technically for low-grade dissolving pulps to be used as raw materials for cellulose acetate production. Therefore, in previous work, cellulose triacetate (CTA) was prepared from low-grade sulfite softwood dissolving pulp in an acetic acid/acetic anhydride/sulfuric acid system. However, a substantial amount of insoluble residues was found to be present in its system; and through a characterization of the insoluble residue,<sup>11</sup> it was found to be composed of CTA and glucomannan triacetate (GTA) in aggregate with each other in the acetylation medium by their compatible nature.

Therefore, some trials were made to reduce such residues. As one of the trials, the pretreatment of the low-grade dissolving pulps with mixtures of acetic acid and sulfuric acid was found to reduce the amount of insoluble residues, due

---

Correspondence to: S. Saka.

Contract grant sponsor: Grant-in-Aid for Scientific Research (Ministry of Education, Science, Sports, and Culture, Japan); contract grant number: 07556102.

*Journal of Applied Polymer Science*, Vol. 67, 289–297 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/020289-09

**Table I Chemical Compositions of Original Hardwood Prehydrolyzed Kraft Pulps Used for Acetylation**

Pulps	$\alpha$ -Cellulose Contents <sup>a</sup> (wt %)	Chemical Compositions (mol %)		
		Glucose	Mannose	Xylose
High grade	99.3	98.5	0.3	1.2
Medium grade	96.5	97.3	0.3	2.4
Low grade	86.2	78.8	0.2	21.0

<sup>a</sup> Determined by 18% NaOH aqueous solution.

perhaps to selective degradation by hydrolysis or acidolysis of glucomannan without degrading cellulose. Furthermore, the use of the higher amount of sulfuric acid as a catalyst was also found to reduce the insoluble residues formed.<sup>12</sup> As another trial, the effect of the addition of a solvent to the acetylation medium on the reduction of the insoluble residues was studied. As a result, some solvents such as nitromethane, nitroethane, and dichloroacetic acid were found to be effective in reducing the insoluble residues,<sup>13</sup> and their optimum conditions of the addition of a solvent to the acetylation medium were studied.<sup>14</sup>

These previous works are all CTA from low-grade sulfite softwood-dissolving pulp, and general basic information could have been achieved. In this study, therefore, hardwood-dissolving pulps were selected as raw materials to prepare CTA, and the obtained results were compared with those from previous works from softwood pulps. Furthermore, the acetylation medium with a solvent added was evaluated to prepare the CTA from hardwood pulps in reducing the insoluble residues.

## EXPERIMENTAL

### Materials and Methods

CTA was prepared from three kinds of hardwood prehydrolyzed kraft pulps (high-grade pulp, Acetkraft,  $\alpha$ -cellulose content 99.3%; medium-grade pulp, Viscokraft, 96.5%; low-grade pulp, Croix, 86.2%) as shown in Table I. The sample (1 part) of these well-defibered pulps was acetylated with a solution of acetic acid (160 parts), acetic anhydride (7 parts), and sulfuric acid (0.1 parts) for 3 h at 40°C, and then stirred overnight at 20°C.

For low-grade hardwood pulps, one part of the pulps was first activated by stirring with a mixture of acetic acid and a solvent with varying ra-

tios [solvent/acetic acid (v/v)] being 0/10, 1/9, 3/7, and 5/5 (totally 160 parts) for 20 min at 40°C. Subsequently, the activated pulps were acetylated with acetic anhydride (7 parts) and sulfuric acid (0.1 part) for 3 h at 40°C, followed by stirring overnight at 20°C. The solvents used in this reaction system are given in Table II.

The reaction solution obtained was then spun in a centrifuge at 7000 rpm for 30 min to separate the soluble portion and insoluble residue. The supernatants were pipetted away, and the precipitated substances were washed repeatedly with fresh acetic acid by centrifugation to obtain the insoluble portions. All supernatants collected were, on the other hand, concentrated, and poured into deionized water to precipitate the soluble por-

