Effects of Solvent Addition to Acetylation Medium on Cellulose Triacetate Prepared from Low-Grade Hardwood Dissolving Pulp

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ABSTRACT: As cellulose triacetate was 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, and it consisted mainly of cellulose triacetate (CTA) and xylan diacetate (XDA). As one of the remedies for reducing the insoluble residue, a solvent was added to the acetylation medium and the effects of the solvent addition on the amount of insoluble residue formed were studied. To do so, 17 different solvents were selected so as to cover a wide range of solubility parameters. The obtained results clearly indicated that the addition of the solvent affects the amount of insoluble residue and that, excluding dichloroacetic acid, nitromethane was effective for its reduction, but that neither methylene chloride nor nitroethane were in spite of their effectiveness for softwood-dissolving pulp, which would be due to the intrinsic properties of XDA on the solubility in the acetylation medium. A new acetylation system with such an appropriate solvent would, therefore, provide a clue as to an industrial usage of the low-grade hardwood-dissolving pulps for cellulose acetate production.
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Key words: cellulose triacetate; hardwood-dissolving pulp; acetylation; insoluble residue; solvent addition; xylan diacetate

INTRODUCTION

Cellulose triacetate, being important in the fiber and textile industries, requires high-quality cellulose as a starting material,[1] because the low-grade dissolving pulps contain more hemicelluloses and the formation of hemicellulose acetates such as xylan acetate and glucomannan acetate results in industrial problems such as filterability, turbidity (haze), and false viscosity. Although a considerable effort has been made since the mid-1950s to explain the relationships between solution properties of the cellulose acetate and contaminated hemicellulose acetate,[2–8] viscose-grade wood pulps with an α-cellulose content of less than 90% still cannot be used for manufacturing cellulose acetate.

In our previous work,[9,10] we studied cellulose triacetate prepared from softwood sulfite-dissolving pulps with an α-cellulose content of 87.5%. The first problem faced was the substantial amount of insoluble residue present in the acetylation medium of the acetic acid/acetic anhydride/sulfuric acid system. This insoluble residue

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retained a fiber structure of a swollen form, resulting in one of the industrial problems: filterability.

Characterization of the insoluble residue[9] showed that it was composed of cellulose triacetate (CTA) and glucomannan triacetate (GTA) aggregated with each other in the acetylation medium due to their compatible nature. In addition to such physicochemical effects of the molecular interactions, ultrastructural effects of the glucomannan distribution in the pulp fibers were found to be involved in the formation of insoluble residues. Therefore, the amount of insoluble residue can be expected to be reduced if physicochemical effects and/or ultrastructural effects are decreased during acetylation.

As one of the remedies, the pretreatment of low-grade dissolving pulps with mixtures of acetic acid and sulfuric acid was found to reduce both the physicochemical and ultrastructural effects of the pulp fibers in the following acetylation, resulting in reducing the amount of the insoluble residue.[10] The use of higher amounts of sulfuric acid as a catalyst was also found to reduce the insoluble residue formed.[10] Furthermore, a solvent-added acetylation medium of the acetic acid/acetic anhydride/sulfuric acid system was found to affect the amount of the insoluble residue, and nitromethane, nitroethane, dichloroacetic acid, and methylene chloride were very effective for its reduction.[11]

These lines of evidence mentioned above are based on the softwood sulfite-dissolving pulp which consists mainly of cellulose and glucomannan. However, hardwood prehydrolyzed kraft pulp is composed of cellulose and glucuronoxylan with a small amount of glucomannan. Therefore, we started studying CTA as prepared from low-grade hardwood-dissolving pulp. As a result, a substantial amount of insoluble residue was found in the acetylation medium, which was composed of CTA and xylan diacetate (XDA).[12]

In this study, therefore, a solvent-added acetylation medium of the acetic acid/acetic anhydride/sulfuric acid system was evaluated for preparing CTA and the effects of the solvent addition on the amount of the insoluble residue formed were studied. To do so, 17 different solvents were selected to cover a wide range of solubility parameters of the solvents.

EXPERIMENTAL

Prehydrolyzed hardwood-dissolving pulp with an α-cellulose content of 86.2% was used for preparing CTA as described in the previous article.[9] To study the effect of the solvent addition to the reaction system on the insoluble residue, a solvent was added to the acetylation medium of the acetic acid/acetic anhydride/sulfuric acid system. The solvents used in this study are given in Table I.

