

# Effect of Concentrated Sulfuric Acid and Nitroethane on Insoluble Residues in Acetylating Medium of Cellulose Acetate Prepared from Low Grade Pulps

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**ABSTRACT:** Cellulose acetate was prepared from locally available low grade pulps containing  $\alpha$ -cellulose in the range of 79–94%. The chemical and spectroscopic characterization confirmed the acetylation of all the cellulosic sources studied in the work. The effect of concentrated sulfuric acid as a catalyst and nitroethane as a solvent in the acetylation medium in reducing the insoluble residues was studied. The

gravimetric analysis has indicated that these reagents reduce the insoluble residues. This was further confirmed by the optical microscopic photographs. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1765–1771, 2005

**Key words:** cellulose acetate; insoluble residue; low grade pulps

## INTRODUCTION

Cellulose acetate (CA) is an important thermoplastic polymer used in applications that require a combination of high melting and glass transition temperature as well as high modulus and good impact strength. The final properties of these polymers may be optimized through the control of the distribution pattern of the acetyl group on the glucose units and the degree of substitution (DS) of the acetyl group. In most of the commercial production of CA, the basic raw material used is cotton linter. The avenues to use wood pulp for the same should bring in more interest and scope for wood pulp. Though there is a mention about the quality of cellulose required for this purpose,<sup>1</sup> not many systematic efforts towards the use of such sources for CA production are found in the literature.

In their study on carbohydrate polymers as extenders and replacements for polymers totally derived from petrochemicals, Fanta et al.<sup>2</sup> have made use of hardwood and softwood pulps with  $\alpha$ -cellulose content 86.3% and 85.8%, respectively, for acetylation. They first grafted the pulps with methyl methacrylate and then acetylated. The resulting products were found to be soluble in acetone. Matsumara et al.<sup>3,4</sup> have reported the preparation of cellulose triacetate (CTA) from low grade wood pulps and have studied the effect of solvent addition on insoluble residue

content. In this study for academic interest, locally available pulps have been examined for the effect of conc. sulfuric acid and nitroethane in diminishing the residue content.

The insoluble residue forms mainly due to the formation of glucomannan triacetate and xylan diacetate in aggregation with CTA. The pretreatment of low grade pulps with the mixture of acetic acid and sulfuric acid is reported as a remedy in reducing the amount of insoluble residue content.<sup>5</sup> It has been found that the use of sulfuric acid in higher amounts has resulted in the reduction of insoluble residue content. Addition of certain solvents, such as nitromethane, nitroethane, dichloro acetic acid, and methylene chloride, is reported to be very effective for softwood and hardwood pulps in reducing insoluble residue.<sup>5,6</sup> In this study, apart from soft and hardwood pulps, mixed wood pulp is also examined.

A study on the suitability of 4 different locally available low grade pulps for CA preparation has been carried out in this work. The CAs prepared from all these sources were characterized by chemical and spectroscopic techniques. The effect of the sulfuric acid catalyst in different amounts and nitroethane on softwood and hardwood pulps was studied. Optical microscopic photographs were taken to visualize the effect of the solvent on insoluble residues.

## EXPERIMENTAL

### CA synthesis

The cellulosic sources (C1 to C5) used in the synthesis of CA are shown in Table I. Among these sources, C5,

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TABLE I  
Cellulose Sources Used

Source	Source type	Supplier
C1	Mixed wood pulp (acacia + bamboo + eucalyptus)	Mysore Paper Mills, Bhadravathi
C2	Hard wood pulp (kraft)	South India Paper Mills, Nanjanagud
C3	Hard wood pulp (particles)	Harihar Polyfibers, Kumarapattanam
C4	Soft wood pulp	South India Paper Mills, Nanjanagud
C5	Bleached cotton linters (BCL)	Mysore Acetate and Chemicals Company, Mandya

the bleached cotton linter (BCL), is used in commercial production of CA and is considered as the control for comparison. The synthesis was carried out in a 1L capacity reaction vessel provided with a flange and provision for stirring and adding reagents in the subsequent steps. The temperature of the reaction was maintained within  $\pm 1^\circ\text{C}$ . The preparation involved essentially 3 steps, namely: pretreatment, acetylation, and hydrolysis. It was followed by precipitation. Table II presents the details of the acetylation of pulps.

