

# High-Quality Cellulose Triacetate Prepared from Bamboo Dissolving Pulp

Jianxin He,<sup>1,2</sup> Ming Zhang,<sup>1</sup> Shizhong Cui,<sup>1</sup> Shan-Yuan Wang<sup>2</sup>

<sup>1</sup>Department of Textile Engineering, College of Textiles, Zhongyuan University of Technology, Zhengzhou 450007, People's Republic of China

<sup>2</sup>Key Laboratory of Textile Science and Technology Ministry of Education, Donghua University, Shanghai 201620, People's Republic of China

Received 2 September 2007; accepted 1 January 2009

DOI 10.1002/app.30008

Published online 19 March 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Cellulose triacetate (CTA) was prepared from high-grade bamboo dissolving pulp in general acetylation medium of acetic acid/acetic anhydride/sulfuric acid system. Despite its properties being improved compared with those of CTA prepared from viscose bamboo pulp, many insoluble residues still remained in its acetylation medium, which resulted in the decrease of the brightness and thermal stability of prepared CTA. Characterization of the insoluble residue indicated that its formation was associated with a higher content of xylan and ash in high-grade bamboo pulp than in high-grade hardwood pulp, in which insoluble residue was negligible. Because of the poor solubility of xylan diacetate (XDA) in acetylation medium, the insoluble residue formed through the aggregation of XDA and CTA by ultrastruc-

tural effects of the pulps during the precipitation of XDA. An addition to the good solvent of XDA, such as 1,2-dichloroethane to acetylation medium of high-grade bamboo pulp, could release the aggregation of XDA and CTA and dissolve the insoluble residue, which could lead to the improvement of the transmittance of reaction solution, as well as the properties of CTA prepared such as brightness and thermal stability. This study showed that high-quality CTA could be prepared from high-grade bamboo dissolving pulp in acetylation with an addition of solvent. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 456–465, 2009

**Key words:** cellulose triacetate; bamboo pulp; thermal stability; insoluble residue

## INTRODUCTION

Cellulose acetate (CA), an important cellulose derivative prepared through acetylation of cellulose, has been widely used in materials such as textiles, plastic film, and cigarette filter tow. Original materials used commercially for preparing cellulose acetate are generally high-quality celluloses with  $\alpha$ -cellulose content of more than 95%, and a hemicellulose content of not more than 2.8%.<sup>1</sup> Many investigations have shown that hemicellulose acetates (HCA), such as glucomannan triacetate (GTA) and xylan diacetate (XDA), behave differently in solution, resulting in industrial problems such as poor filterability, turbidity, and false viscosity.<sup>2,3</sup> Therefore, cellulose materials capable of being used for preparing CA are

usually cotton linters, as well as high-grade wood dissolving pulps, which come from high-quality hardwoods or softwoods of more than 20 years.

Some workers attempted to prepare CA from low-grade wood pulp to decrease material costs. Barkalow et al. presented an approach of producing CA through acetylation of mechanical pulp with subsequent isolation of CA by different solubility.<sup>4</sup> Saka et al. have reported the preparation of cellulose acetate from low-grade wood dissolving pulps in general acetylation medium and found that an addition of appropriate solvent to acetylation medium was able to reduce insoluble residues in reaction solution.<sup>5,6</sup> However, a great amount of acetic acid, as well as sulfuric acid as catalyst, were employed in their studies.<sup>7</sup> Moreover, there was no report about the degree of polymerization (DP) and brightness of CA prepared. Although considerable effort has been made to find other sources of cellulose for CA preparation, up to now, these works still stop at the lab stage.

Bamboo, an abundant regenerative resource in Asia, is a kind of rapidly grown and early harvested vegetable with high adaptability, which can be felled every year for one hundred years after growing for 3 years. Unfortunately, bamboo is only employed in

Correspondence to: J. He (hejianxin771117@163.com).

Contract grant sponsor: Programme of Introducing Talents of Discipline to Universities, China; contract grant number: B07024.

Contract grant sponsor: Natural Science Research Program of Education Office of Henan Province of China; contract grant number: 2008A540005.

conventional fields such as furniture, construction, and the paper industry throughout the Asian region, and there are limited reports in the scientific literature concerning the use of bamboo pulp. Little research has focused on that bamboo pulps are used as reinforcing materials of composite or employed in paper making.<sup>8,9</sup> Recently, bamboo pulps have been utilized in preparing viscose fibers in some Asia countries, but there is no report about bamboo pulps used in CA preparation.

High-grade bamboo dissolving pulp with  $\alpha$ -cellulose content of more than 95% had been prepared from bamboo Cizhu (*Dendrocalamus affinis*) in our previous work.<sup>10</sup> In this study cellulose triacetate (CTA) was first synthesized from high-grade bamboo dissolving pulp in a general acetylation medium comprising acetic anhydride, acetic acid, and sulfuric acid, and the formation mechanism of insoluble residues in reaction solution were elucidated in this work. The effect of the addition of solvent to the acetylation medium on the reduction of insoluble residues and the improvement of the properties of prepared CTA was also studied. The investigation showed that high-quality CTA could be prepared from high-grade bamboo pulp in general medium with an addition of only 15% 1,2-dichloroethane.

## EXPERIMENTAL

### Materials

High-grade bamboo dissolving pulps were prepared from Cizhu (*D. affinis*) by prehydrolyzed kraft pulping and three stages of hydrogen peroxide bleaching with xylanase pretreatment and DMD pretreatment in our lab.<sup>10</sup> High-grade hardwood pulp used for commercial preparation of CA from Rayonier Inc. of Florida (USA), and viscose bamboo dissolving pulp prepared from bamboo Maozhu (*Phyllostachys pubescens*) from Shanghai Pulp Factory (China) were also used in experiments for comparison. All chemical reagents were of reagent grade and used without further purification.