**Table II Solvents Used in Acetylation Mediums and Resultant Insoluble Residue Contents**

Solvents	Solubility Parameter (MPa <sup>1/2</sup> )	Insoluble Residue (%)
1. <i>n</i> -Butyl chloride	16.6	42.6
2. <i>p</i> -Chlorotoluene	18.0	68.3
3. 1,2-Dichloroethane	18.2	35.0
4. Methylcellosolve acetate	18.8	43.1
5. Chloroform	19.0	40.0
6. Ethylbromide	19.6	48.7
7. Methylene chloride	19.8	46.4
8. 2-Nitropropane	20.3	24.8
9. Bromobenzene	20.3	25.6
10. Nitrobenzene	20.5	20.2
11. Acetic acid (control)	20.7	23.8
12. 1-Nitropropane	21.1	24.5
13. Methylbenzoate	21.5	33.3
14. 1-Bromonaphthalene	21.7	31.5
15. Dimethyl phthalate	21.9	31.1
16. Dichloroacetic acid	22.5	4.5
17. Nitroethane	22.7	19.9
18. Nitromethane	26.0	10.3

tions. The soluble and insoluble portions were washed with saturated NaCl solution three times for stabilization, and the remaining NaCl was washed away thoroughly with deionized water. These were successively washed with ethanol, and dried under a vacuum for more than 12 h.

To isolate xylan, a low-grade hardwood prehydrolyzed kraft pulp was extracted under a nitrogen atmosphere with 24% KOH. Four volumes of ethanol containing excess of acetic acid to neutralize the base were added to the extracted portion for precipitating xylan.<sup>6</sup> The obtained xylan was subsequently acetylated to prepare xylan diacetate (XDA).

Cellulose triacetate I (CTA-I) and cellulose triacetate II (CTA-II) were prepared for studying the crystallographic nature and thermal properties of the insoluble residue. CTA-I was prepared by a general fibrous process,<sup>16</sup> while CTA-II by dissolving the CTA-I in a  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (9:1) solvent mixture and precipitating it in MeOH.<sup>17</sup> The degree of substitution (DS) of acetate samples was determined by a titration method.<sup>18</sup>

To study neutral sugar compositions, the samples were hydrolyzed by 72%  $\text{H}_2\text{SO}_4$  at 110°C for 3 h and neutralized by barium carbonate, after ribose was added. Filtrating by filter paper and diluting it by superpure water in 10 volumes, neutral sugar compositions were determined with DI-ONEX ion chromatograph (DX-AQ1120) to which CarboPac PA1 was attached. DX-AQ1120 was operated with a flow of 20 mM NaOH as a carrier solvent at 10 mL/min.

To study the crystallographic nature, the sam-

ples were annealed at 220°C<sup>19,20</sup> for 20 min under a vacuum and nonoriented samples on a glass plate were prepared to obtain X-ray diffraction patterns by a Rigaku RINT 2000V (Cu-K $\alpha$ ,  $\lambda = 1.542 \text{ \AA}$ ) at 40 kV and 30 mA.

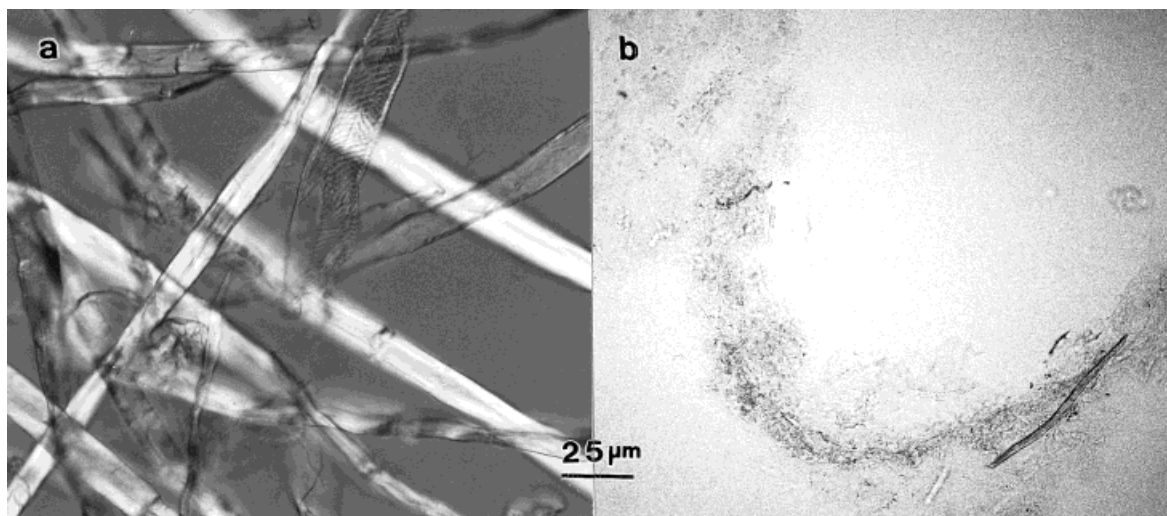
For investigating thermal properties, the dried samples were studied by a differential scanning calorimetry (DSC) and thermogravimetry (TG) with Shimadzu DSC-50 and TGA-50 instruments with a flow of nitrogen gas, 30 mL/min. The temperature was raised from 350 K (77°C) to 600 K (327°C) at a heating rate of 5 K/min (5°C/min).