### Characterization

The composition of cellulose is classically designated as  $\alpha$ ,  $\beta$ , and  $\gamma$  cellulose. Ideally these components may be viewed as:  $\alpha$ , long chain relatively undamaged cellulose;  $\beta$ , degraded short chain cellulose; and  $\gamma$ , non cellulosic impurities. The  $\alpha$ -cellulose content of the cellulose samples was determined by the titration method. About 10 g of sample was weighed and its moisture content was determined. Separately, about 1.6 g of sample was weighed to the nearest mg and placed in a 500 mL conical flask. This sample was soaked with 100 mL of 10% sodium hydroxide solution at  $20 \pm 2^\circ\text{C}$  for 7 min. During this period the contents were continuously stirred to ensure complete disintegration of the pulp sample. The flask was covered and maintained at  $20 \pm 2^\circ\text{C}$  for 1 h. At the end of 1 h the extract was filtered through a sintered glass crucible. The first 10 mL of the filtrate was rejected, and the rest was collected and allowed to attain room

temperature. A 20 mL portion of this extract was measured carefully into an iodine flask. 25 mL of 2% aqueous potassium dichromate solution was added to this flask and cooled for 10 min at  $20^\circ\text{C}$ . After carefully adding 30 mL of conc. sulfuric acid, the contents were boiled for 10 min and then cooled to room temperature. The contents of the iodine flask were washed into a beaker with a measured quantity of water and diluted to a known volume. Using *n*-phenyl anthralinic acid indicator (2 mL), the contents were titrated against 0.1N ferrous ammonium sulfate (FAS) until the color changed from violet to pale green. A blank titration was carried out in a similar manner, and the percent alkali solubility was calculated using the relation:

$$\% \text{ Alkali solubility} = \frac{(B - A) \times N \times 6.85 \times 100}{w \times 1000} \quad (1)$$

where *B* and *A* are the volumes (in ml) of FAS required for titration of the blank and sample, respectively; *N* is the normality of the FAS solution; 6.85 is the mg of cellulose equivalent to 1 milli equivalent of potassium dichromate; and *w* is the weight of the oven dried sample in the aliquot taken, in g. Then,  $[100 - (\% \text{ Alkali solubility})]$  gives the  $\alpha$ -cellulose content in wt %.<sup>7,8</sup>

Purification of cellulose acetate requires extensive washing to remove the residual acids. Even so, trace levels of acidity exist. This analysis is a water extraction and direct titration method with dilute sodium hydroxide. About 5 g of sample, corrected for moisture content, was weighed to 1 mg and ground to pass a No. 20 sieve, into a 250 mL flask. 150 mL freshly boiled water was added and cooled to room temperature. The flask was stoppered and allowed to stand for 3 h. Then, CA was filtered off and washed with 25 mL of water in three portions. The combined filtrate and washings was titrated with 0.01N sodium hydroxide solution, using phenolphthalein indicator. A blank titration was also run on the same volume of water used for the sample.

Free acidity was determined using the relation:

$$\text{Free acetic acid} = \frac{(A - B)(N)(6.005)}{w} \quad (2)$$

TABLE II

### Procedure Used for the Preparation of Cellulose Acetate

Stage	Process details
Pretreatment	Treat with 225 g glacial acetic acid (duration – 30 min; temp. – $50^\circ\text{C}$ ).
Acetylation	Add precooled acetylation mixture containing 135 ml acetic anhydride and 4.5 ml conc. sulphuric acid (duration – 2h; temp. – $50\text{--}55^\circ\text{C}$ ).
Hydrolysis	Add 54 ml of glacial acetic acid and 24 ml of water (duration – 6h; Temp. – $50\text{--}55^\circ\text{C}$ ).
Precipitation	Precipitate using 4.5 L of deionized water.