### CTA preparation

CTA was prepared from the three pulps. The well-defibered pulps with a weight of 50 g were pretreated with 500 mL of acetic acid at room temperature; subsequently 250 mL acetic anhydride and 1.5 mL H<sub>2</sub>SO<sub>4</sub> were added and the pulps were acetylated for 80 min at 50°C.

To reduce the insoluble residue in reaction solution of high-grade bamboo pulp, a solvent was added to the control acetylation medium with acetic acid, acetic anhydride, and sulfuric acid. The pulp was first activated by stirring with a mixture of acetic acid and a

solvent with various solvent contents for 60 min at room temperature and subsequently acetylated under the same condition mentioned above,

$$\text{Solvent content} = \frac{V_{\text{solvent}}}{V_{\text{solvent}} + V_{\text{acetic}}} \times 100\% \quad (1)$$

where  $V_{\text{solvent}}$  (mL) is the volume of solvent added, and  $V_{\text{acetic}}$  (mL) is the volume of acetic acid.

The solutions obtained by acetylation were then spun in a centrifuge at 7000 rpm for 30 min to separate the soluble portion and the insoluble residue. The supernatant portions were pipetted out, and the precipitated mass was washed three times with fresh acetic acid by centrifugation; the obtained insoluble residue was stored separately. All supernatants were collected in a beaker, concentrated, and poured into deionized water to precipitate the soluble portion. The soluble and insoluble portions were washed three times with saturated NaCl solution for stabilization. The remaining NaCl was washed thoroughly with deionized water. Finally, these were washed with methanol and dried under vacuum for 12 h.

### Chemical analysis

DP of pulp samples was determined from the intrinsic viscosity  $[\eta]$  (mL/g) measured in a cupriethylene-diamine solution according to TAPPI T206, by the following formula:

$$\text{DP}^{0.905} = 0.75[\eta] \quad (2)$$

DP of CTA was calculated from the  $[\eta]$  (dL/g) measured in a mixture of dichloromethane and methanol (90/10, w/w) according to ASTM D-871-96, by the following formula:

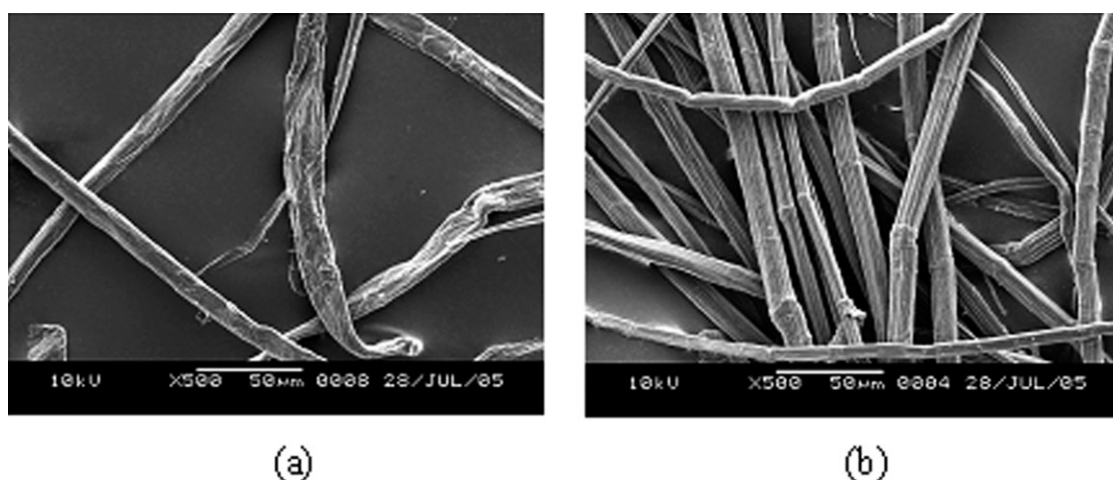
$$\text{DP} = 147[\eta]^{1.2} \quad (3)$$

The neutral sugar compositions were determined by an alditol-acetate procedure<sup>11</sup> with a Shimadzu GC-2010 gas chromatograph to which a 10% Silar-10C column (2 m) was attached. The carrier gas used was helium with a flow rate of 40 mL/min. An injection temperature of 260°C was set with a column temperature of 230°C.

The degree of substitution (DS) of CTA was determined by the titration method according to ASTM standard. Brightness of pulps and CTA produced were measured according to ISO 3688/2470. Other parameters of pulp samples were determined by using TAPPI standard methods.

### Measurement of transmittance of reaction solution

The obtained reaction solutions were subject to a photometric analysis to determine the degree of transmittance of the solution by the formula below



**Figure 1** SEM photographs of (a) high-grade hardwood pulp and (b) high-grade bamboo pulp.

with a monochromatic light of 670-nm wavelength on a Shimadzu recording spectrophotometer UV-365:

$$\text{Transmittance} = \frac{I_{\text{solution}}}{I_{\text{medium}}} \times 100(\%) \quad (4)$$

where  $I_{\text{solution}}$  and  $I_{\text{medium}}$  refer to the transmittances of the reaction solution and the acetylation medium without CTA, respectively.

#### Scanning electron microscopy and light microscopy

A JEOL JSM-5600LV electron microscopy with an accelerating voltage of 15 kV was used to study the morphology of bamboo and wood pulp fibers. A Carton optical microscope was used to observe insoluble residue in acetylation medium by placing the samples of reaction solution on glass slides.

#### FTIR spectroscopy

FTIR spectra of the samples were recorded with a Nicolet Nexus 670 FTIR spectrometer, using the KBr disc technique (1 mg power of samples/300 mg KBr). One hundred scans were taken with a resolution of  $2 \text{ cm}^{-1}$ .