## RESULTS AND DISCUSSION

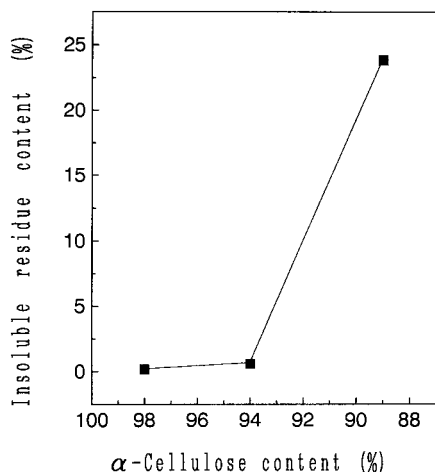
### Insoluble Residue of Acetylated Low-Grade Hardwood Prehydrolyzed Kraft Pulp

The light microscopic observations of the pulps during acetylation revealed that the high-grade hardwood-prehydrolyzed kraft pulp fibers dissolved almost completely at the end of acetylation. However, some of the low-grade pulp fibers remained in the swollen state with fiber structure (Fig. 1). A comparison with the nonacetylated original hardwood pulp fibers can show the degree of fiber swelling of the insoluble residue after acetylation.

Figure 2 show a relationship between  $\alpha$ -cellulose contents of original hardwood pulps and the amounts of insoluble residues after acetylation. It is surprising that low-grade hardwood pulp resulted in the insoluble substances more than over 100 times that of high-grade hardwood pulp. Therefore,



**Figure 1** Light micrographs of the low-grade hardwood pulp fibers in which a vessel element is present (a) and insoluble-fiber residue after acetylation (b).



**Figure 2** A relationship between cellulose content of the original hardwood dissolving pulp and the amounts of the insoluble residue in acetylation medium.

the  $\alpha$ -cellulose content cannot be a direct indication of the amounts of insoluble residue formed.

These lines of results, as seen in Figures 1 and 2, were also observed in a previous study of low-grade softwood dissolving pulp. However, the softwood-dissolving pulps contains more galactoglucomannan than xylan, while the hardwood dissolving pulps, in turn, contain more xylan. Therefore, it is of interest to characterize the insoluble residues in the acetylation medium of the low-grade hardwood dissolving pulps, compared with the previous results from the low-grade softwood pulps.

### Characterization of Soluble Portion and Insoluble Residue

#### Chemical analysis

For acetylated low-grade hardwood pulp, the soluble portion and insoluble residue were collected

separately for their characterization. Table III shows the obtained DS and chemical compositions of these fractions. On chemical compositions, the xylose content of the insoluble residue was found to be much greater than that of the soluble portion. The values in parentheses were calculated from the data of soluble and insoluble portions with known weight fractions. These results are close enough to the values for the original pulp as well as the whole CTA (whole = Sol. + Ins.). Therefore, the large content of xylose for insoluble residue must be valid. Because of the presence of xylan acetate, the DS of the insoluble residue must be less than 3, even if it was fully acetylated. The calculated value of the DS for the insoluble residue, as it was fully acetylated, is therefore 2.35 [= 3.00 (0.348 + 0.004) + 2.00  $\times$  0.648]. In fact, the DS of the insoluble residue was 2.22 so that the insoluble residue must be fairly acetylated and rich in xylan diacetate (XDA). This indicates that its insolubility is not due to a lack of acetylation. Therefore, the residual xylan in hardwood pulp plays an important role in the formation of insoluble-fiber residue during acetylation.