Basis: weight of cellulose taken in each batch = 45g.

where  $A$  is the volume of sodium hydroxide to the titrate sample, in ml;  $B$  is the volume of sodium hydroxide to the titrate blank, in ml;  $N$  is the normality of the sodium chloride solution; and  $w$  is the weight of the oven dried sample, in g.

The degree of polymerization (DP) of the cellulose samples was determined by the viscometric method<sup>9</sup> using a Fenske–Ostwald viscometer. The acetyl value of the CA produced was determined by the titration method as per ASTM D-871–63.<sup>10</sup>

The IR spectrum of the CA samples prepared was recorded by running the samples as thin films on NaCl discs. Dilute solutions (2%) of CA samples in  $N,N$ -dimethylacetamide were placed on a clean, polished NaCl disc, and the solvent was slowly evaporated. A transmission spectrum of the sample was then obtained from 4000 to 400  $\text{cm}^{-1}$  range using a Perkin–Elmer IR 2000 FTIR spectrometer, UK.

### Treatment of sulfuric acid and nitroethane

To begin with, the samples were well defibered. To 1 part of the defibered pulp, 60 parts of acetic acid was added and the pulp was activated by agitating with a magnetic stirrer for 20 min at 40°C. Then it was treated with 7 parts of acetic anhydride and 0.1 part of sulfuric acid, and stirring continued for 3 h at 40°C. It was followed by stirring overnight at 20°C. The solution obtained was 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 3 times with fresh acetic acid by centrifugation; the resulting 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. The same procedure was followed by varying the amount of sulfuric acid and nitroethane (as a solvent) in the acetylation mixture for all the pulps mentioned.

**TABLE III**  
Quantities of Reagents, Sulphuric Acid, and Nitroethane Used

Reagents	Amount (g)			
	Expt. 1	Expt. 2	Expt. 3	Expt. 4
Acetic acid	160	160	160	120
Acetic anhydride	7	7	7	7
Sulfuric acid	0.1	0.2	0.3	0.1
Nitroethane	—	—	—	40

Basis: weight of cellulose taken in each batch = 1g.

**TABLE IV**  
Important Parameters of the Raw Material

Source	Moisture content (wt %)	Ash content (wt %)	$\alpha$ -Cellulose content (on moisture free basis) (wt %)	Degree of polymerization (DP)
C1	23.83	0.590	93.62	820
C2	6.52	0.430	88.55	860
C3	7.19	0.107	79.00	800
C4	6.92	0.715	85.46	880
C5*	4–6	0.100	98.00	900–1300

\* Values supplied by BCL producer, M/s Mysore Acetate & Chemicals Co., Mandya, India.

The exact amount of various reagents used is presented in Table III.

To visualize the effect of the solvent in dissolving the fibers, optical microscopic pictures of the acetylation medium were taken using a WILD LIETZ inverted transmitted-light microscope, Italy. These pictures were taken by placing the samples of acetylation medium on glass slides.

## RESULTS AND DISCUSSION

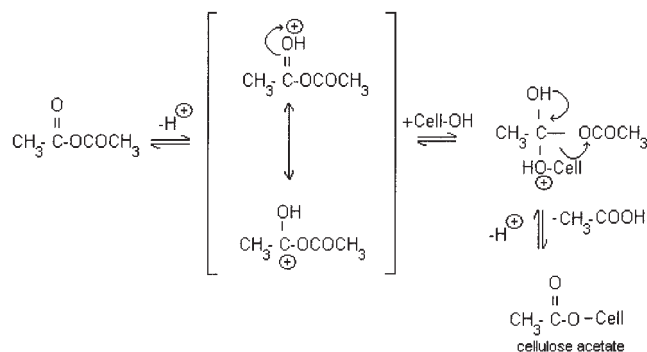
### Pulp properties

The different characteristic parameters of cellulose, such as moisture content, ash content,  $\alpha$ -cellulose content, and degree of polymerization, are presented in Table IV. The  $\alpha$ -cellulose content, an important parameter in signifying the value of a cellulosic material, was found to be in excess of 80% except in C3. The DP was in the range of 800–900 for sources C1–C4. In the case of the bleached cotton linter, DP was in the range of 900–1300.

