

Modified Cellulose Acetate Prepared from Acetic Anhydride Reacted with Cellulose Dissolved in a Chloral-Dimethylformamide Mixture

L. P. CLERMONT AND N. MANERY, *Department of The Environment, Canadian Forestry Service, Eastern Forest Products Laboratory, Montreal Road, Ottawa*

Synopsis

A bleached sulfite pulp (85.0% α -cellulose) was dissolved in dimethylformamide containing anhydrous chloral and pyridine as catalyst. The clear cellulose solution was then reacted with acetic anhydride under various conditions. The reaction products contained both acetyl groups and chlorine in amounts varying from 20% to 38%. Curves of reaction rates with respect to chlorine and acetyl groups under various conditions of temperature and reactant ratios were similar in appearance, and all the products contained approximately 2 moles of acetyl groups per mole of chloral. Yields varied from 180% after treatment at room temperature (25°C) for 1 hr to 250% after 4 hr. The products could be hydrolyzed in acid with some difficulty but very easily in dilute alkali. The products had low flammability and hygroscopicity. Films cast from acetone solutions had higher permittivity and lower a.c. conductivity than similar films made from cellulose diacetate.

INTRODUCTION

It was recently reported that cellulose could be dissolved in dimethyl sulfoxide, dimethylformamide (DMF), dimethylacetamide, and N-methyl-2-pyrrolidone in the presence of 5-10 moles anhydrous chloral per glucose residue.¹ These solutions were found to be miscible with synthetic high polymers. Tepteleva² reported on the reaction of free hydroxyl groups in cellulose acetate with chloral in methylene chloride and in chloroform. In DMF, little reaction was found to take place. In previous work,³ modified cellulose triacetates were prepared by reacting either secondary cellulose acetate or cellulose with chloral in methylene chloride, benzene, or acetic acid followed by acetylation of the reaction product in the same reaction medium. Products with interesting properties were obtained containing up to 17% chlorine.

In the present work, cellulose was first dissolved in DMF containing chloral and pyridine and reacted with a mixture of acetic anhydride and pyridine. Reaction rates were studied and the products were characterized as to their acetyl and chlorine contents, elementary composition, and degree of polymerization (D.P.).

EXPERIMENTAL

Materials

A commercial, bleached sulfite pulp with a D.P. of 800 and 85.0% α -cellulose was used. Sheets of pulp were disintegrated in a Waring Blendor, air dried, and fluffed in a small hammer mill.

The DMF was purified by drying over sodium sulfate and distilling under vacuum at 60°C. However, it was observed that technical-grade DMF could also be used as a medium for the reactions described in this work.

The anhydrous chloral (bp 97–98°C), acetic anhydride, methylene chloride, acetic acid, and pyridine used were reagent-grade chemicals.

Analyses

Chlorine analyses were carried out by the microcombustion method described by White.⁴

Acetyl groups were determined by a modification of the semimicromethod described by Lin and Schuerch.⁵ A sample (20–30 mg) was weighed into a 25-ml flask. Then, 3 ml of 70% 2,2,2-trifluoroethanol solution containing 0.195 meq/ml sodium hydroxide was added to the sample, and the flask was heated loosely stoppered for 10 min at 60°C. Pyridine, 3 ml, was then added, and the solution was saponified for 3 hr at 60°C. The excess alkali was back-titrated to a phenolphthalein endpoint with 0.05 *N* HCl. Blanks were run with every batch of samples.

The D.P. of the original sulfite pulp and of some of the modified acetate derivatives were determined in cadoxen prepared according to Donetzhuber⁶ using the equation

$$[\eta] = 1.85 \times 10^{-2} \text{ D.P.}^{0.76}.$$

Prior to D.P. determinations, the cellulose derivatives were saponified in 10% ammonium hydroxide at room temperature for 24 hr.

Carbon, hydrogen, and nitrogen analyses were carried out by microcombustion. Infrared spectra were determined with a Beckman IR8 using the KBr disc technique. Differential thermal analyses were carried out in a nitrogen atmosphere using aluminum oxide as reference material and a heating rate of 10°C/min.