#### X-Ray Diffractometry

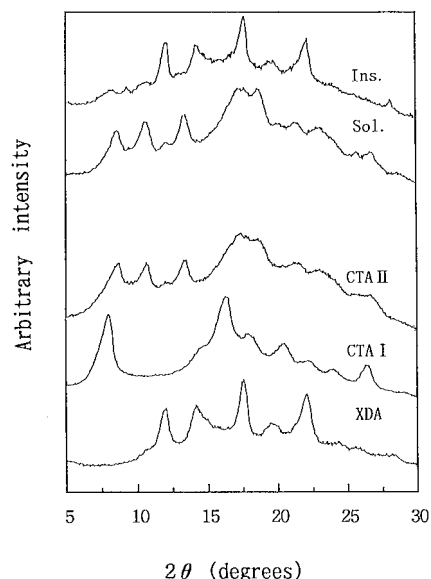
The insoluble residue of low-grade hardwood pulp was studied by X-ray diffractometry after annealing at 220°C. The obtained X-ray diffraction profiles are shown in Figure 3. For comparison, CTA-I, CTA-II, and XDA annealed at the same temperature were included as control samples. It is quite apparent that the diffraction profile from the soluble portion (Sol.) is very similar to that of CTA-II with diffraction peaks appearing at  $2\theta$  around 8.5, 10.5, and 13.4°. However, the insoluble residue (Ins.) does not exhibit any characteris-

**Table III** DS and Chemical Composition of Soluble and Insoluble Portions in CTA Prepared from Low-Grade Hardwood Dissolving Pulp

Samples	Weight Fractions (%)	DS	Chemical Compositions (mol %)		
			Glucose	Mannose	Xylose
Pulp	100.0		78.8	0.2	21.0
Whole <sup>a</sup>	2.78		79.3	0.3	20.4
		(2.77) <sup>b</sup>	(80.3)	(0.2)	(19.5)
Soluble	76.2	2.94	94.5	0.2	5.3
Insoluble	23.8	2.22	34.8	0.4	64.8

<sup>a</sup> "Whole" refers to the total prior to the separation of soluble and insoluble portion.

<sup>b</sup> Values in parentheses were calculated from ones of soluble and insoluble portions with their weight fractions.



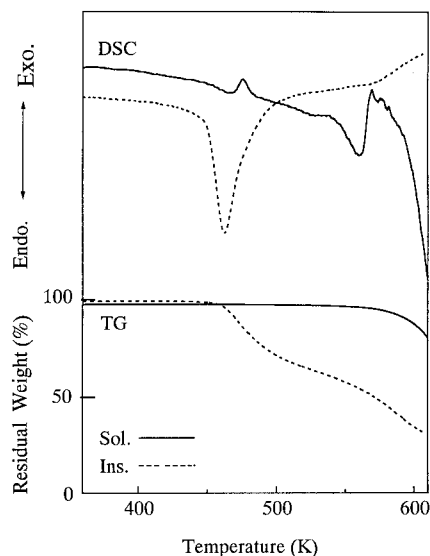
**Figure 3** X-ray diffraction profiles of insoluble residue (Ins.) and soluble portion (Sol.) in cellulose triacetate prepared from the low-grade hardwood dissolving pulp CTA I; cellulose triacetate I, CTA II; cellulose triacetate II, XDA; xylan diacetate.

tic peak derived from either CTA-I or CTA-II, but resembles XDA in the diffraction profile. Because the insoluble residue is rich in XDA, this suggests that XDA is present without any aggregation with CTA, but that the presence of XDA would prevent CTA molecules from being crystallized because of the absence of X-ray diffraction originating from CTA.