### Cellulose acetate synthesis and properties

The course of the acetylation reaction is largely controlled by the rates of the diffusion of the reactant and the catalyst into the cellulose fiber.<sup>11</sup> The reaction between one of the hydroxyl groups of the cellulose molecule and the anhydride is given in Scheme 1.

The diluent, which is usually a solvent for the acetate, facilitates the reaction, particularly with respect to temperature control. The probability of acetylation of any one cellulosic group is strongly dependent on its position in the fiber. Since they cannot be dissolved before acetylation, it will be realized that some molecules will be completely acetylated while others may be untouched. It is thus necessary first to acetylate the cellulose completely; and the resultant triacetate material, which is soluble in certain solvents, may then be hydrolyzed back in solution. Under these conditions, probabilities of these groups in another molecule and



Scheme 1

products with an even degree of substitution, less than three, may be obtained. Therefore, preparation of CA involves three steps, namely: pretreatment, acetylation, and hydrolysis.

The pretreatment of pulp is an important step wherein the cellulosic matter is opened up to achieve even substitution and to accelerate the main substitution reaction. Glacial acetic acid, being nonaqueous in nature, has been found to be an effective pretreatment agent.<sup>12</sup> The reaction conditions followed for acetylating cellulose are shown in Table II. The precipitation of the hydrolyzed mass was carried out with 1.5 L of water.

The properties of CAs obtained are shown in Table V. All the cellulose acetates prepared were white and powdery in nature. The moisture content was found below that of CA from BCL (control) except in the case of CA from softwood (C4). Free acidity, as percent acetic acid, was found 0.012 for all CAs prepared, which is slightly higher than that for CA from BCL. This slightly higher content of free acidity may be attributed to the use of the same amount of deionized water (4.5 L) in the precipitation stage. More washing could have resulted in further reduction in free acidity.

The acetone solubility of CAs prepared was low. This is attributed to the fact that the degree of substitution is far from the region of acetone solubility. The acetyl content, as % acetic acid, should be in the range of 52–56 for acetone solubility.<sup>13</sup> The acetyl content for CA from mixed wood pulp (C1) was much lower at

TABLE VI  
Characteristic Infrared Absorption Peaks of CA

Group	Wave number (cm <sup>-1</sup> )
(OH) stretching	3400–3200
(C=O) stretching	1700–1780
(CH <sub>3</sub> ) asymmetric deformation	1430–1470
(CH <sub>3</sub> ) symmetric deformation	1365–1385
Acetate C—C—O stretching	1210–1250
(C—O) stretching	≈ 1050

46.56%. The DS for all the CAs prepared is shown in Table V. Since a common procedure for hydrolysis was adopted for the control as well as for other wood pulps, there is marked variation in % acetyl content of CA obtained from C1–C4 compared to that from C5.

### Infrared (IR) spectroscopic characterization

To confirm the formation of CA from different cellulosic sources, IR spectroscopy has been used in this study. The characteristic peaks of CA are given in Table VI.<sup>14–17</sup> The IR spectra of all the five CAs synthesized in the present study (dissolved in *N,N*-dimethylacetamide) are shown in Figure 1. The IR spectrum of the CA supplied by MACC (control) is also presented in the same Figure. All the prominent peaks, namely C—O (1050 cm<sup>-1</sup>), C—C—O (1235 cm<sup>-1</sup>), CH<sub>3</sub> symmetric deformation (1370 cm<sup>-1</sup>), CH<sub>3</sub> asymmetric deformation (1432 cm<sup>-1</sup>), and C=O (1750 cm<sup>-1</sup>) corresponding to CA are seen in all the five types of CA, thus confirming the formation of CA. In the present IR studies, the OH stretching (corresponding to about 3400 cm<sup>-1</sup>) is not clearly seen. This may be attributed to the fact that water absorbs strongly near 3710 cm<sup>-1</sup>. These absorptions obscure absorptions of the substance being analyzed or may more frequently lead to erroneous assignment.<sup>17</sup>

