

A New Approach for the Production of Cellulose Acetate: Acetylation of Mechanical Pulp with Subsequent Isolation of Cellulose Acetate by Differential Solubility

D. G. BARKALOW,* R. M. ROWELL,† and R. A. YOUNG,
*University of Wisconsin, Department of Forestry, 1630 Linden Drive,
Madison, Wisconsin 53706, and USDA Forest Products Laboratory,
1 Gifford Pinchot Drive, Madison, Wisconsin, 53705*

Synopsis

A heretofore uninvestigated approach to the production of cellulose acetate, the acetylation of whole wood pulp with subsequent isolation of the cellulose derivative by differential solubility, is described. The mechanical pulp used was produced by refining aspen wood chips with a disc refiner. Two conventional acetylation techniques, the fibrous and solution process, were employed to acetylate all components of the pulp. The cellulose acetate was isolated from the acetylated lignin and hemicellulose by dissolving in dichloromethane/methanol (9:1, v/v). The advantage of this new approach is that the high cost involved in using an extensively purified dissolving pulp are avoided. Both acetylation techniques yielded a product that was about 84% cellulose acetate. The remaining acetylated components were lignin and hemicellulose. The yield of cellulose acetate, based on the cellulose content of the original pulp and the product, was 75–80%.

INTRODUCTION

Cellulose acetate is one of the oldest manmade macromolecules used extensively in the textile and polymer industries. It has an inherent advantage in that the starting material, cellulose, is a renewable natural resource. The current applications of cellulose acetate include textiles, cigarette tow, lacquers, cellulose films, and packaging. Since it is nontoxic, cellulose acetate is widely used in food packaging.

In 1865, Schutzenberger reacted cellulose in sealed tubes at 180°C with acetic anhydride and is generally attributed with the discovery of cellulose acetate. But it was not until 1904, when Miles found that partially saponified triacetate was soluble in acetone, that the commercial feasibility was recognized. The first cellulose acetate fiber was made by British Celanese Ltd. in 1920 and in the United States in 1924.¹

Cellulose acetate has been produced from both cotton and wood pulp. Economics have dictated that wood pulp dominates the current market source. The purity of the pulp is very high, consisting of 95–98% α -cellulose². Dissolving pulp is generally used in circumstances that dictate the need of a

*Present address: Purdue University, Whistler Center for Carbohydrate Research, Smith Hall, West Lafayette, Indiana 47907.

†To whom correspondence should be addressed.

high level of purity. The hemicellulose component of wood is removed by pre- or postpulping chemical treatment and the lignin is removed by chemical pulping and bleaching. As a consequence of the extensive purification treatments, the pulp yield may be as low as 29%.² The low yield and the chemical treatments make this material a high-cost wood pulp. The expense of the starting material will be borne in the price of the cellulose acetate.

We have worked on a heretofore uninvestigated approach to the production of cellulose acetate by direct acetylation of a whole wood pulp, such as mechanical pulp, with subsequent isolation of the cellulose derivative by differential solubility. The mechanical pulp chosen for this study was produced by disc-refining aspen wood. The three major components of wood, cellulose, lignin, and hemicellulose, exist in the pulp in the same proportions as in wood. By using mechanical pulp as the starting material, the high costs incurred in first generating a nearly pure cellulose dissolving pulp are avoided.

Two conventional acetylation techniques, the fibrous and solution processes, were employed to fully acetylate the mechanical pulp. The reaction media for acetylating pulp by the fibrous process consisted of xylenes, acetic anhydride, and sulfuric acid. Xylenes acted as a nonsolvent, diluent. The acetylated pulp was never dissolved in the liquor and the product retained the original fibrous nature of the pulp. With the solution procedure the pulp was reacted in a mixture of acetic acid, acetic anhydride, and sulfuric acid. As the reaction proceeded, part of the pulp became soluble in the liquor and was recovered by precipitation into water. The cellulose acetate was isolated from the remainder of the acetylated wood components by differential solubility in dichloromethane/methanol (9 : 1, v/v).