#### X-ray diffractometry

X-ray diffraction was recorded at a scanning speed of  $0.02^\circ/\text{s}$  with a Rigaku-D/Max-2550PC diffractometer using Ni-filtered Cu  $K\alpha$  radiation with a wavelength of 0.1542 nm. The operating voltage and current were 40 kV and 30 mA, respectively.

#### Thermal analysis

Differential thermal gravimetry (DTG) and differential thermal analysis (DTA) were carried out by

using a Perkin-Elmer Diamond TG/DTA analyzer under nitrogen gas at a flow rate of 30 mL/min and a heating rate of  $10^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

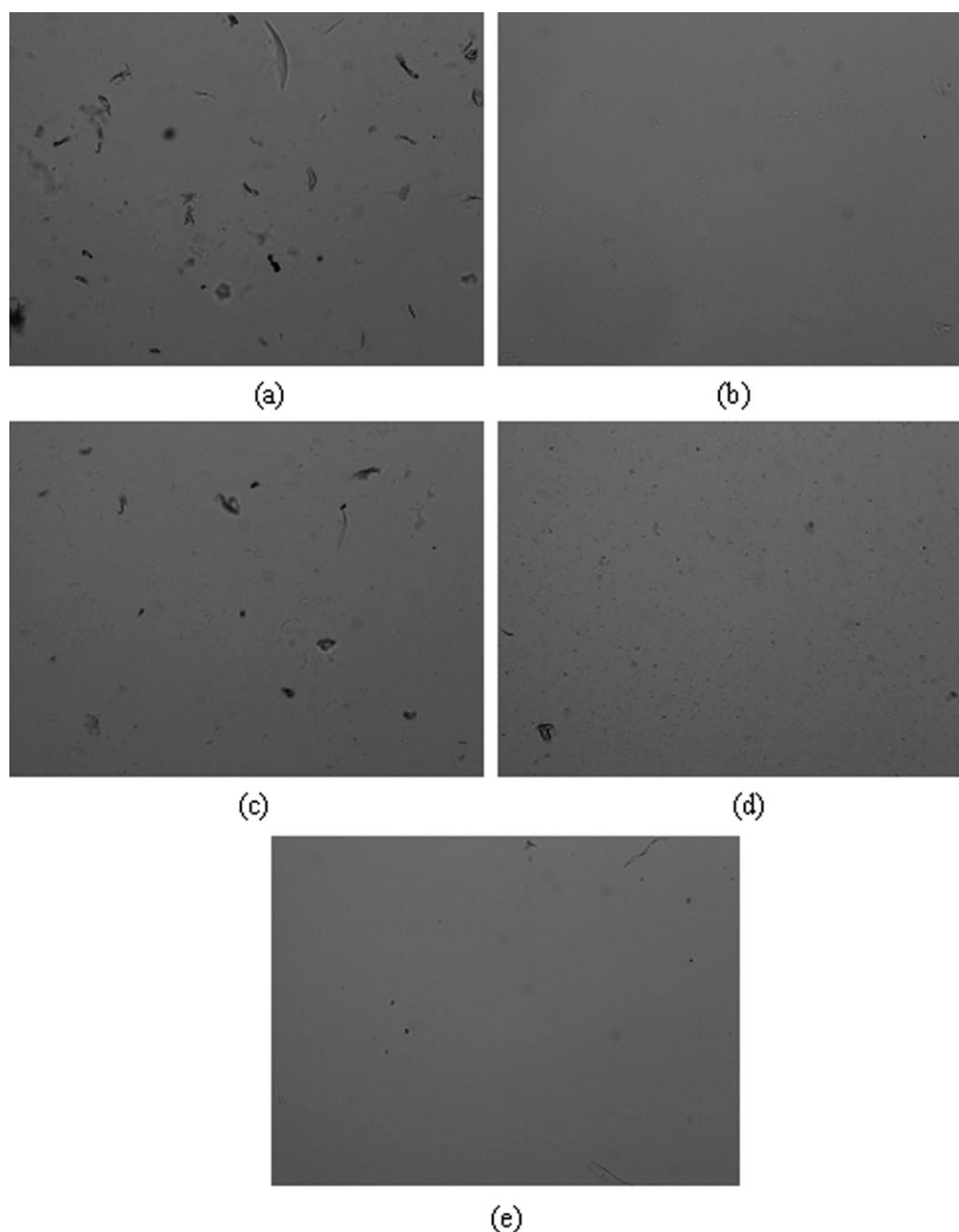
### Morphology and properties of pulps

High-grade wood dissolving pulps, especially hardwood pulp, are widely used commercially for preparing CA. As shown in Figure 1(a), hardwood pulp fiber is flat with no distinct nodes, while bamboo pulp fiber is long, cylindrical, and uniform in size with distinct nodes [Fig. 1(b)].

As compared with viscose bamboo pulps, high-grade bamboo pulps show the properties with prominent improvement, among which  $\alpha$ -cellulose content, DP, and brightness have been accessible to those of high-grade hardwood pulp (Table I). However, two important parameters affecting acetylation, xylan content and ash content, are more than several times those of high hardwood pulps, and this is

**TABLE I**  
Comparison of Chemical Composition and Physical Properties of High-Grade Bamboo Pulp with High-Grade Hardwood Pulp and Viscose Bamboo Pulp

Parameters	High-grade bamboo pulp	High-grade hardwood pulp	Viscose bamboo pulp
Alpha cellulose (%)	96.24	98.20	85.43
Degree of polymerization	1021	1134	512
DCM extractive (%)	0.08	0.013	0.22
Xylose (%)	3.9	1.3	6.8
Mannose (%)	0	0.3	0
Brightness (%)	88.4	92.7	75.5
Ash (%)	0.10	0.02	0.22
Moisture (%)	6.70	6.81	6.96
Crystallinity (%)	58.27	54.92	52.08
Crystallite size (nm)	6.10	5.85	5.33



**Figure 2** Light micrographs of insoluble residue in acetylation medium of (a) viscose bamboo pulp, (b) high-grade hardwood pulp, and (c) high-grade bamboo pulp without solvent addition, as well as in acetylation medium of high-grade bamboo pulp with an addition of (d) 5% and (e) 15% 1,2-dichloroethane.