Permittivity and conductivity measurements on films were carried out according to Venkateswaran.⁷

Preparation of Cellulose Derivatives

To 1 g of sulfite pulp (6.0% moisture) were added 50 ml DMF, 5 ml anhydrous chloral, and 2.5 ml pyridine. The suspension was shaken at room temperature overnight (about 18 hr) and a clear solution obtained. The solution was then diluted by adding a further 50 ml DMF. Acetic anhydride and pyridine were added to give the desired anhydride/pyridine ratio, taking into account the amount of pyridine already present in the solution. The reacted product was recovered by adding hot water to the

reaction mixture, filtering, and washing with hot water. The sample was purified by dissolving it in acetone, adding hot water, filtering, and washing. Samples were dried in a vacuum oven at 50°C.

For the preparation of films, a purified sample was prepared as described above. The reaction with acetic anhydride was carried out using a 5:1 anhydride/cellulose ratio at 25°C for 1 hr. The derivative contained 33.1% chlorine and 29.1% acetyl. The films were cast on a glass plate and dried at room temperature from a 6% solution in acetone.

When methylene chloride was the reaction medium, the following procedure was used: 2 g cellulose was activated by soaking in glacial acetic acid for 1 hr at room temperature. The excess acid was drained and 50 ml methylene chloride and 9.1 g (6.0 ml) chloral were added, i.e., a ratio of chloral to cellulose of about 4.5:1 was used. The mixture was allowed to react overnight. Equimolar amounts of pyridine and acetic anhydride were added to the suspension. The weight ratio of anhydride to cellulose was 8:1. When sulfuric acid or perchloric acid was used as the catalyst, an amount equal to 1% of the weight of anhydride was used. The suspension was allowed to react at room temperature for 3–4 hr, then poured into water, filtered immediately, washed thoroughly, and dried in a vacuum oven at 50°C.

RESULTS AND DISCUSSION

It has been observed that a mixture of DMF and chloral containing approximately 5% chloral (v/v) at a chloral/cellulose ratio of 5:1 (v/w) will dissolve cellulose very slowly, about three weeks being required for complete solution. However, it was found that the addition of small amounts of pyridine (2.5 ml/100 ml DMF) resulted in a clear solution after about 18 hr at room temperature. The dissolved cellulose could be easily recovered by pouring it into water, filtering it, and washing it with water and acetone. The recovered cellulose contained 1.93% chlorine, and its D.P. was unchanged (800). The infrared spectrum showed a small, broad absorption band near 810 cm^{-1} , thought to be the absorption region of compounds containing a carbon atom linked to more than one chlorine atom.⁸ This would indicate that chloral is incorporated into the cellulose, probably as a hemiacetal.

Figure 1 shows the yield of purified product obtained when cellulose dissolved in the DMF–chloral–pyridine mixture is acetylated at 25°C for various times at a ratio of acetic anhydride to cellulose of 3:1 (v/w) and an equimolar mixture of anhydride and pyridine. After 4 hr, the acetyl content was 27.3%, the chlorine content 34.8%, and the yield of product was about 250%.

Figures 2 and 3 show the rate of increase in acetyl and chlorine content of the reacted products for various ratios of anhydride to cellulose and equimolar amounts of pyridine and anhydride. All these curves are similar, i.e., there is a fast reaction during the first hour of treatment followed by a

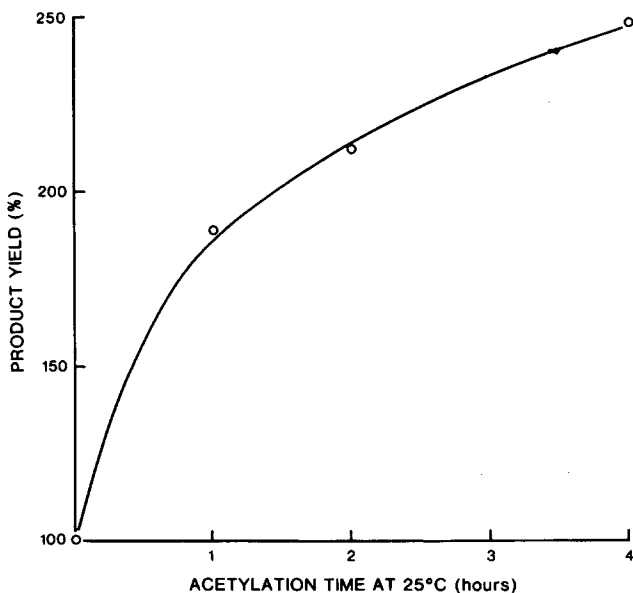


Fig. 1. Yield increase with acetylation time at 25°C.