### Effect of treatment of sulfuric acid and nitroethane

While preparing CA from C1–C4, it was observed that a considerable amount of insoluble residue was formed. This may be due to the simultaneous formation of hemicellulose acetates, such as glucomannan

TABLE V  
Yield and Properties of CA Prepared

Source	Yield (g)	Moisture (%)	Free acidity (%)	Acetyl content as % acetic acid	Acetyl content as % acetyl group	DS
C1	54.99	3.87	0.012	46.56	33.37	2.23
C2	52.5	2.50	0.012	62.10	44.50	2.98
C3	52.5	0.80	0.012	60.62	43.44	2.91
C4	62.25	4.20	0.012	61.31	43.94	2.94
C5	69.99	4.00	<0.01	53.5–55.5	38.34–39.77	2.57–2.66

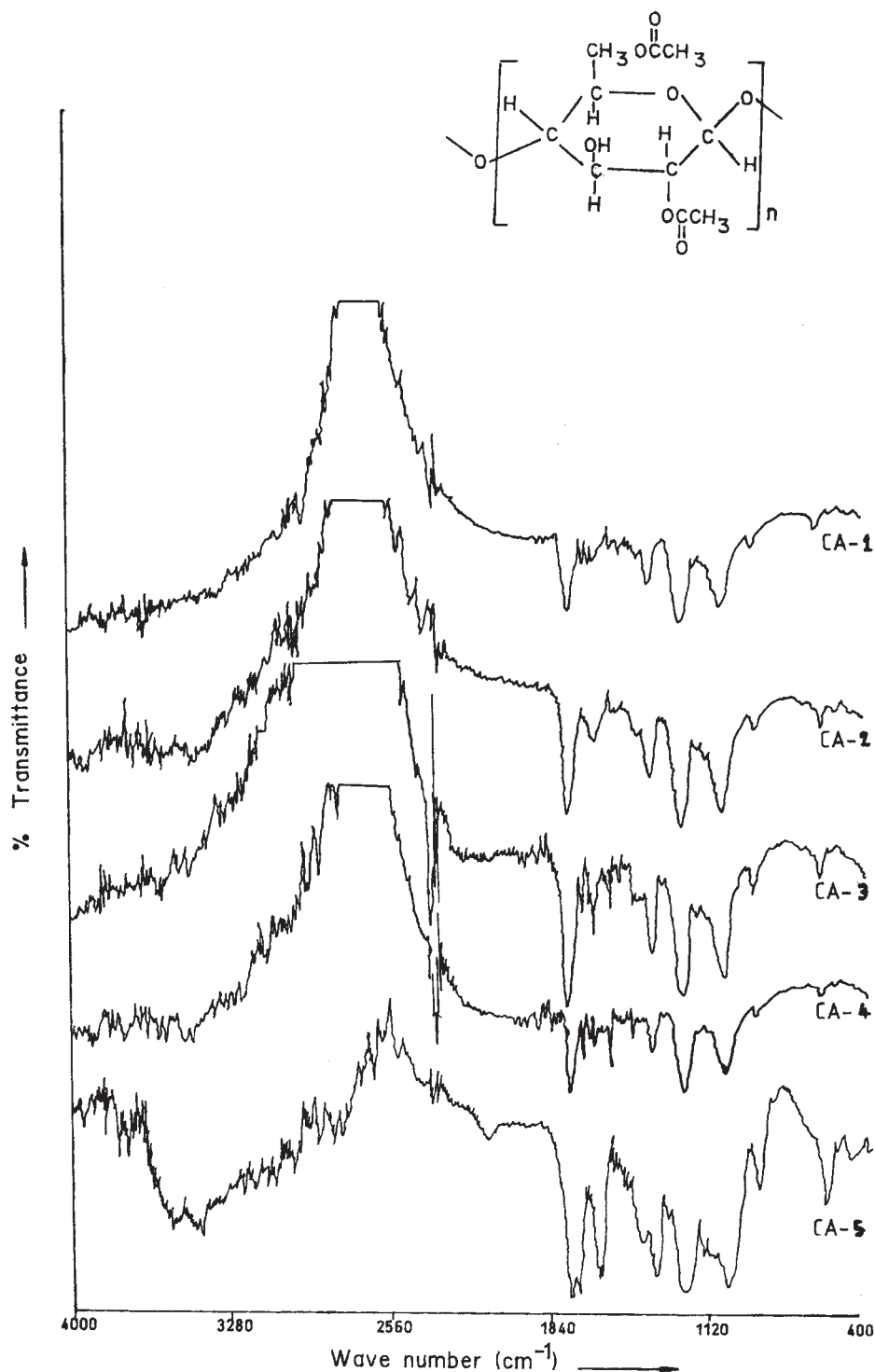


Figure 1 IR spectra of cellulose acetates prepared.