EXPERIMENTAL

Materials

Aspen refiner mechanical pulp was produced with a Sprout-Waldron 12 inch disc refiner. The pulp had a Canadian Standard of Freeness of 130 mL and a Fiber Length Index of 0.106 mm. All chemicals were reagent grade. The water used was deionized.

Acetylation of Mechanical Pulp

The fibrous and solution procedures were modifications of those discussed by Tanghe et al.³ and are described separately below.

Fibrous Process

About 3.3 g of pulp (30% consistency) was dewatered two times with glacial acetic acid. Xylenes (25 mL), 6.0 mL acetic anhydride, and 25, 50, 100, or 200 μ L of 96% sulfuric acid were combined in a 100 mL round-bottom flask. The flask was stoppered and placed in an oil bath at 55°C. The reaction mixture was stirred slowly with a magnetic stirring bar for either 1, 2, or 4 h. At the completion of the reaction, the material was filtered on a coarse ground glass disc. The fibrous acetylated pulp was washed with xylenes, then methanol. The acetylated pulp was washed extensively with water, then methanol, and

dried at 60°C under vacuum.

Solution Process

About 3.3 g of pulp (30% consistency) was dewatered two times with glacial acetic acid. Acetic acid (20 mL) was combined with the desired amount of 96% sulfuric acid (50, 100, or 200 μ L) in a 100 mL round-bottom flask with ground glass stopper. The pulp was added to this solution and shaken for 1 min. Acetic anhydride (6.0 mL) was added and the flask shaken 1 min. The flask was stoppered and placed in an oil bath at 55°C. The reaction mixture was stirred slowly with a magnetic stirring bar for the designated time (1, 2, or 3 h). The flask was then placed in an ice bath (about 15°C), and a solution of 1.0 mL water and 2.2 mL acetic acid was slowly added. The material was slowly stirred for 10 min. The acetylated pulp and liquor were added dropwise to 600 mL water with rapid stirring to precipitate soluble components. The acetylated pulp was recovered by filtration on a coarse fritted glass disc. This material was washed extensively with water, then methanol, and dried at 60°C under vacuum.

Isolation of Cellulose Acetate by Differential Solubility

A product with very high cellulose acetate content was obtained by differential solubility. The acetylated pulp obtained by either process was stirred in 40 mL dichloromethane/methanol (9 : 1, v/v) for 2 h. The soluble fraction was isolated by filtration through Whatman #4 filter paper, concentrated to 15 mL, and precipitated in 50 mL *n*-hexane (Skelly B). The precipitate was washed with 95% ethanol and dried at 60°C under vacuum.

Analysis of Acetylated Material

Acetyl content was determined by titration.³ The lignin was measured using the micro-Klason technique developed by Effland.⁴ Sugar analysis was done by high performance liquid chromatography (HPLC) (Biorad HPX87P column, 48°C) after digestion in 72% sulfuric acid and neutralization with aqueous barium hydroxide.

Degree of Polymerization

The molecular weight distribution of the dichloromethane/methanol soluble product was done by: (1) saponification of the acetyl with 0.25 *N* sodium hydroxide,³ (2) holocellulose isolation by the acid chlorite method,⁵ (3) carbanilation of the holocellulose in pyridine and phenyl isocyanate,^{6,7} and (4) HPLC of the carbanilate. The HPLC system included a Perkin-Elmer Sigma Series 2 pump, Sigma Series 15 data station, and LC-85 UV detector operated at 235 nm for the carbanilate and 284 nm for the polystyrene standards. The columns were Shodex A/805 and Styragel 500A connected in series. The mobile phase was tetrahydrofuran and the injected sample concentration was less than 0.01%. To obtain weight-average and number-average molecular weight values, the universal calibration procedure was used with polystyrene standards. The Mark-Houwink coefficients, *K* and *a*, used for polystyrene were 0.0141 and 0.7, respectively.⁷ The cellulose tricarbanilate *K* and *a* values