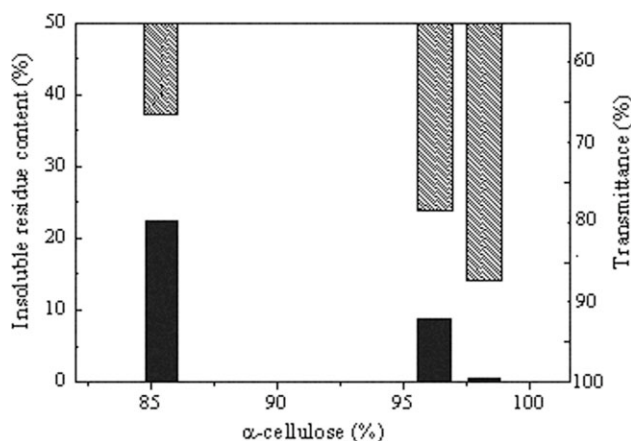
likely associated with the fact that bamboo is a herbaceous plant.<sup>12</sup> In addition, crystallinity and crystallite size in high-grade bamboo pulp are greater than those in other two pulps.

#### Insoluble residues in acetylation medium

Observations by optical microscope revealed that for two bamboo pulps some of fibrous matter remained in acetylation medium comprising acetic anhydride, acetic acid, and sulfuric acid [Fig. 2(a,c)], whereas

for high hardwood pulp no any insoluble residue was found [Fig. 2(b)]. In contrast with viscose bamboo pulp with an insoluble residue content of 22.4%, the insoluble residue in acetylation medium of high-grade bamboo pulp evidently reduced (8.7%) with an increase of  $\alpha$ -cellulose (Fig. 3); however, high-grade bamboo pulp resulted in insoluble residue more than almost 20 times that of high-grade hardwood pulp, which was negligible (0.44%).

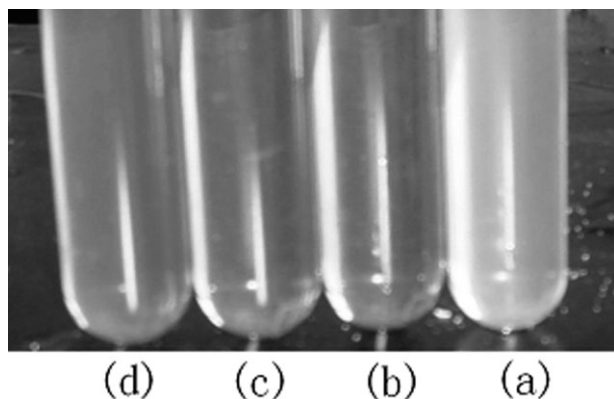
The transmittance is inversely dependent on the content of insoluble residues in reaction solution



**Figure 3** Relationship between  $\alpha$ -cellulose contents of the three pulps and the amount of insoluble residues in acetylation medium, as well as the transmittances of reaction solutions.

because of the light scattering by the insoluble residues. As shown in Figure 3, there was still a considerable difference in the transmittances of reaction solutions between high-grade bamboo pulp and hardwood pulp, although the transmittance of high-grade bamboo pulp had been improved obviously compared with that of viscose bamboo pulp. This can be seen from the reaction solution photographs of the three pulps presented in Figure 4. The reaction solution of high-grade bamboo pulp was rather turbid in contrast with that of high-grade hardwood pulp.

Properties of CTA prepared from the three pulps, which were acetylated under the same conditions in acetylation medium without solvent addition, are listed in Table II. Insoluble residues in reaction solution also resulted in the lowering of CTA brightness synthesized from the two bamboo pulps. The bright-



**Figure 4** Reaction solutions of (a) high-grade hardwood pulp, (b) high-grade bamboo pulp, (d) viscose bamboo pulp acetylated in acetylation medium without solvent addition, as well as (c) high-grade bamboo pulp acetylated in acetylation medium with an addition of 15% 1,2-dichloroethane.

**TABLE II**  
Properties of CTA Prepared from Three Pulps in Acetylation System Without Solvent Addition and from High-Grade Bamboo Pulp in Acetylation Medium with an Addition of Solvent

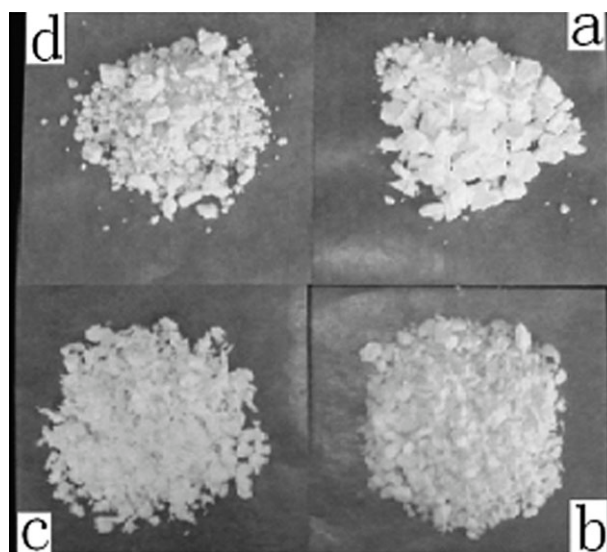
Pulps	DP	DS	Brightness
High-grade bamboo pulp	164	2.90	83.6
High-grade hardwood pulp	145	2.97	93.2
Viscose bamboo pulp	123	2.88	74.3
High-grade bamboo pulp <sup>a</sup>	158	2.93	90.4

<sup>a</sup> Acetylation in acetylation medium with 15% 1,2-dichloroethane.

ness of CTA prepared from high-grade bamboo pulp had been improved as compared with that of CTA from viscose bamboo pulp, which was russet in appearance [Fig. 5(d)]; however, it was less than about 9.6% that of CTA prepared from high-grade hardwood pulp, which was white, while CTA prepared from high-grade bamboo pulp was yellowish [Fig. 5(a,b)]. A lower DP for CTA synthesized from high-grade hardwood pulp, as shown in Table II, is likely because of the lower crystallinity and crystallite size in the pulp.