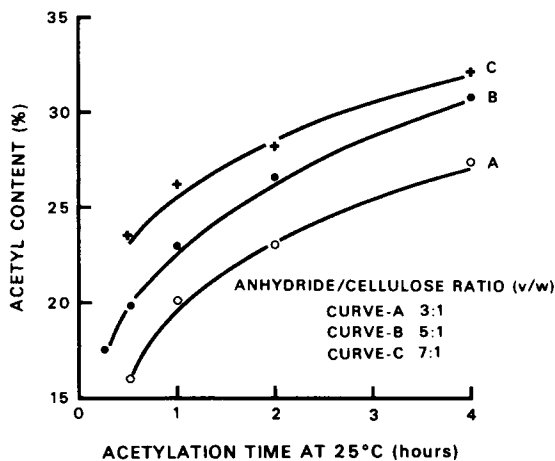


Fig. 2. Rate of acetylation at 25°C at various acetic anhydride/cellulose ratios.

3-hr slower reaction. The curves of Figure 2 are similar to those reported in the literature for the commercial acetylation of cellulose by the acetic acid-acetic anhydride-sulfuric acid process.⁹

The effect of temperature on reaction rate is shown in Figures 4 and 5. As expected, increasing the temperature from 25° to 70°C greatly increased the rate of reaction. At 45° and 70°C, most of the reaction takes place in the first hour of treatment. At 70°C, maximum contents of about 35% acetyl and 38% chlorine are reached after 4 hr.

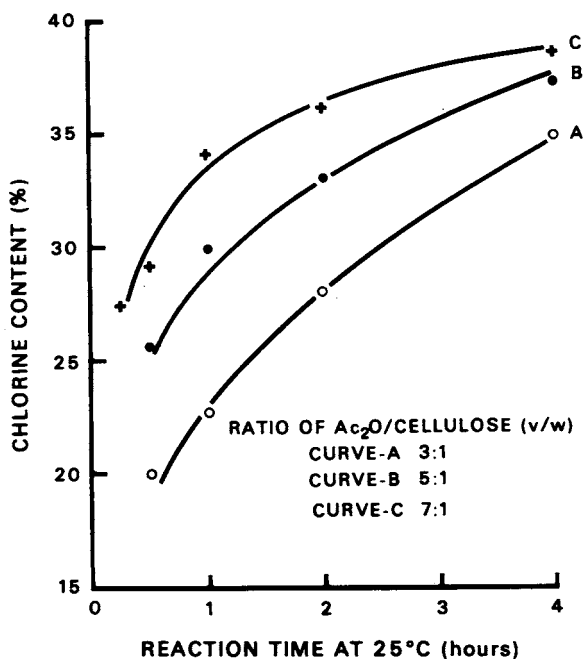


Fig. 3. Rate of chlorination at 25°C at various acetic anhydride/cellulose ratios.

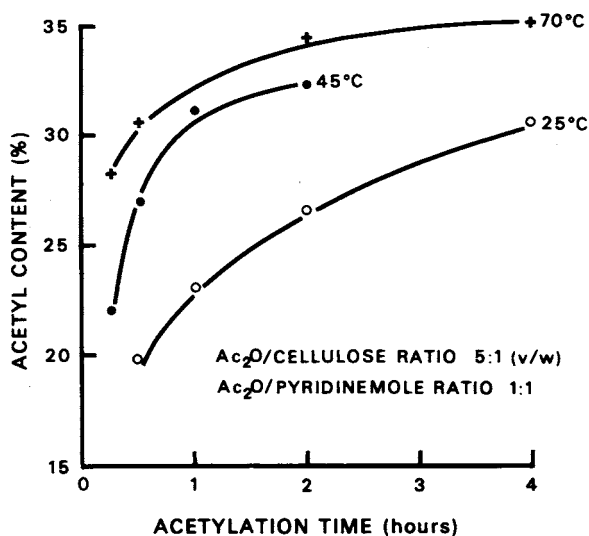


Fig. 4. Effect of temperature on the rate of acetylation at 5:1 acetic anhydride/cellulose ratio.

