

ISOLATION AND CHARACTERIZATION OF ACETONE-INSOLUBLE SUBSTANCES IN CELLULOSE ACETATE PREPARED BY AN ACETIC ACID ACETYLATION PROCESS

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Cellulose acetate fibers are commonly made by a dry-spinning process, in which cellulose acetate is firstly dissolved in acetone and then the cellulose acetate acetone solution is extruded through spinneret orifices that have extremely small diameters. Any insoluble substances in acetone solutions could cause disruptions in fiber extrusion, and are not tolerated. In this work, acetone-insoluble substances in cellulose acetates prepared from several kinds of pulps with varying cellulose content were isolated by ultracentrifugation, and characterized by using chemical, spectroscopic and chromatographic techniques. According to the results, acetone-insoluble substances are enriched in hemicellulose acetates, lower in the degree of substitution and higher in crystallinity in comparison with corresponding cellulose acetates. Based on analysis, a possible mechanism for the formation of insoluble substances is proposed. Hemicelluloses residues in pulps and insufficient acetylation of crystalline cellulose play important roles in forming the insoluble substances in cellulose acetate acetone solutions.

Keywords: cellulose acetates, insoluble substances, formation mechanism

INTRODUCTION

Cellulose acetate (CA), one of the most commercially important cellulose derivatives, has been utilized in a wide variety of applications, such as coatings, fibers, optical films, filtration membranes, composites, laminates, and medical and pharmaceutical products.¹⁻⁶ Among these applications, cellulose acetate fibers are commonly spun from acetone solutions in a so-called “dry extrusion process”, in which cellulose acetate is firstly dissolved in acetone and then the cellulose acetate solution is extruded through spinneret orifices that have extremely small diameters and spun in hot air with resultant acetone vaporization and cellulose acetate coagulation. Any insoluble substances in polymer solutions would reduce the filterability, cause disruptions in fiber extrusion and are not tolerated, and these industrial problems should be even worse when some low-grade cellulose resources are used to make cellulose acetate.⁷⁻⁹ Therefore, it seems quite important to investigate

the compositions and formation of insoluble substances in cellulose acetate solutions. Some literatures have reported researches on the insoluble substances in cellulose acetate solutions.¹⁰⁻¹⁶ For example, Russo *et al.* prepared cellulose acetate from lower purity wood pulps and characterized the soluble and insoluble fractions of cellulose acetate in acetone. Ueda *et al.* characterized the acetone-insoluble substances in cellulose acetate and proposed a possible model of the gel in acetone, indicating that the gel is in molecular aggregates of cellulose acetates with regions of cellulose diacetate and cellulose triacetate I. Fleury *et al.* analyzed the solutions of cellulose diacetate by size exclusion chromatography, and characterized the series of humps in the chromatogram. In spite of their pioneering works, the exact nature of acetone-insoluble substances is not fully understood, and little related literature has been published in recent years.

In this work, cellulose acetates were prepared by an acetic acid acetylation/ripening process from several different pulps with varying cellulose content. Acetone-insoluble substances in the cellulose acetates were collected by ultracentrifugation, and characterized by using chemical, spectroscopic and chromatographic techniques, such as titration method, ion chromatography (IC), nuclear magnetic resonance (NMR), X-ray diffraction (XRD) etc. Based on analysis, influences of hemicelluloses and the degree of substitution (DS) on the formation of acetone-insoluble substances are discussed, and a possible mechanism for the formation of insoluble substances is proposed in this article, which can help us understand what the acetone-insoluble substances are, how they form and how to reduce them. This is beneficial to cope with the industrial problems in the spinning process and is meaningful for enabling the use of low-grade cellulose resources, such as bamboo fibers and agricultural by-products.

EXPERIMENTAL

Materials

Cotton linter, Rayonier hardwood pulp, Borregaard softwood pulp and paper pulp have been purchased commercially. Their main components are shown in Table 1. Acetic anhydride, acetic acid, sulfuric acid, and anhydrous magnesium acetate have been purchased from Nanjing Chemical Reagent Co., Ltd. All above materials were used without purification.