The low-grade dissolving pulps (1 part) were thus acetylated with a solution of acetic acid (160 parts), acetic anhydride (7 parts), and sulfuric acid (0.1 part) with a solvent (51 parts) in a closed vial for 3 h at 40°C, followed by stirring overnight at 20°C. The solutions were then spun in a centrifuge at 7000 rpm for 30 min with a Hitachi high-speed microcentrifuge RT15D (rotor type RT15A6 with dimensions of 18.2 cm diameter $\times$ 10.2 cm height). After the tubes were removed carefully, the supernatants were pipetted away and precipitated substances were washed repeatedly with mixtures of fresh acetic acid and the solvent used in the system (160 : 51 in a weight ratio) by centrifugation to obtain the insoluble portions. The supernatants collected were, on the other hand, concentrated and poured into deionized water to precipitate the soluble portions. The insoluble and soluble portions were washed as described previously.[9]

The degree of substitution (DS) of these samples was determined by a titration method,[11] while neutral sugar compositions were determined by an alditol–acetate procedure[13] using conditions described in a previous article.[9]

RESULTS AND DISCUSSION

It is known from our previous work,[9,12] that when CTA is prepared from low-grade dissolving pulps a substantial amount of the insoluble residue is present in the acetylation medium of the acetic acid/acetic anhydride/sulfuric acid system and that the insoluble residue is composed of CTA and GTA in softwood pulp, while of CTA and XDA in hardwood pulp. Furthermore, an addition of the appropriate solvent to the acetylation medium for softwood-dissolving pulp was known to reduce the insoluble residues.[10,11] Therefore, in this study, a solvent was added to the above acetylation medium with 51 : 160 weight ratio of solvent to acetic acid to study the effects of the solvent addition on the reduction of the insoluble residue in the acetylation medium for hardwood-dissolving pulp.

Table I shows the selected solvents excluding the alkaline, unstable, and reactive solvents in

Table I Insoluble Residue Content in the Acetylation Medium with a Solvent Added and Its Chemical Composition

No.	Solvent	Solubility Parameter [(MPa)$^{1/2}$]	Insoluble Residue (wt %)	Chemical Compositions (mol %)		
				Glucose	Mannose	Xylose
1	*n*-Butyl chloride	16.6	42.6	66.9	0.3	32.8
2	4-Chlorotoluene	18.0	68.3	60.9	0.3	38.8
3	1,2-Dichloroethane	18.2	35.0	58.3	0.2	41.5
4	Methylcellosolve acetate	18.8	43.1	57.1	0.4	42.5
5	Chloroform	19.0	40.0	48.3	0.3	51.5
6	Ethylbromide	19.6	48.7	65.8	0.3	33.9
7	Methylene chloride	19.8	46.4	56.5	0.1	43.4
8	2-Nitropropane	20.3	24.8	42.1	0.4	57.6
9	Bromobenzene	20.3	25.6	41.7	0.4	57.9
10	Nitrobenzene	20.5	20.2	21.0	0.3	78.7
11	Acetic acid	20.7	23.8	34.8	0.4	64.8
12	1-Nitropropane	21.1	24.5	26.8	0.3	72.9
13	Methylbenzoate	21.5	33.3	35.2	0.4	64.4
14	1-Bromonaphtalene	21.7	31.5	29.1	0.4	70.4
15	Dimethyl phthalate	21.9	31.1	35.6	0.4	64.0
16	Dichloroacetic acid	22.5	4.5	8.4	0	91.6
17	Nitroethane	22.7	19.9	23.1	0.1	76.9
18	Nitromethane	26.0	10.3	11.3	0	88.7

the reaction medium. The acetylation system with acetic acid (No. 11 in Table I) was also included just for comparison as a control reaction system without any addition of the solvent. Compared with acetic acid, 20.7 (MPa)$^{1/2}$ in its solubility parameter (SP), the selected solvents could cover a wide range of the SP values from 16.6 to 26.0 (MPa)$^{1/2}$.[14] Also included in Table I is the insoluble residue content in the acetylation medium with a designated solvent.