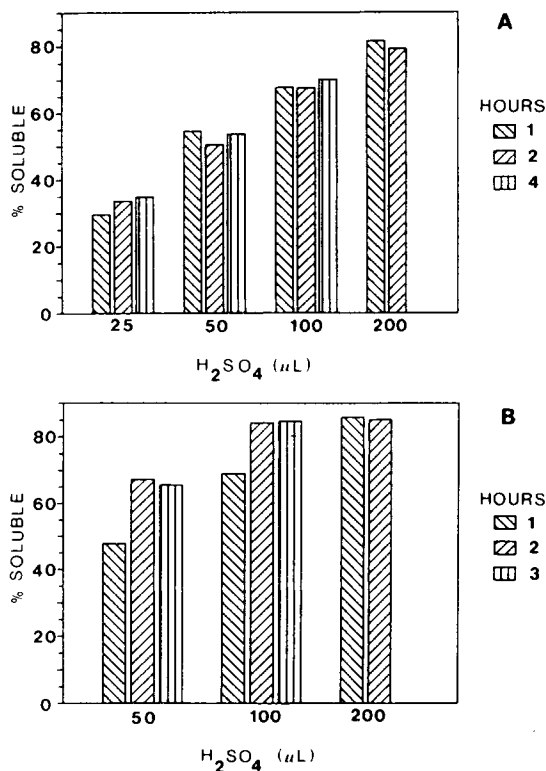


Fig. 1. Percent of acetylated pulp soluble in dichloromethane/methanol. (A) Fibrous process, (▨) 1h; (▩) 2h; (▧) 4h, (B) solution process (▨) 1h; (▩) 2h; (▧) 3h.

were 0.00343 and 0.869, respectively.⁸⁻¹² The degree of polymerization (\overline{DP}_w) was calculated by dividing the weight-average molecular weight by 519 g/mol, the formula weight of a tricarbanilated anhydroglucose unit.

RESULTS AND DISCUSSION

Solubility and Acetyl Content

The proportion of cellulose acetate in the product was greatly improved by isolating the fraction of acetylated pulp soluble in dichloromethane/methanol (9 : 1, v/v). The fibrous process showed a greater dependence on acid concentration than reaction time [Fig. 1 (A)]. There was a steady rise from an average of 33% to 77% soluble as the acid content increased from 25 to 200 μL. A plausible explanation for the larger effect associated with initial sulfuric acid concentration, rather than reaction time, was the aprotic environment of the fibrous process. The acid was more easily regenerated in a reaction liquor composed mostly of acetic acid (solution process) as opposed to xylenes (fibrous process). The relationship between solubility and reaction time for the solution process at 1 and 2 hour reactions with 50 or 100 μL sulfuric acid is shown in Figure 1(B). For the 50 μL reaction, the solubility increased from 48% to 67% when the time was raised from 1 to 2 h. However, between the 2

and 3 h reactions, no improvement in solubility was noted. The maximum solubility was about 83%.

The range of acetyl content for the fibrous and solution acetylated pulps was 39–44%. Assuming complete recovery of all acetylated pulp components, the theoretical maximum acetyl content was 38.3%. As the acetylated hemicellulose and lignin components were removed, the acetyl should have approached that of cellulose triacetate, 44.8%. The acetyl content of the dichloromethane methanol-soluble fraction of the acetylated pulp range was 43–45%. This was indicative of the higher concentration of cellulose acetate in the soluble component. The high levels of acetyl were consistent with the conclusion that the conditions employed for both the fibrous and solution methods resulted in complete acetylation of the mechanical pulp.

Chemical Composition of the Acetylated Products

The acetylated pulp and dichloromethane/methanol-soluble fractions were analyzed for Klason lignin and carbohydrate composition. The values were on a weight basis of the acetylated material, and thus, included the acetyl contribution. For example, the fibrous reaction at 1 h, 50 μ L sulfuric acid produced acetylated pulp with 41% acetyl, 39% glucose, 9.4% xylose, 0.4% galactose, 2.7% mannose, and 10% lignin. The mechanical pulp starting material for all acetylations contained 4.6% acetyl, 52.9% glucose, 18.8% xylose, 0.6% galactose, 1.3% mannose, and 19.1% lignin. The major hemicellulose sugar was D-xylose arising from the hardwood hemicellulose *O*-acetyl-4-*O*-methyl-