### Thermal Analyses

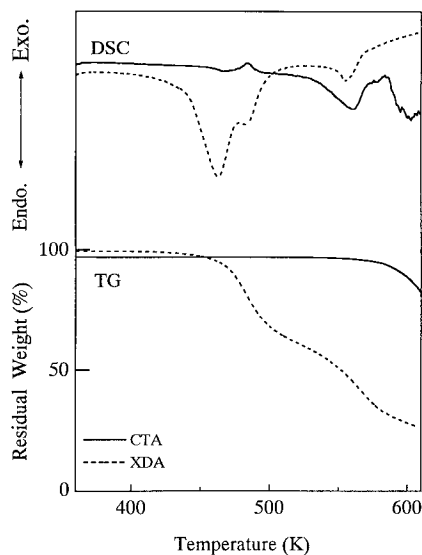
Figure 4 shows the DSC and TG thermograms, under a flow of nitrogen, of the soluble portion and insoluble residue of the CTA prepared from hardwood low-grade dissolving pulp. The DSC and TG thermograms of pure CTA prepared from cotton linters and XDA are also shown in Figure 5. From these results, it is clear that the soluble portion reveals a similar pattern to that of CTA. Therefore, an exothermic peak at about 475 K and an endothermic peak at 575 K, respectively, correspond to the peaks of crystallization and melting of CTA as in the literature,<sup>15</sup> whereas the insoluble residue reveals neither of them for the soluble portion.

For the TG thermograms in Figure 4, the soluble portion was fairly stable against a temperature rise up to about 580 K, but the insoluble

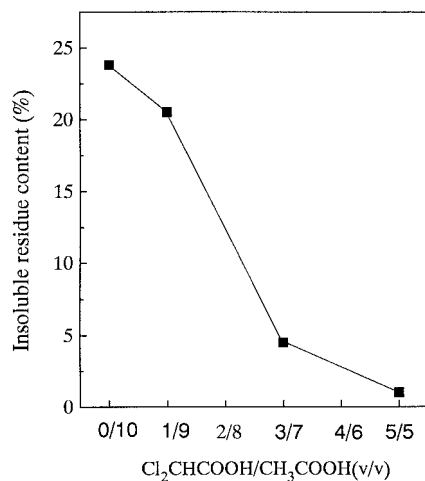


**Figure 4** DSC (upper) and TG (lower) curves of the soluble portion and insoluble residue from hardwood low-grade dissolving pulp.

residue revealed some weight decrease started from about 460 K due to its pyrolysis.<sup>14</sup> Because XDA in its pure state is unstable against a temperature rise as in Figure 5, the observed degradation of the insoluble residue in Figure 4 would be due to that of XDA molecules, rich in its residue.



**Figure 5** DSC (upper) and TG (lower) curves of cellulose triacetate from linter (CTA) and xylan diacetate (XDA).



**Figure 6** The insoluble residue contents in dichloroacetic acid added acetylation mediums.

### CTA in Dichloroacetic Acid Added Acetylation Medium

Based on these results, it may be concluded that the presence of XDA leads to the formation of the insoluble residue in an acetylation system and a lack of its thermal stability. Therefore, 17 different solvents were selected to find one to dissolve the XDA. The selected solvents could cover a wide range of the solubility parameters as shown in Table II. As a result, only dichloroacetic acid dissolved XDA, and insoluble residue content was lowest in an acetylation medium with dichloroacetic acid added. This solvent can dissolve CTA as well, so that an acetylation medium with dichloroacetic acid added was evaluated to reduce the insoluble residues in preparing CTA.

### Soluble Portion and Insoluble Residue

Figure 6 shows the relationship between the insoluble residue content and the acetylation medium with an addition of various amounts of dichloroacetic acid with volumetric ratios of 0/10, 1/9, 3/7, and 5/5 to acetic acid (v/v). It is apparent that with an increase of dichloroacetic acid added to the acetylation medium, the insoluble residue content was decreased. Particularly, 3/7 and 5/5 solutions of dichloroacetic acid added systems revealed a significant decrease in its residue, and its content of the latter system was equivalent to the acetylation system of CTA without a solvent added prepared from high-grade hardwood dissolving pulp. Therefore, the addition of

the dichloroacetic acid to the acetylation medium is very effective in reducing insoluble residues.

Table IV shows chemical compositions of the soluble portions in CTA prepared in dichloroacetic acid added acetylation medium. Inversely to the results of the insoluble residues in Figure 6, the weight fractions of the soluble portions increase. It is also clear that increasing the amount of dichloroacetic acid added, glucose content decreases and xylose content increases with keeping mannose content constant. Furthermore, in 5/5 solution, xylose content is 20.8%, which is very close to the value of 21.0% in that of the original low-grade hardwood pulp (Table I). These results indicate that XDA present in the insoluble residue was moved to the soluble portion, with increasing its solubility.