triacetate and xylan diacetate, in aggregation with CTA.<sup>5</sup> In this study, the effect of the sulfuric acid catalyst at different amounts and nitroethane (solubility parameter,  $\delta = 22.7 \text{ MPa}^{1/2}$ ) was studied, to bring down the insoluble residue. The reaction conditions and the amount of insoluble residue obtained are presented in Tables III and VII, respectively.

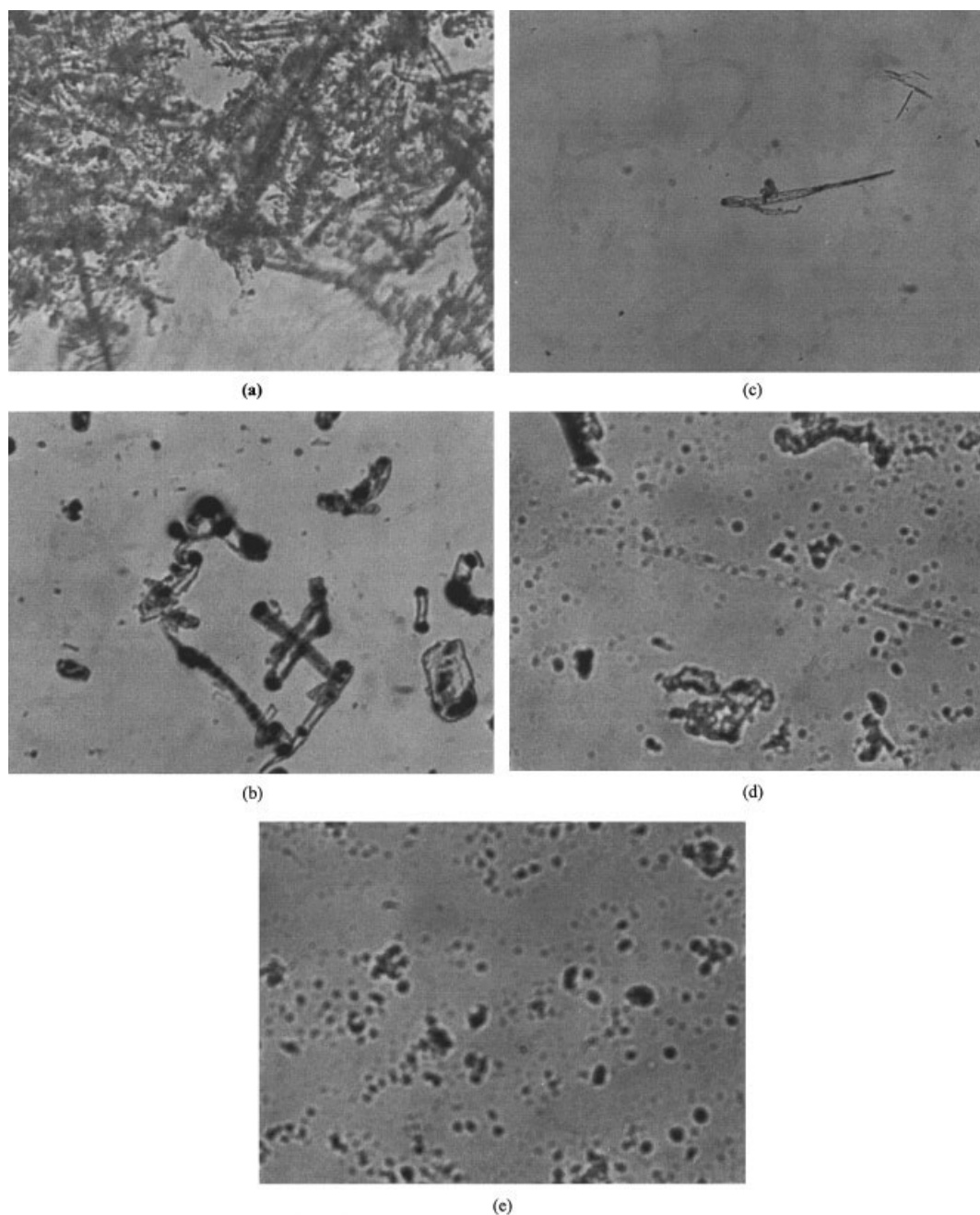
It is apparent that with an increase in the amount of sulfuric acid added to the acetylation medium, the insoluble residue was decreased. When the solvent nitroethane was incorporated in the acetylation medium, the insoluble residue was further decreased. A similar trend was found in the case of all the four cellulosic sources considered in this study. Therefore,