TABLE I
Glucose and Xylose Content of the Acetylated Pulp and Soluble Fraction

Reaction parameters		Acetylated pulp		Soluble fraction	
Acid (μ L)	Time (h)	Glucose	Xylose	Glucose	Xylose
Fibrous process					
25	1	38.2	11.4	51.0	5.1
25	2	34.5	12.0	51.2	5.0
25	4	36.7	12.1	50.4	6.2
50	1	38.0	9.5	49.0	6.8
50	2	39.0	10.0	51.1	7.3
50	4	35.8	9.8	50.3	6.6
100	1	42.4	6.3	48.1	5.7
100	2	42.0	4.1	49.8	6.0
100	4	45.4	4.8	47.4	5.5
200	1	48.4	2.2	53.5	2.5
200	2	47.0	2.1	51.9	2.4
Solution process					
50	1	36.7	11.2	49.0	5.0
50	2	38.1	8.9	46.0	6.0
50	3	37.5	9.4	40.8	7.8
100	1	39.0	8.0	47.7	6.6
100	2	40.7	5.1	47.2	4.9
100	3	41.5	4.4	47.7	3.6
200	1	42.2	3.5	48.0	3.1
200	2	44.5	4.4	49.0	1.9

glucuronoxylan. The low concentration of D-mannose indicated only a small amount of glucomannan present. Since the technique used for sugar analysis did not measure methylglucuronic acid as glucose, and since there was only a small amount of glucomannan, the cellulose content could be estimated from the percent glucose.

In comparing the amount of xylose in the acetylated pulp for reactions done at 25 and 50 μL sulfuric acid with those at 200 μL , a significant difference was noted (Table I). The xylose declines from 12% to 2% in the case of the fibrous process, and from 11% to 3.5% for the solution process with the increase in acid catalyst. This was a direct result of the higher acid concentration causing more degradation of the hemicellulose xylan. The acetylated, degraded xylan was dissolved and lost during workup of the acetylated pulp.

The purification of cellulose acetate by dissolution in dichloromethane/methanol, isolation from the insoluble component, and reprecipitation was evident in the increased concentration of glucose in the soluble fraction (Table I). For example, the acetylated pulp, obtained by reacting for 2 h with 50 μL sulfuric acid, contains 39.0% glucose (fibrous process) and 38.1% (solution process). The associated glucose levels for the soluble fraction were 51.1% (fibrous process) and 45.9% (solution process). As the glucose level rose in the soluble fraction, the lignin and hemicellulose levels declined. The lignin content in the acetylated pulp was fairly constant at 9–10% for all reaction

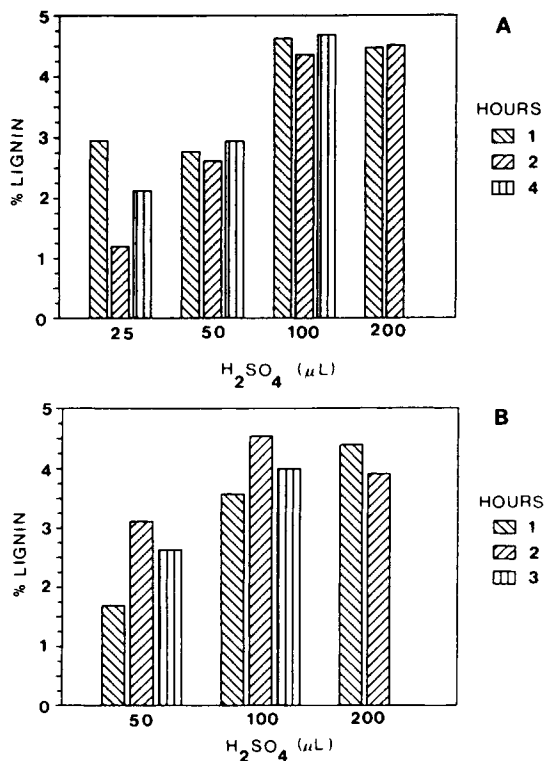


Fig. 2. Percent lignin in the dichloromethane/methanol-soluble fraction. (A) Fibrous process, (B) solution process (see Fig. 1 for key).