These soluble portions in Table IV were studied by X-ray diffractometry after annealing at 220°C. The obtained X-ray diffraction profiles shown in Figure 7 reveal a similar pattern to that of CTA-II, with diffraction peaks appearing at  $2\theta$  around 8.5, 10.5, and 13.4°. Additionally, the diffraction peak at  $2\theta = 12.5^\circ$ , shown by an arrow, seems to be more intense with an increase of the amount of dichloroacetic acid added. Regardless of the addition of dichloroacetic acid, X-ray diffraction patterns do not change so that CTA would not be aggregated with XDA in acetylation medium, as observed in the CTA prepared from softwood dissolving pulps.<sup>11,12</sup>

### Thermal Properties of the Soluble Portion

Figure 8 shows DSC and TG thermograms, under a flow of nitrogen, of the soluble portion in dichloroacetic acid added acetylation mediums. In spite of the presence of XDA as in Table IV, these soluble portions are more thermally stable compared with the soluble portion obtained from an acetylation system without dichloroacetic acid added (Fig. 4).

To clarify the reason for this, the extracted xylan from the low-grade hardwood prehydrolyzed kraft pulps (Croix) was acetylated in an acetylation system with dichloroacetic acid added with a volumetric ratio of 5/5 (v/v) to acetic acid. The extracted xylan was, respectively, 95.5, 0.8, and 3.7% in xylose, mannose, and glucose contents in its chemical composition. The prepared XDA was then studied by DSC and TG (Fig. 9). As it is apparent in Figure 9, the thermal stability was improved and weight loss was restrained up to the higher temperature with an increase of the

**Table IV Chemical Composition of Soluble Portions Prepared from Dichloroacetic Acid Added Acetylation Mediums**

Samples	Weight Fractions (%)	Chemical Compositions (%)		
		Glucose	Mannose	Xylose
Sol. [0/10] <sup>a</sup>	76.2	94.5	0.2	5.3
Sol. [1/9]	79.5	95.7	0.4	4.0
Sol. [3/7]	95.5	89.5	0.4	10.1
Sol. [5/5]	99.0	78.9	0.3	20.8

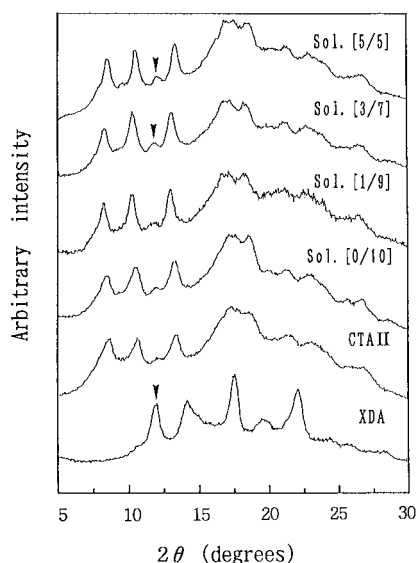
<sup>a</sup> Volumetric ratios of dichloroacetic acid to acetic acid in acetylation medium.

amount of dichloroacetic acid added to the acetylation system. Additionally, an endothermic peak in the DSC thermograms by pyrolysis was weakened and shifted to the higher temperature accordingly. This result suggests that even if the chemical composition of the XDA is the same, its dissolving state in an acetylation medium will affect the thermal properties of the XDA.

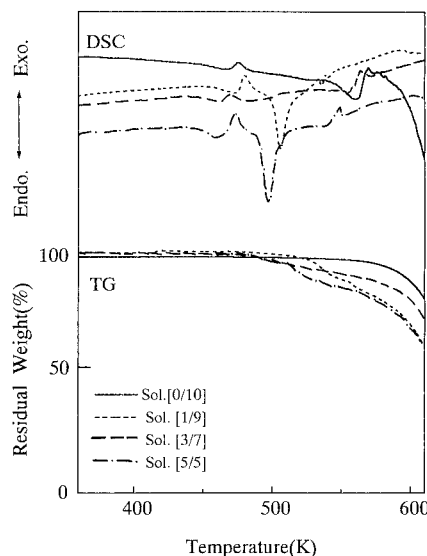
#### Properties of Solvent-Treated Insoluble Residue