Cellulose acetates preparation and insoluble substances isolation

Cellulose acetates have been prepared by an acetic acid process with several different pulps,¹⁸ cotton linter (C-CA), Rayonier hardwood pulp (R-CA), Borregaard softwood pulp (B-CA) and paper pulp (P-CA). In this acetic acid process, a pulp (1 part) is firstly swelled in acetic acid (0.4 parts) at room temperature, and then acetylated to cellulose triacetate with acetic anhydride (3 parts) in the presence of sulfuric acid (0.07-0.15 parts) as catalysts at 40-55 °C for 1 hour. After neutralization of sulfuric acid, a ripening is done with the addition of water to make cellulose acetate with a degree of substitution of approximately 2.4 in 2-3 hours. Then, the solution is poured into distilled water to precipitate the cellulose acetate. Finally, the resulting cellulose acetate is washed thoroughly with distilled water and dried in a vacuum oven at 60 °C for about 24 hours.

To isolate insoluble substances, the obtained cellulose acetate is dissolved in acetone to prepare a

3.0% solution. The solution is then transferred into ultracentrifugation tubes and spun in a Sigma 3-18K Sartorius high speed centrifuge at 10000 rpm for 2-3 hours at 5 °C to collect acetone-insoluble substances. The obtained insoluble substances are washed with acetone 3 times and dried at 60 °C for 24 hours prior to characterization.

Characterization

Solution properties

Haze measurements of the cellulose acetate acetone solutions and the supernatant after centrifugation were performed on a spectrophotometric colorimeter at room temperature. In addition, the undissolved micro-particles and their diameters in solution were analyzed with a HIAC/ROYCO 3000A (Mcount-200/MC-05) particle sizer.

Ion Chromatography

The compositions of different sugars in pulps, cellulose acetates and the corresponding acetone-insoluble substances were analyzed with Ion Chromatography (DIONEX ICS-5000). Firstly, pulp samples were fluffed in a blender, cellulose acetates and acetone-insoluble substances samples were ground into powder, and dried overnight. Then a hydrolysis process was carried out as follows: a sample prepared above (0.355±0.005 g) was immersed in 3.0 ml 72% sulfuric acid with periodical agitation in a 30 °C water bath for 2-3 hours, until the sample was dissolved. After the sample was removed from the water bath, 84.0 ml of deionized water was added to the sample, and then heated in an autoclave at 120 °C for 10 minutes. After the sample was cooled to room temperature, a 50% sodium hydroxide solution was added to neutralize the sulfuric acid, and then the sample was filtered with a 0.45 micron ion chromatography filter. The filtrate was analyzed with a Dionex ICS 5000, using a CarboPac PA20 analytical column.

Degree of substitution

Degrees of substitution of cellulose acetates prepared from several different pulps were determined by a titration method. Firstly, a sample of 2 g dried powder was dissolved into 150 ml acetone with periodical agitation. Subsequently, 30 ml sodium hydroxide solution (1 mol/L) was added and the resulting solution was kept at 25 °C for 30 minutes. Then the solution was titrated with 0.5 mol/L sulfuric acid solution with a small amount of phenolphthalein as an indicator until the red color faded to obtain a volume of sulfuric acid (A). A blank experiment was also tested to obtain the volume of sulfuric acid (B). The mass of acetic acid and degree of substitution of cellulose acetate were calculated from the following

equations:

$$AV = (B - A) \times C_{\text{H}_2\text{SO}_4} \times 0.06005 \times 100 / W$$

$$DS = 162.14 \times AV / (6005 - 42 \times AV)$$

where AV is acetic acid content of cellulose acetates (%), A is the volume of sulfuric acid for cellulose acetates (ml), B is the volume of sulfuric acid for blank (ml), $C_{\text{H}_2\text{SO}_4}$ is the concentration of sulfuric acid (mol/L), W is the weight of sample in grams (g).

DS of acetone-insoluble substances were

determined by ^1H nuclear magnetic resonance spectra. Insoluble substances were first reacted with propionic anhydride using pyridine as solvents for 24 hours in order to convert hydroxyl groups on the molecules of the insoluble substances to propionyl groups. ^1H nuclear magnetic resonance spectra were recorded of the reaction product on a Varian Unity spectrometer in chloroform- d at room temperature with tetramethylsilane as an internal standard.