#### Effect of solvent addition on the amount of insoluble residue in the acetylation medium of high-grade bamboo pulp

Chemical compositions of the insoluble residues of the two bamboo pulps in the reaction solution without solvent addition are given in Table III. It is apparent that, in addition to glucose, the residues



**Figure 5** CTA prepared from (a) high-grade hardwood pulp, (b) high-grade bamboo pulp, and (d) viscose bamboo pulp in acetylation medium without solvent addition, as well as from (c) high-grade bamboo pulp in acetylation medium with 15% 1,2-dichloroethane.

**TABLE III**  
**Chemical Composition of Insoluble Residue in Acetylation Solution of Viscose Bamboo Pulp and High-Grade Bamboo Pulp**

Pulps	Solvent content (%)	Weight fractions (%)	Chemical compositions (%)		
			Glucose	Xylose	Ash
Viscose bamboo pulp	0	22.4	73.8	25.4	0.8
High-grade bamboo pulp	0	8.7	64.3	34.7	1.0
High-grade bamboo pulp	5	4.4	31.8	66.3	1.9
High-grade bamboo pulp	10	1.5	10.6	82.9	6.5

contained a high proportion of xylose. This indicates that XDA was involved in the formation of insoluble residue in acetylation medium of bamboo pulp. Acetic acid, a major part of acetylation medium, is known not to be a good solvent for either CTA or HCA, especially for the HCAs such as GTA and XDA, which are almost insoluble.<sup>13</sup> In the study on CTA prepared from low-grade wood pulps, Saka et al. considered the information of insoluble residue as the result of these insoluble HCA in aggregation with CTA by the physicochemical effects of the molecular interactions of HCA and CTA, as well as by the ultrastructural effects of pulp fibers.<sup>5,7</sup>

These HCAs can be preferably degraded when running hydrolysis under acidic conditions leading to cellulose diacetate prepared from CTA by hydrolysis with sulfuric acid as catalyst having no or a small aggregate,<sup>14</sup> especially for high-grade bamboo pulps, which have a lower content of xylan (3.9%). The experimental results of brightness and particle distribution in acetone also indicated that cellulose diacetate (DS = 2.5) prepared from high-grade bamboo pulps had a higher quality accessible to that prepared from high-grade hardwood pulp (no shown).

However, for CTA obtained by acetylation of high-grade bamboo pulp, these aggregates including XDA decrease its properties. To reduce the amount of insoluble residues in acetylation medium, it is necessary to add good solvent of HCA to acetylation medium to decrease the two effects as mentioned above.

In this work, the selected solvents, as shown in Table IV, were added to acetylation medium to study the effects of solvent addition on the reduction of insoluble residues in acetylation medium of high-grade bamboo pulp. The acetylation system with acetic acid was also included just for comparison as a control reaction system without any additional solvent.

Table IV presented insoluble residue content in acetylation medium with 15% solvent and corresponding transmittance of reaction solution. It is obvious that, compared with an insoluble residue content of 8.7% in a control reaction system of acetic acid, the results in acetylation medium with various solvents are varied from 0.69 to 15.44%, while the corresponding transmittances are varied from 76.83

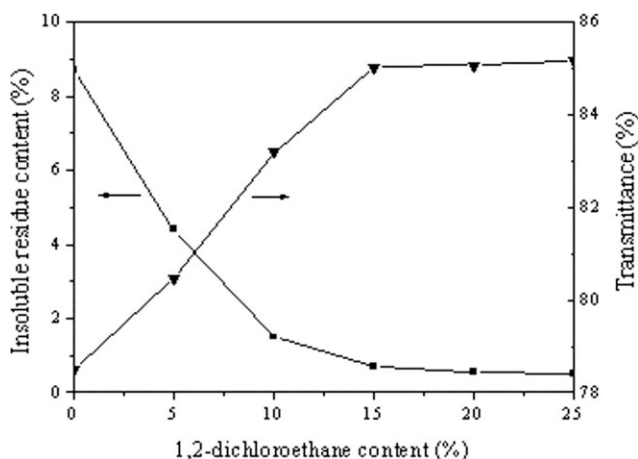
to 85.03%, indicating a large effect of solvent addition on the amount of insoluble residue in reaction solution of high-grade bamboo pulp. The additions of dichloromethane, nitromethane, or chloroform to acetylation medium were effective for reducing insoluble residues in reaction solution, but the most effective solvent was 1,2-dichloroethane.

The effect of the content of 1,2-dichloroethane on the amount of insoluble residue in acetylation medium and the transmittance of reaction solution was further investigated, as shown in Figure 6. With an increase of solvent content, transmittance of reaction solution was improved; on the other hand, the amount of insoluble residue in acetylation was decreased markedly, and when solvent content was beyond 15%, it was constant for the transmittance and negligible for the insoluble residue, indicating a mutual dissolution of CTA and XDA at the molecular level and the complete releasing of the aggregation existing in acetylation medium without an addition of solvent.