To study the effect of the solvent on the properties of the insoluble residues, three solvents were selected such as dichloroacetic acid, nitromethane, and chloroform. The insoluble residue formed in an acetylation medium without a solvent was treated with these solvent. Subsequently, it was

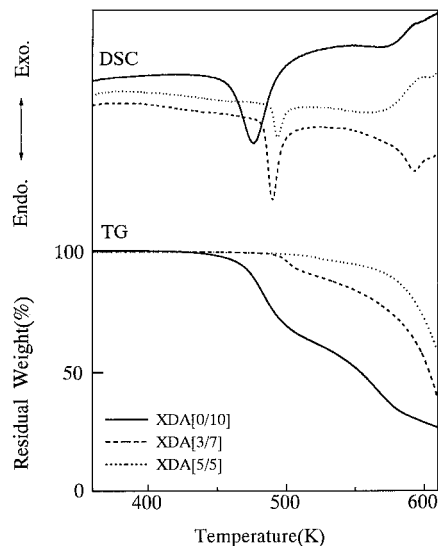
poured into water to be precipitated. The collected precipitates were then studied. The chemical compositions shown in Table V indicate that all these solvent-treated insolubles are basically the same in the chemical nature. However, these are significantly different in their thermal properties as seen in DSC and TG thermograms (Fig. 10); compared with the insoluble residue (Ins.) not treated with a solvent, the insoluble residues could improve their thermal properties in the order of nitromethane, chloroform, and dichloroacetic acid. Because nitromethane and chloroform are only a good solvent for CTA, but dichloroacetic acid is good for both CTA and XDA, the improvement of the thermal properties in the insoluble residues requires a complete solubilization in the acetyla-



**Figure 7** X-ray diffraction profiles of soluble portion in dichloroacetic acid added acetylation mediums.



**Figure 8** DSC (upper) and TG (lower) curves of soluble portion in dichloroacetic acid added acetylation mediums.

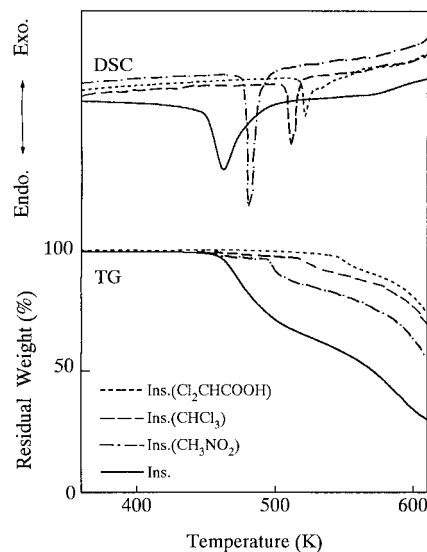


**Figure 9** DSC (upper) and TG (lower) curves of XDA prepared from dichloroacetic acid added acetylation mediums.

tion medium. Furthermore, as shown in Figure 11, insoluble residues treated with dichloroacetic acid [Ins. ( $\text{Cl}_2\text{CHCOOH}$ )] and chloroform [Ins. ( $\text{CHCl}_3$ )] are both revealing a characteristic diffraction peak of CTA-II at  $2\theta = 8.5^\circ$  (see an arrow in Fig. 11), in addition to the diffraction pattern of XDA. However, such a peak cannot be observed in either insoluble residue treated with nitromethane [Ins. ( $\text{CH}_3\text{NO}_2$ )] or those not treated with a solvent (Ins.). As shown in Figure 1, the insoluble residues in the acetylation system keep the fiber structure originated from the pulp fibers. The thermal properties may be, therefore, improved by deminishing such a fiber structure by an appropriate solvent added. Therefore, by an addition of dichloroacetic acid to the acetylation

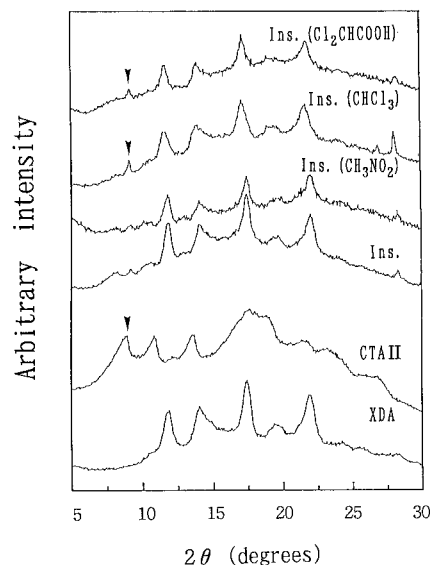
**Table V** Chemical Composition of Insoluble Residue in Acetylation Medium and Its Dissolved Portion with Dichloroacetic Acid, Chloroform, or Nitromethane