times and acid concentrations. The soluble fraction had reduced lignin content, 1.2-5.2% (Fig. 2). The lowest lignin contents were obtained at the lowest levels of sulfuric acid, 25-50 μ L. At these low acid concentrations the lignin and hemicellulose existed as a matrix held together by covalent bonding. As the acid was increased, the degradation of xylan by acetolysis increased, as noted above. The destruction of the matrix rendered the acetylated lignin more soluble. Apparently the dichloromethane/methanol solvent had difficulty dissolving an acetylated hemicellulose-lignin matrix. This may have been related to the basic structural differences of lignin and xylan. It also may have been a molecular size phenomenon, in that a matrix that was undegraded would have been much larger.

The purity of the soluble fraction was calculated from the amount of glucose in relation to the remaining components. Thus, the percent cellulose acetate in the soluble fraction ranged from 80.3 to 88.7%, with an average of 83.6%, for the fibrous process. The soluble fraction from the solution process reactions contained 77.7-88.5% cellulose acetate, with an average of 83.6%.

Product Yield

The total yield for the fibrous process was independent of reaction time, but dependent on the sulfuric acid concentration. Maximum yields of 150% were

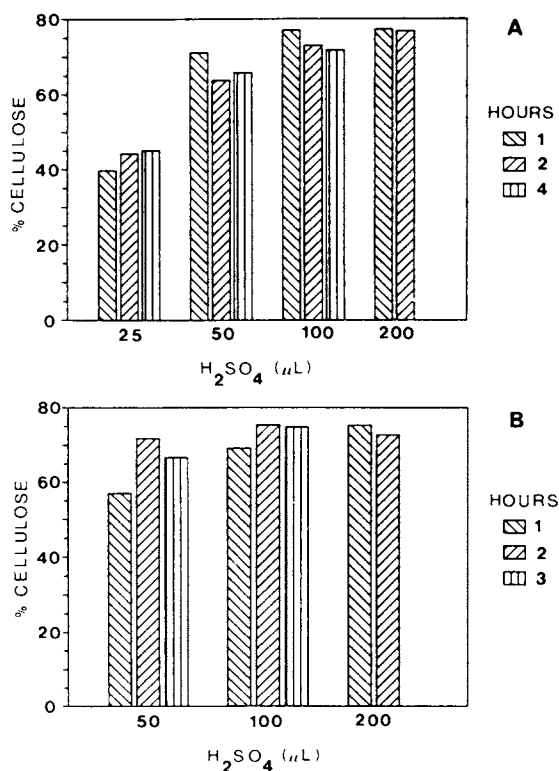


Fig. 3. Yield of cellulose in dichloromethane/methanol-soluble fraction. (A) Fibrous process, (B) solution process (see Fig. 1 for key).

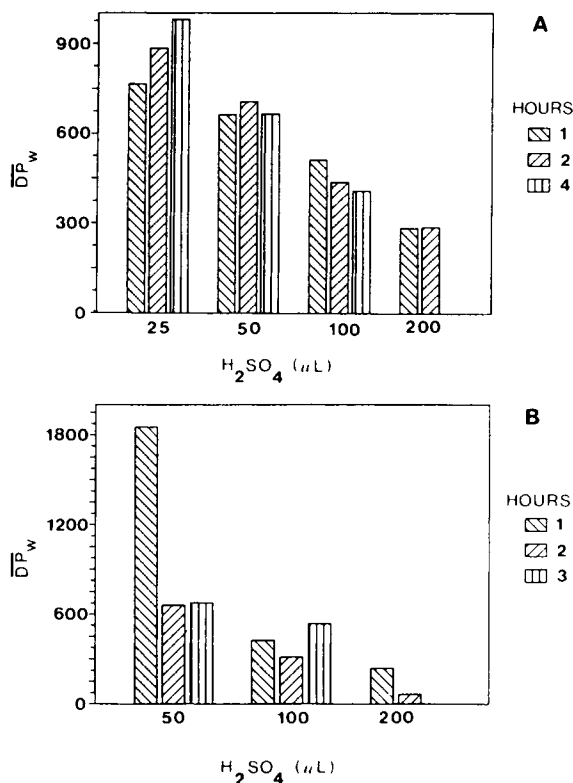


Fig. 4. Weight-average DP of cellulose acetate in the dichloromethane/methanol-soluble fraction. (A) Fibrous process, (B) solution process (see Fig. 1 for key).