Table 1
Main components of four pulps

Pulps	Cotton linter	Hardwood pulp	Softwood pulp	Paper
α -Cellulose content	~98%	~97%	~95%	~80%
Hemicelluloses content	~2%	~3%	~5%	~20%

X-ray diffraction analysis

X-ray diffraction was used to investigate the crystallographic nature of pulps, cellulose acetates prepared from four different pulps and corresponding acetone-insoluble substances by a Bruker D8 ADVANCE (Cu-K α , $\lambda = 0.154$ nm) at 40 kV and 40 mA with a scanning speed of $0.02^\circ \text{ min}^{-1}$ and scanning angle range of 5° - 40° .

RESULTS AND DISCUSSION

Solution properties

The solution properties of cellulose acetate in acetone were characterized by haze and particle size before and after ultracentrifugation. The results of the haze measurement are shown in Table 2. The haze value of the solutions decreased sharply after centrifugation, indicating that the vast majority of hazy substances were separated by ultracentrifugation. In addition, the haze values of cellulose acetate solutions before centrifugation showed a positive correlation with the hemicelluloses contents in the pulps used to make the cellulose acetates. For example, the P-CA (cellulose acetate from paper pulp) solution was much hazier than the other cellulose acetate solutions, due to the higher hemicelluloses content in the paper pulp than in the other pulps used in this study.

The same tendency was observed by the particle size measurement. Undissolved particles and their size distribution in cellulose acetate acetone solutions before and after centrifugation are shown in Table 3. It can be seen that the number of undissolved micro-particles decreased significantly in a broad size range from 2 μm to 75 μm . The particles of the P-CA acetone solution

before centrifugation were not investigated because the solution was too hazy to be measured.

The results of the particle measurement are in good agreement with the haze measurement, and this confirmed that ultracentrifugation is an effective method for the separation and collection of the acetone-insoluble substances in cellulose acetate solutions.^{10,11}

Percentage of insoluble substances in cellulose acetates

The collected acetone-insoluble substances were weighed and the percentage of insoluble substances was calculated by the weight of insoluble substances divided by the weight of cellulose acetates used for collecting insoluble substances, as shown in Table 4. It is apparent that the amount of residual hemicelluloses in pulp is related to that of insoluble substances in acetone. More hemicelluloses in pulps result in higher content of insoluble substances in cellulose acetates. This suggests that residual hemicelluloses in pulps play an important role in the formation of acetone-insoluble substances in cellulose acetate. This result is consistent with the conclusion of previous reports.^{12,17}

Analysis of natural sugar compositions

Natural sugar compositions of pulps, cellulose acetates and the corresponding acetone-insoluble substances were analyzed by Ion Chromatography, as shown in Table 5. It can be seen that the glucose content of the cellulose acetates is slightly higher than that of the pulps, which may be owing to the degradation of hemi-

celluloses in the acetylation process. Comparing the sugar compositions in Table 5, it can be clearly seen that the content of hemicelluloses in the acetone-insoluble substances is much higher than that in the corresponding cellulose acetates (the hemicelluloses content is estimated by the sum of the xylose and mannose contents). The enrichment of hemicelluloses in the insoluble substances is clear evidence that hemicellulose

acetates have poor solubility in acetone. Hemicellulose acetates formed by acetylation of hemicelluloses residues in pulps are difficult to dissolve in acetone and result in haze and undissolved particles in the acetone solutions. Hemicelluloses in pulps play an important role in the formation of insoluble substances in acetone solutions. This result is again consistent with the conclusion of previous reports.