The dissolution of insoluble residue in acetylation medium with an addition of 1,2-dichloroethane was observed by light microscope. The fibrous matter in control acetylation medium of high-grade bamboo pulp without additional solvent began to be dissolved into tiny spots dispersed over reaction solution after 5% solvent was added [Fig. 2(c,d)]. As the added solvent increased to 15%, almost no insoluble

**TABLE IV**  
**Transmittance and Insoluble Residue Content in Acetylation Medium of High-Grade Bamboo Pulp with an Addition of Solvent**

Solvent	Solubility parameter [(MPa) <sup>1/2</sup> ]	Transmittance (%)	Insoluble residue (%)
Acetic acid	20.7	78.50	8.7
Dichloromethane	19.8	81.27	3.24
Bromobenzene	20.3	81.65	7.83
Ethyl bromide	19.6	75.81	15.44
Nitromethane	26.0	81.98	3.50
Nitroethane	22.7	76.83	10.44
1,2-Dichloroethane	18.2	85.03	0.69
Chloroform	19.0	82.14	2.71
Nitrobenzene	20.5	84.22	1.04
Toluene	21.5	77.68	9.57



**Figure 6** The effect of 1,2-dichloroethane content on the amount of insoluble residue in acetylation medium of high-grade bamboo pulp and the transmittance of reaction solution.

residue in acetylation medium was observed [Fig. 2(e)]; on the other hand, the reaction solution became more transparent, as seen in Figure 4(c). Figure 5(c) displays the CTA prepared in acetylation medium with an addition of 15% 1,2-dichloroethane, brightness of which was improved and exceeded 90% (Table II), approaching that of CTA prepared from high-grade wood pulp in control reaction system.

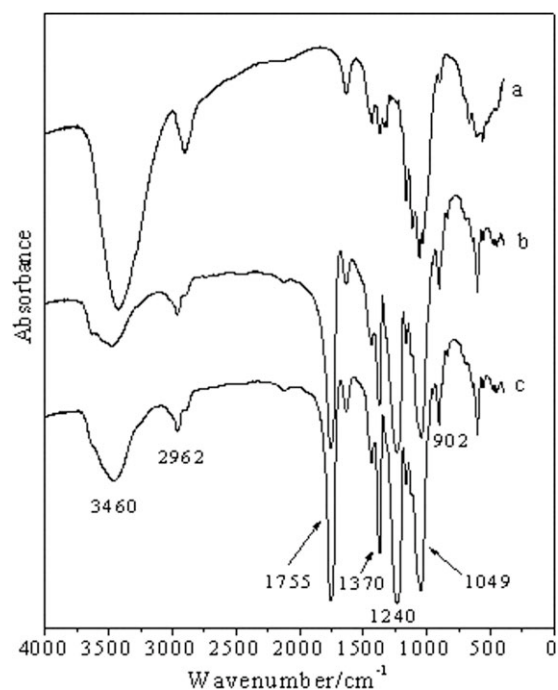
Because bamboo belongs to the herbaceous plants family, not including glucomannan, the insoluble residue in reaction solution of bamboo pulp is composed of XDA and CTA (Table III). A discovery is that with an increase of the content of 1,2-dichloroethane, the amount of insoluble residue in reaction solution of high-grade bamboo pulp was reduced, while the XDA content in the insoluble residue enhanced greatly, just the reverse for the CTA content (i.e., the ratio of CTA to XDA decreased apparently, indicating that the mutual interaction between CTA and XDA molecules is much weaker). Therefore, the formation of insoluble residue in reaction solution of high-grade bamboo pulp is mostly due to the ultrastructural effects of pulp fibers, which originate from ultrastructural distribution of residual xylan in the dissolving pulp.<sup>5</sup> Because of poor solubility in acetylation solution, XDA tended to precipitate and CTA was involved in the precipitate due to the ultrastructural effects of pulp fibers. Moreover, a higher proportion of ash was found in the insoluble residue of high-grade bamboo pulp, and the ash content increased largely with the decrease of the amount of insoluble residue in acetylation medium, showing that a majority of ash in the pulp was shifted to the insoluble residue (Table III). The insoluble ash likely acted as a “crystalline nucleus” for the aggregation of XDA and CTA; as a result, higher ash content in high-grade bamboo

pulp contributed to the formation of the insoluble residue in acetylation solution too. In the experiment carried out by Shashidhara et al., CTA was prepared from local low-grade wood pulps and they found that for the pulps with higher ash content more insoluble residue remained in acetylation solution even though they had a greater  $\alpha$ -cellulose content and lower hemicellulose content.<sup>15</sup>

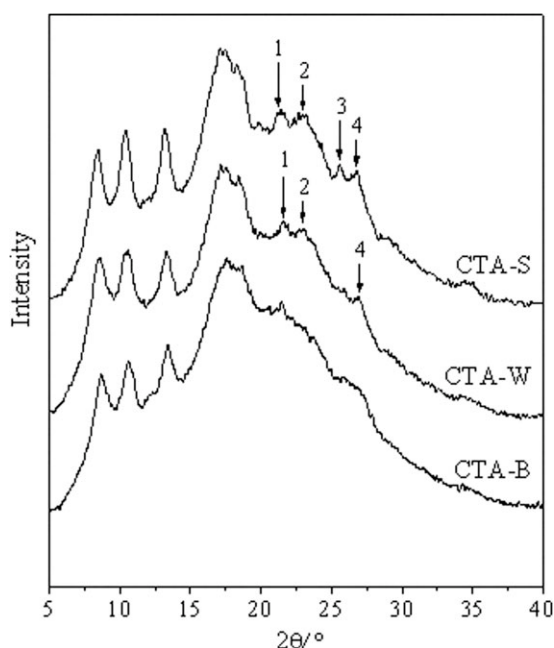
The analysis of chemical composition of the pulps has indicated a xylose content of 3.9% in high-grade bamboo pulp. Thus, the amount of xylose in the soluble part was also calculated according to the data presented in Table III. As solvent content in acetylation medium increased to 10%, the amount of xylose in the soluble part increased from 0.9% in control acetylation medium to 2.7% (total xylose content, 3.9%). This demonstrated that most XRD, which had formed insoluble residue in acetylation medium, was no longer involved in its formation and had moved into the soluble part. Therefore, the improvement of the brightness for CTA prepared from high-grade bamboo pulp in acetylation medium with an addition of solvent (Table II and Fig. 5) was not due to the removal of XRD from acetylation medium but depended on its dissolving state.