Samples	Chemical Compositions (mol %)		
	Glucose	Mannose	Xylose
Ins.	34.8	0.4	64.8
Ins. ( $\text{Cl}_2\text{CHCOOH}$ )	32.9	0.4	66.8
Ins. ( $\text{CHCl}_3$ )	38.3	0.5	61.3
Ins. ( $\text{CH}_3\text{NO}_2$ )	38.1	0.4	61.5



**Figure 10** DSC (upper) and TG (lower) curves of insoluble residue of the cellulose triacetate prepared from the low-grade hardwood pulp after dissolving in dichloroacetic acid, nitromethane, or chloroform.

medium, CTA may be improved in its thermal properties even if a substantial amount of XDA is contained in the soluble portion. These lines of the results, therefore, suggest that the thermally stable CTA may be manufactured even from low-



**Figure 11** X-ray diffraction profiles of insoluble residue of the cellulose triacetate prepared from the low-grade hardwood pulp after dissolving in dichloroacetic acid, nitromethane, or chloroform.



grade hardwood dissolving pulps, by modifying the acetylation reaction system.

This research was supported by a Grant-in-Aid for Scientific Research (A) (2) (07556102, 1995–1997) from the Ministry of Education, Science, Sports, and Culture, Japan. The authors thank the research scientists at the Research Center, Daicel Chemical Industries, Ltd., for their valuable discussion.

## REFERENCES

1. M. Ichino, *Nikkakyo Geppo*, **39**, 25 (1986).
2. J. K. Watson, and D. R. Henderson, *TAPPI*, **40**, 686 (1957).
3. F. L. Wells, W. C. Schattner, and A. Walker, Jr., *TAPPI*, **46**, 581 (1963).
4. C. J. Malm and L. J. Tanghe, *TAPPI*, **46**, 629 (1963).
5. J. L. Neal, *J. Appl. Polym. Sci.*, **9**, 947 (1965).
6. P. E. Gardner and M. Y. Chang, *TAPPI*, **57**, 71 (1974).
7. J. D. Wilson and R. S. Tabke, *TAPPI*, **57**, 77 (1974).
8. K. Ueda, S. Saka, Y. Funaki, and S. Soejima, *Mokuzai Gakkaishi*, **34**, 346 (1988).
9. K. Ueda, S. Saka, and S. Soejima, *TAPPI*, **71**, 183 (1988).
10. Y. Funaki, K. Ueda, S. Saka, and S. Soejima, *J. Appl. Polym. Sci.*, **48**, 419 (1993).
11. H. Matsumura and S. Saka, *Mokuzai Gakkaishi*, **38**, 270 (1992).
12. H. Matsumura and S. Saka, *Mokuzai Gakkaishi*, **38**, 862 (1992).
13. S. Saka and T. Takahashi, in *Cellulose and Cellulose Derivatives*, J. F. Kennedy, G. O. Phillips, P. O. Williams, and L. Piculell, Eds., Woodhead Publishing Ltd., Cambridge, 1995, p. 219.
14. S. Saka and K. Ohmae, *J. Appl. Polym. Sci.*, **62**, 1003 (1996).
15. K. Kamide and M. Saito, *Polym. J.*, **17**, 919 (1985).
16. N. Migita, Y. Yonezawa, and T. Kondo, in *Mokuzai Kagaku*, Wood Chemistry, Kyoritsushuppan, 1968, p. 184.
17. B. S. Sprague, J. L. Riley, and H. D. Noether, *Text. Res. J.*, **28**, 275 (1958).
18. A. Katsumoto, in *Sen'isokagaku Oyobi Kogyo*, Maruzen, Tokyo, 1956, p. 418.
19. S. Watanabe and M. Takai, *Kogyokagaku Zasshi*, **71**, 1883 (1968).
20. H. Bittiger and R. H. Marchessault, *Carbohydr. Res.*, **18**, 469 (1971).