Table 2
Haze value of cellulose acetate acetone solutions before and after centrifugation

Haze	C-CA	R-CA	B-CA	P-CA
Before	8.6	9.8	11.7	94.4
After	1.4	1.4	1.3	15.2

Table 3
Particles and their size distribution in cellulose acetate acetone solutions before and after ultracentrifugation

Samples		2 μm	5 μm	10 μm	25 μm	50 μm	75 μm
C-CA	Before	47007	18048	7098	795	8	1
C-CA	After	107	47	23	2	0	0
R-CA	Before	46358	20873	8843	1794	64	2
R-CA	After	330	108	88	10	0	0
B-CA	Before	65007	27977	8736	1198	82	3
B-CA	After	361	114	90	10	0	0
P-CA	Before	/	/	/	/	/	/
P-CA	After	2144	558	92	3	0	0

Table 4
Percentage of insoluble substances in cellulose acetates

Cellulose acetates	C-CA	R-CA	B-CA	P-CA
Insoluble substances content (%)	0.54	0.64	0.81	22.15

Table 5
Natural sugar compositions of pulps, cellulose acetates and insoluble substances

Samples	Natural sugar compositions (%)								
	Pulps			Cellulose acetates			Insoluble substances		
	Glu.	Xyl.	Man.	Glu.	Xyl.	Man.	Glu.	Xyl.	Man.
Cotton	99.6	0.4	/	99.7	0.3	/	86.3	13.7	/
Rayonier	97.7	1.9	0.4	98.7	1.3	/	80.9	19.1	/
Borregaard	97.2	1.7	1.1	97.5	1.5	1.0	66.4	26.4	7.2
Paper	80.8	18.8	0.3	81.4	18.6	/	31.7	68.3	/

Degree of substitution analysis

In addition to hemicelluloses in pulps, the DS of cellulose acetate is another important factor for the occurrence of the acetone-insoluble

substances. The DS of cellulose acetate is determined by a titration method, while the DS of insoluble substances is determined by ^1H NMR spectra. The ^1H NMR spectra of four insoluble

substances are shown in Figure 1. The spectra of the four insoluble substances are similar and all show three kinds of hydrogen atoms in three clusters of peak signals – the proton resonance of the ring ($\delta = 3.20$ - 5.20), and the corresponding resonance for the methyl protons of the acetyl groups ($\delta = 1.70$ - 2.20) and the propionyl groups ($\delta = 0.90$ - 1.20). Among the proton resonance of the ring, the peaks appearing at $\delta = 5.00$, 4.74 , 4.35 , 4.00 , 3.64 , 3.47 correspond to the proton resonance of the glucose ring, and other small peaks appearing at $\delta = 3.22$, 3.84 , 5.26 may be attributed to the proton resonance of the xylose ring. Due to the high content of xylose in insoluble substances, and xylose has two hydroxyl groups, and hence the degree of substitution calculated commonly by the peak

area of proton resonance of the ring and acetyl groups⁹ is not precise. In this work, the degree of substitution of insoluble substances is indicated by the percentage of the number of hydroxyl substituted by acetyl groups accounting for all hydroxyl groups on molecules (DSp). The DSp is calculated by the peak area of the proton resonance of acetyl groups divided by the sum of the peak area of acetyl and propionyl groups, while the DSp of cellulose acetates is calculated by the DS determined by the titration method divided by 3, which is the number of hydroxyl groups in glucose units. The DSp values of cellulose acetates and insoluble substances are shown in Table 6. In comparison with the cellulose acetates, the DSp values of acetone-insoluble substances are slightly lower.

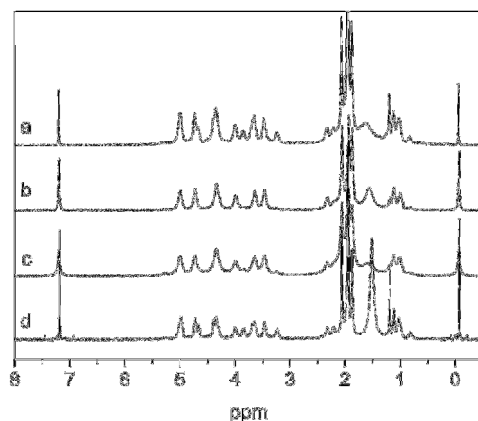


Figure 1: ^1H NMR spectra of acetone-insoluble substances in C-CA (a), R-CA (b), B-CA (c) and P-CA (d)