#### FTIR spectra characterization

As illustrated in Figure 7, infrared spectra proved the formation of CTA after high-grade bamboo pulp



**Figure 7** FTIR spectra of (a) high-grade bamboo pulp and (b) CTA prepared from it in acetylation medium with 15% 1,2-dichloroethane, as well as (c) CTA prepared from high-grade hardwood pulp in control acetylation medium.



**Figure 8** X-ray diffractograms of CTA prepared from high-grade bamboo pulp (CTA-B) and high-grade hardwood pulp (CTA-W) in control acetylation medium, as well as from high-grade bamboo pulp (CTA-S) in *n*-acetylation medium with 15% 1,2-dichloroethane.

was acetylated in the acetylation medium with 15% of 1,2-dichloroethane, because it shows a similar spectrum to that of CTA prepared from high-grade hardwood pulp in control reaction system. As compared with the infrared spectrum of high-grade bamboo pulp, evidence of acetylation of the pulp in acetylation medium with an addition of solvent is provided by the increase of the intensity of the bands related to the acetyl group at  $1754\text{ cm}^{-1}$ , attributed to C=O stretching,  $1245\text{ cm}^{-1}$  attributed to C—O stretching of acetyl group, and  $1375\text{ cm}^{-1}$  attributed to C—H bending in the methyl of acetyl group. Moreover, the lowering of the absorbance of the OH stretching band in the region of  $3100\text{--}3750\text{ cm}^{-1}$  also presents further evidence of acetylation,<sup>16</sup> and the wavenumber at the maximum absorbance of the pulp in this region shifts from  $3425\text{ cm}^{-1}$  up to  $3460\text{ cm}^{-1}$  after acetylation in the medium with an addition of solvent, indicating OH stretching was induced primarily by water molecules.

#### X-ray diffraction analysis

CTA prepared from high-grade bamboo pulp in acetylation medium with 15% of 1,2-dichloroethane (CTA-S) and from high-grade hardwood pulp (CTA-W) and high-grade bamboo pulp (CTA-B) in control acetylation medium without an addition of solvent were studied by X-ray diffraction; the results are

shown in Figure 8. The three samples reveal a similar X-ray diffraction curve attributed to the crystalline modification of CTAII.<sup>17</sup> However, it can be found by further observation that the curve of CTA-W appears highly resolved compared with that of CTA-B. The three diffraction peaks in the range of  $8^\circ\text{--}14^\circ$  and the principal peak at  $17.12^\circ$  for CTA-W display a higher intensity than these for CTA-B, and the three escape peaks marked with the number 1, 2, and 4 in the curve of CTA-W can be resolved clearly, while they cannot in the curve of CTA-B, suggesting that the insoluble XDA in the control acetylation system of high-grade bamboo pulp can affect the crystallization of CTA prepared despite its lower content. This was also proven by the calculating results for crystallite sizes, as shown in Table V; CTA-B has minimal values of crystallite sizes except the lattice plane at  $2\theta$  of  $10.42^\circ$ .

As mentioned above, with an addition of good solvent for XDA such as 1,2-dichloroethane, the aggregation of XDA and CTA existing in acetylation medium of high-grade bamboo pulp was released and the molecules of XDA and CTA were separated completely. This is favorable for forming a perfect crystalline structure of CTA during precipitation, which was demonstrated by X-ray diffraction. CTA-S shows a most resolved diffraction profile, in which the three sharpest peaks with the minimal full width half-maximum appear in the range of  $8^\circ\text{--}14^\circ$ . In the X-ray diffraction profile of CTA-S, not only three peaks marked with the number 1, 2, and 4 can be resolved distinctly but also a peak signed with number 3 appears. As compared with CTA-B, marked increase in crystallite sizes provided further evidence of more perfect crystalline structure for CTA-S.

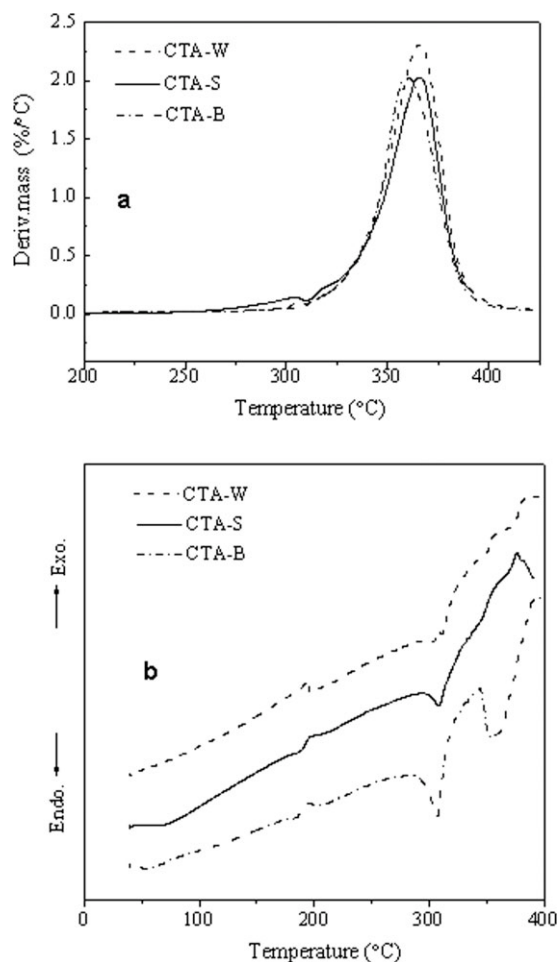
#### Thermal analysis

DTG analysis under nitrogen indicates the improvement of thermal stability for CTA prepared from high-grade bamboo pulp in acetylation medium with 15% 1,2-dichloroethane, because compared with CTA-B the maximum peak position in DTG