Figure 1 shows a relationship between the amount of insoluble residue and the SP of the solvent added to the acetylation medium. Numbers correspond to the solvents in Table I. It is very apparent that compared with 23.8% in a control reaction system (acetic acid, No. 11) the results are varied from 4.5 to 68.3% in insoluble residue contents, indicating that large effects of the solvent addition exist on the amount of the insoluble residue in the acetylation medium. Furthermore, it is noted that with increase in the SP values the amount of insoluble residue has a tendency to decrease. The effective solvents for reducing the insoluble residue were only dichloroacetic acid (4.5%) and nitromethane (10.3%). The other solvents which were effective in softwood-dissolving pulp were not effective for this hardwood pulp, such as methylene chloride (46.4%) and nitroethane (19.9%). However, it was very unfortunate that the analysis of CTA prepared in a dichloroacetic acid-added acetylation medium revealed the presence of 2.03% chlorine. By as-

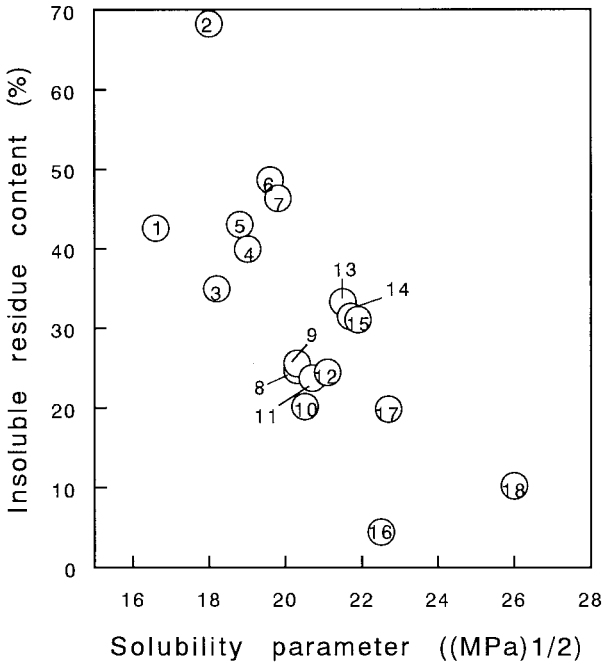

Figure 1 Soluble residue content versus solubility parameter of the solvent added to the acetylation medium. Nos. correspond to the solvents in Table I.

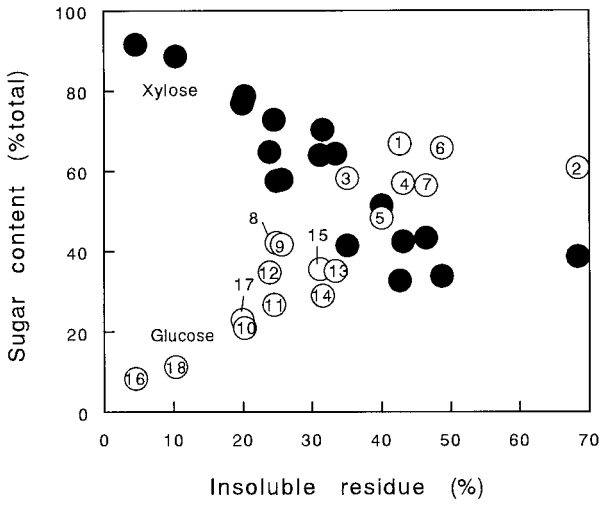

Figure 2 Sugar content versus insoluble residue content for acetylation medium with a solvent added. Nos. correspond to the solvents in Table I.

suming that all of the chlorine is derived from the dichloroacetic acid cellulose ester formed, its DS value is about 0.08. Therefore, dichloroacetic acid must be excluded as a solvent to be added to the acetylation systems.

The chemical compositions of the insoluble residue in each reaction system are also given in Table I. It is apparent that, in addition to glucose, the insoluble residue contains a high proportion of xylose, with a limited amount of mannose. This result is in good agreement with the findings of our previous work[12] that the insoluble residue is composed of CTA and XDA. Therefore, XDA is involved in the formation of the insoluble residue for all the acetylation systems studied.