Table 6
DSp of cellulose acetates and insoluble substances

Samples	Cellulose acetates		Insoluble substances
	DS (titration)	DSp (%)	DSp (%)
Cotton	2.45	81.7	75.7
Rayonier	2.47	82.3	78.9
Borregaard	2.49	83.0	81.1
Paper	2.42	80.7	75.8

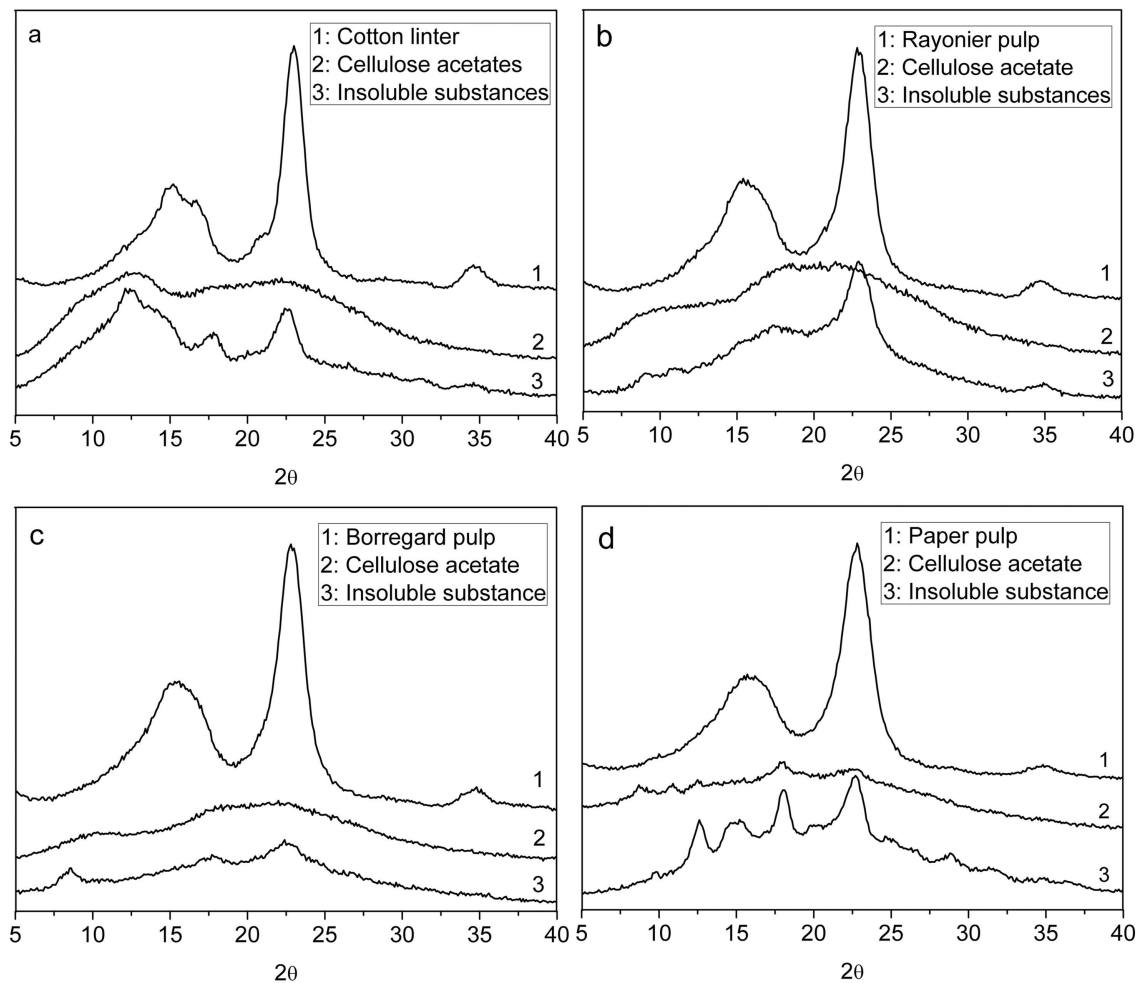


Figure 2: XRD of cotton linter (a), Rayonier hardwood pulp (b), Borregaard softwood pulp (c) and paper pulp (d), cellulose acetates prepared from four pulps and corresponding insoluble substances