**TABLE V**  
Crystallite Size of CTA Prepared from High-Grade Bamboo Pulp in Acetylation Medium with 15% of 1,2-Dichloroethane (CTA-S) and from High-Grade Hardwood Pulp (CTA-W) and High-Grade Bamboo Pulp (CTA-B) in Control Acetylation Medium

	Crystallite size (nm)			
$2\theta$ ( $^\circ$ )	8.48	10.42	13.16	17.12
CTA-B	3.60	4.87	3.01	2.35
CTA-W	3.97	4.80	4.10	3.41
CTA-S	5.31	5.67	5.60	3.42





**Figure 9** DTG (a) and DTA (b) curves of CTA prepared from high-grade bamboo pulp (CTA-B) and high-grade hardwood pulp (CTA-W) in control acetylation medium, as well as from high-grade bamboo pulp (CTA-S) in *n*-acetylation medium with 15% 1,2-dichloroethane.

curve of CTA-S shifts from 360 up to 366°C and overlaps with the peak position of CTA-W [Fig. 9(a)]. As shown in Figure 9(b), CTA-S shows a similar DTA curve to that of CTA-W, where an endothermic loop below 80°C is associated with moisture evaporation; as well as an exothermic peak at 196°C and an endothermic peak at 308°C, respectively, correspond to the peak of crystallization and melting of CTA.<sup>18</sup> As compared to CTW-B, the two peaks corresponding crystallization and melting of CTA-S shifted to a higher temperature. However, an evident endothermic peak appears at 355°C in the DTA curve of CTA-B prepared from high-grade bamboo pulp in acetylation medium without solvent addition, while in the curve of CTA-W and CTA-S the peak is inconspicuous because of the narrow interval between the melting and decomposition temperature and the overlap of the two peaks in CTA-W and CTA-S. Owing to less perfect and smaller crystallites

in CTA-B, which are induced by insoluble XDA in the acetylation system, more facile motility for the molecule chains or chain segment within its crystalline region resulted in the melting peak appearing in a lower temperature, and the interval between the melting and decomposition temperature enlarged. Accordingly, the endothermic peak corresponding to decomposition temperature can be observed in the DTA curve of CTA-B.

By an addition of 1,2-dichloroethane to acetylation medium, CTA prepared from high-grade bamboo pulp may also be improved in its thermal property even if XDA is not removed from reaction solution because of a complete solubilization of the insoluble residue.

## CONCLUSIONS

Although the properties of CTA prepared from high-grade bamboo pulp in general acetylation medium of the acetic acid/acetic anhydride/sulfuric acid system had been improved compared with these of viscose bamboo pulp, abundant insoluble residue in its acetylation medium could be observed by light microscope, which resulted the decrease of the transmittance of reaction solution and the brightness of CTA prepared as compared to these of high-grade hardwood pulp. The insoluble residue of high-grade bamboo pulp is composed of XDA and CTA because of a poor solubility of XDA in acetylation medium, which tends to precipitate from acetylation medium and CTA is involved in the precipitation due to the ultrastructural effects of the pulp fibers. The aggregation of XDA and CTA can be released and the insoluble residue can be reduced evidently with the addition of a good solvent such as 1,2-dichloroethane to acetylation medium. This was proved by the observation of light microscope. Therefore, the brightness of CTA prepared from high-grade bamboo pulp could be improved after adding solvent to the acetylation medium. In addition, because of the improvement of the dissolving state of XDA in acetylation medium with an addition of solvent, a more perfect crystalline structure of prepared CTA was shown in the X-ray diffraction profile and thermal analysis indicated its thermal stability was also enhanced.

## References

1. Saka, S.; Matsumura, H. *Macromol Symp* 2004, 208, 37.
2. Funaki, Y.; Ueda, K.; Saka, S.; Soejima, S. *J Appl Polym Sci* 1993, 48, 419.
3. Neal, J. L. *J Appl Polym Sci* 1965, 9, 947.
4. Barkalow, D. G.; Rowell, R. M.; Young, R. A. *J Appl Polym Sci* 1989, 37, 1009.

5. Saka, S.; Takanashi, K.; Matsumara, H. *J Appl Polym Sci* 1998, 69, 1445.
6. Saka, S.; Ohmae, K. *J Appl Polym Sci* 1996, 62, 1003.
7. Saka, S.; Takanashi, K. *J Appl Polym Sci* 1998, 67, 289.
8. Tommy, Y. L.; Cui, H. Z.; Leung, H. C. *Mater Lett* 2004, 58, 2595.
9. Okubo, K.; Fujii, T.; Yamamoto, Y. *Compos A* 2004, 35, 377.
10. He, J. X.; Cui, S. Z.; Wang, S. *J Appl Polym Sci* 2008, 107, 1029.
11. Borchardt, L. G.; Piper, C. V. *TAPPI* 1970, 53, 257.
12. Scurlocka, J. M. O.; Daytonb, D. C.; Hamesb, B. *Biomass Bioenergy* 2000, 19, 229.
13. Gardner, P. E.; Chang, M. Y. *TAPPI* 1974, 57, 71.
14. Steinmeier, H. *Macromol Symp* 2004, 208, 49.
15. Shashidhara, G. M.; Guruprasad, K. H. *J Appl Polym Sci* 2005, 98, 176.
16. Adebajo, M. O.; Frost, R. L.; Kloprogge, J. T.; Kokot, S. *Spectrochim Acta A* 2006, 64, 448.
17. Ryskina, I. I.; Fedorova, I. Y. *Polym Sci* 1986, 28, 680.
18. Kamide, K.; Saito, M. *Polym J* 1985, 17, 919.