However, a closer inspection of the results in Table I shows a large variation in xylose content from a maximum of 91.6% to a minimum of 32.8%. Therefore, a relationship between the insoluble residue content and its sugar content for glucose and xylose was studied. It is apparent from Figure 2 that the glucose content decreases with decrease in the insoluble residue content, whereas the xylose content increases. Therefore, the contents of the XDA and CTA were computed for all insoluble residues, based on the chemical compositions of the insoluble residue. Figure 3 shows the obtained ratio of CTA to XDA against the insoluble residue content. It is apparent that with a decrease in the insoluble residue content the ratio of CTA to XDA decreases, and below 10% of the insoluble residue content, the ratio becomes nearly zero, indicating that the insoluble residue is almost pure XDA. This finding, therefore, suggests that the mutual aggregation between CTA and XDA is much weaker, compared with that between CTA and GTA as prepared from low-grade softwood sulfite pulp.[12]

Comparative studies of the acetylation in the model experiments[10] indicated that the insoluble residue from the low-grade softwood-dissolving pulp is formed by ultrastructural effects of the pulp fibers and the physicochemical effects of the molecular interactions of CTA and GTA. The former effects originate from the ultrastructural distribution of residual glucomannan in the dissolving pulp, whereas the latter effects are due to molecular aggregation of CTA and GTA by their compatible nature. It is, therefore, possible to get a reduction in the amount of the insoluble residue if physicochemical effects and/or ultrastructural effects are decreased during acetylation.

With this concept in mind, an interaction of CTA and XDA from hardwood-dissolving pulp is so weak, as in Figure 3, that the formation of the insoluble residues from hardwood pulp are due only to the ultrastructural effects of the pulp fibers in which intrinsic properties of XDA on the solubility in the acetylation medium are involved.

The determination of the chemical compositions of the original pulps used in this study indicated that they contain 21.0% xylose. Thus, the proportions of the total xylose in the soluble portion and insoluble residue were computed as shown in Figure 4. It is apparent from Figure 4 that as the insoluble residue decreases in content

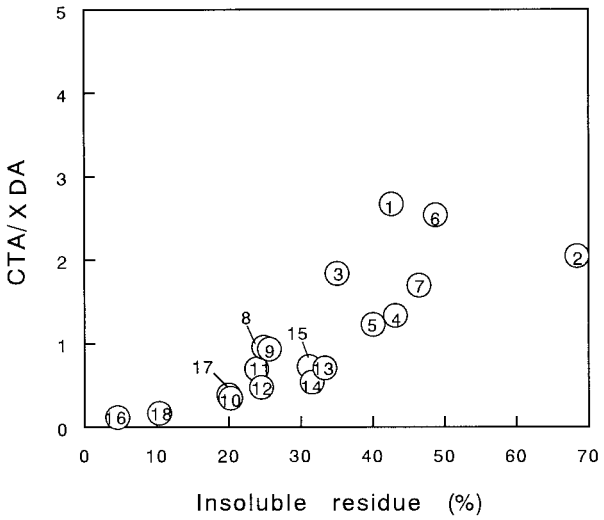

Figure 3 Ratio of CTA to XDA content in the insoluble residue versus insoluble residue content. Nos. correspond to the solvents in Table I.

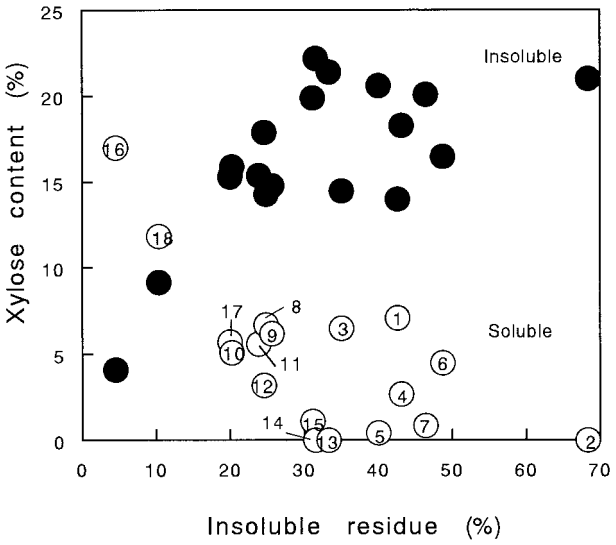

Figure 4 Insoluble residue content versus xylose content of the original pulp (21.0%) divided into soluble and insoluble portions.

the proportion of the xylose in the insoluble portion decreases, whereas that in the soluble portion, in turn, increases. This implies that some of the XDA which has formed the insoluble residue in the acetylation medium is no longer involved in its formation and has moved to the soluble portion. Therefore, the addition of the appropriate solvent to the acetylation medium could solve a problem with the formation of the insoluble residue as the low-grade hardwood-dissolving pulps are used to prepare cellulose acetate.

In conclusion, therefore, a new acetylation system with an appropriate solvent can provide a clue as to an industrial usage of the low-grade dissolving pulps from both softwood[12] and hardwood for cellulose acetate production.

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