**TABLE VII**  
**Insoluble Residue Content Obtained in Different Experiments**

Expt. no.	Insoluble residue content (wt %)				
	C1	C2	C3	C4	C5
1	24.50	4.66	4.98	23.85	0.47
2	16.73	3.96	4.78	14.93	—
3	16.44	3.95	1.70	14.41	—
4	6.15	1.46	0.31	9.58	—

the addition of nitroethane to the acetylation medium is very effective in reducing insoluble residues. For the control, C5, the insoluble residue was found to be negligible (0.47%), even without nitro ethane treatment.

The representative microscopic photographs taken during the acetylation of mixed wood pulp (C1) and softwood pulp (C4) are shown in Figure 2. It is clear from these micrographs that the fibrous nature of the cellulose is retained. However, with higher amounts



**Figure 2** Optical micrographs of fibers in the acetylation medium: (a) C1/0.2 g conc. sulfuric acid, (b) C1/0.3 g conc. sulfuric acid, (c) C1/0.1 g conc. sulfuric acid + nitroethane, (d) C4/0.3 g conc. sulfuric acid, and (e) C4/0.1 g conc. sulfuric acid + nitroethane.

of conc. sulfuric acid, the fibric matter is considerably dissolved. With the use of nitroethane in the acetylation medium, the fibric matter is further dissolved.

### CONCLUSIONS

Preparation of CA from low grade hardwood, softwood, and mixed wood pulps ( $\alpha$  cellulose content in the range 79–94%) has been done in this work, and the reaction conditions were optimized. Formation of CA was confirmed by IR spectroscopic studies. The degree of substitution, determined by chemical methods, was found to be in the range 2.23–2.98. It was observed that a considerable amount of insoluble residue was formed with all the pulps considered, which may be due to the formation of glucomannan acetate and xylan acetate, as suggested by Saka et al.<sup>5</sup> The presence of conc. sulfuric acid (catalyst) and nitroethane (solvent) in the acetylation medium were found to be effective in reducing these insoluble residues. This has been confirmed by the gravimetric analysis and optical micrographs.

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