obtained when 1 g pulp (dry basis) was reacted with 25 or 50 μL of sulfuric acid catalyst. The lowest yields, 103%, were seen at 200 μL . The weight gains at high yields were due to the addition of acetyl groups. At high acid levels, the hemicellulose fraction was degraded and lost during workup, which reduced the yield. The solution process gave total yields that were dependent on reaction time and catalyst concentration. For example, the total yield with 50 μL sulfuric acid was 132% for a 1 h reaction, and 120% for 2 h. In general, the total yield was less for the solution as compared to the fibrous process.

As mentioned above, the average percent cellulose acetate in the dichloromethane/methanol soluble fraction was 83.6%. The yield, based on cellulose in the original mechanical pulp and that in the soluble product, is plotted in Figure 3. The yield of cellulose for the fibrous reactions ranged from 39.7% (1h, 25 μL sulfuric acid) to 80.6% (2h, 200 μL). The range for the solution process was 53.0% (1h, 50 μL) to 75.7% (1h, 200 μL). For both processes, the cellulose yield was similar at 100 and 200 μL sulfuric acid (about 74%).

Degree of Polymerization

Figure 4 shows the weight-average degree of polymerization (\overline{DP}_w) of the dichloromethane/methanol-soluble cellulose acetate product. The \overline{DP}_w of the

cellulose acetate was dependent on the initial acid concentration and, in the case of the solution process, on the reaction time. The \overline{DP}_w for the fibrous reactions ranged from 980 (4h, 25 μ L sulfuric acid) to 284 (1h, 200 μ L). The maximum and minimum \overline{DP}_w for the solution reactions were 1853 (1h, 50 μ L sulfuric acid) and 65 (2h, 200 μ L). In the solution process, the \overline{DP}_w was decreased at a given acid concentration by an increase in reaction time from 1 to 2 h. However, there was no observed decrease between the 2 and 3 h reactions. Except for the 1 h, 50 μ L sulfuric acid reaction, the fibrous process yielded a higher \overline{DP}_w than the solution process. The solution reactions were more stringent due to the increased regeneration of sulfuric acid and the homogeneous acetolysis conditions.

CONCLUSIONS

The acetylation of mechanical pulp was investigated with the aim of finding an alternative, cost-efficient means of producing cellulose acetate. We found that both the fibrous and solution processes resulted in complete acetylation of the pulp. The acetylated pulp was dispersed in dichloromethane/methanol (9:1, v/v) to dissolve and extract the cellulose acetate. Using this technique, both the fibrous and solution procedures gave a product that was approximately 84% cellulose acetate. The other 16% consisted of acetylated lignin and hemicelluloses.

With either process, the dichloromethane/methanol-soluble fraction had a similar chemical composition for a given reaction time and sulfuric acid concentration. The solution procedure, however, resulted in a greater degradation of the carbohydrate component at higher acid concentrations and longer reaction times. For example, the weight-average degree of polymerization for the cellulose acetate produced using 200 μ L sulfuric acid and a 2 h reaction time was 286 for the fibrous reaction and 65 for the solution reaction.

The commercial application of this new approach to producing cellulose acetate from mechanical pulp will depend upon consumer preference, market needs, and a cost evaluation. The new process has a greater yield than conventional acetylation of dissolving pulp. The cost of the starting material, mechanical pulp, is much lower than a dissolving pulp because the cellulose is not first isolated by extensive pretreatment, pulping, and bleaching of wood. There is, however, a greater expense associated with increased amounts of acetylating chemicals necessary to derivatize the lignin and hemicellulose constituents, as well as the cellulose.

The cellulose acetate product could be used in the current market for cellulose films and packaging materials. The acetylated pulp is whitened by the dichloromethane/methanol dissolution step because much of the lignin remains insoluble and is not carried over with the soluble product. To obtain a snow-white material, we found that the product could be bleached by a mild acid chlorite treatment without loss of acetyl content.

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