X-ray diffraction analysis

The XRD results for cotton linter, Rayonier hardwood pulp, Borregaard softwood pulp and paper pulp, cellulose acetates prepared from four pulps and the corresponding acetone-insoluble substances are shown in Figure 2. The XRD spectra indicate changes in the crystallinity and structure of the samples after the acetylation process.¹⁹ For pulps (lines 1), the sample peaks located at around 15.6 and 22.8 are assigned to cellulose I, because the 22.8 is assigned to the 002 plane and 15.6 is due to the 101 and 10-1 plane. The cellulose acetates (lines 2) have broad peaks, indicating a low degree of crystallinity. The reduction of crystallinity compared with the original pulps is due to the conversion of hydroxyl groups to acetyl groups, which breaks the inter- and intra-molecular hydrogen bonds of cellulose. In contrast with the broad peaks for the cellulose acetates, the spectra of acetone-

insoluble substances (lines 3) show sharp peaks, indicating higher crystallinity than that of the corresponding cellulose acetates, which indicates that some cellulose crystalline structures may be present in the insoluble substances. This could be explained according to the diffusion mechanism of the acetylation process employed in this study. In the acetylation process, it is believed that acetic anhydride reacts first with the amorphous region and outer surface of crystals, and then diffuses to the crystalline nucleus of cellulose. This leaves some of the inner hydroxyl groups of crystalline cellulose unavailable to react with acetic anhydride at the end of the reaction. Therefore, insufficiently acetylated microcrystalline cellulose is retained in cellulose acetates, which is difficult to dissolve in acetone and isolate by ultracentrifugation. This can explain the lower DSp of insoluble substances.

Formation mechanism of acetone-insoluble substances

Based on the results above, a possible formation mechanism of insoluble substances in cellulose acetate acetone solution is proposed. The insoluble substances in acetone solutions are mixtures of hemicellulose acetates and cellulose microcrystals. Hemicelluloses residues in pulps were acetylated to hemicellulose acetates during the esterification process. Such hemicellulose acetates have poor solubility in acetone. In addition, the high crystallinity of cellulose and the diffusion mechanisms in the heterogeneous acetylation process made some of the inner hydroxyl groups of crystalline cellulose unavailable to react with acetic anhydride and caused the formation of insufficiently acetylated cellulose microcrystals, which are difficult to dissolve in acetone. Therefore, the acetone insoluble substances comprise mostly hemicellulose acetates and cellulose microcrystals, which can be separated by ultracentrifugation and collected as a mixture.

In the manufacturing of cellulose acetate, the development of the process to reduce the insoluble substances in acetone solutions is of great interest and commercial importance. The formation mechanism of acetone-insoluble substances established in this work could help us to reduce them, especially when low-grade pulps are used.

CONCLUSION

In this work, acetone-insoluble substances were successfully isolated by ultracentrifugation from cellulose acetates prepared from four different pulps with varying cellulose content ranging from 80% to 98%. The properties of the cellulose acetate solutions were characterized before and after ultracentrifugation. Then the isolated insoluble substances were characterized by using chemical, spectroscopic and chromatographic techniques. The relationship between the percentage of insoluble substance in cellulose acetates and the hemicelluloses content in pulps indicated that hemicelluloses residues in pulps play an important role in the formation of insoluble substances, because of the poor solubility of hemicellulose acetates in acetone. Moreover, the results of spectroscopic measurement suggested that the DS_p values of insoluble substances were lower and the crystallinity was higher in comparison with those of

cellulose acetates. A good explanation to this is that the corresponding insoluble substances contain insufficiently acetylated cellulose microcrystals that are formed during the acetylation process. Such cellulose microcrystals are difficult to dissolve in acetone. The hemicellulose acetates and cellulose microcrystals are the major components of the insoluble substances in cellulose acetates acetone solutions. This work is helpful in providing more insights in understanding the formation of acetone-insoluble substances.

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