Figures 6 and 7 show that increasing the mole ratio of pyridine to acetic anhydride from 1:1 to 1.3:1 at room temperature and at an anhydride/cellulose ratio of 5:1 (v/w) increases the rates of acetylation and chlorination. Again all curves are similar in appearance. Obviously, pyridine has a pronounced effect on the reaction rate.

Table I shows the composition of products obtained at room temperature at an equimolar ratio of pyridine to acetic anhydride under various treatment conditions. These acetylations were carried out on 1-g cellulose samples dissolved in 100 ml DMF containing 7.5 g (5 ml) anhydrous chloral

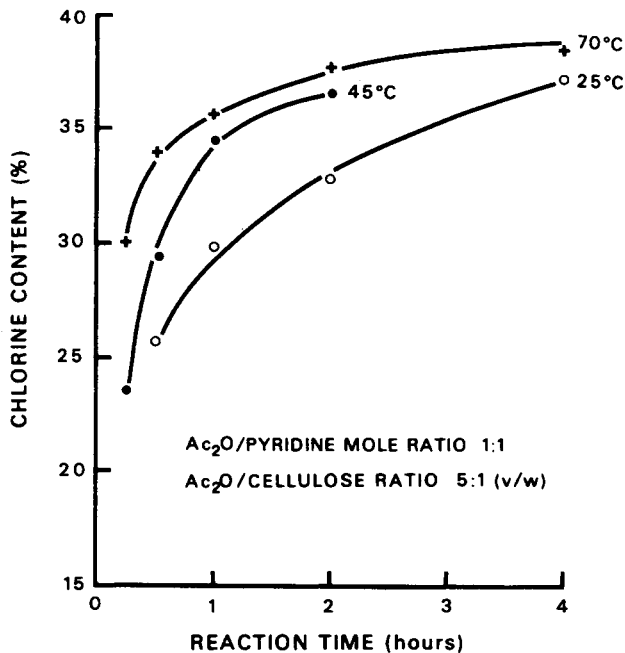


Fig. 5. Effect of temperature on the rate of chlorination at 5:1 acetic anhydride/cellulose ratio.

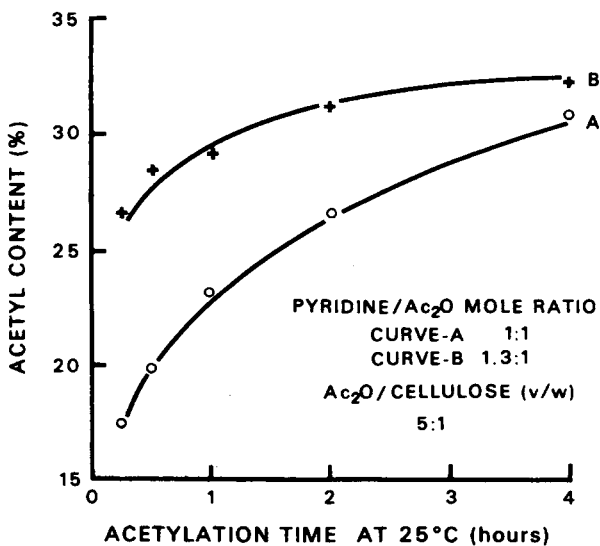


Fig. 6. Effect of pyridine/acetic anhydride mole ratio on the rate of acetylation at 25°C.

TABLE I
Mole Ratios of Acetyl to Chloral Groups in Modified Cellulose Acetates^a

Acetic anhydride/ cellulose ratio (v/w)	Acetylation time, hr	Chlorine content, %	Acetyl content, %	Acetyl/chloral mole ratio
3:1	0.5	20.0	15.9	1.97
	1	22.6	20.0	2.19
	2	27.9	22.9	2.04
	4	34.8	27.3	1.93
5:1	0.25	23.6	17.5	1.83
	0.5	25.6	19.8	1.92
	1	29.8	23.1	1.92
	2	32.8	26.5	2.00
7:1	4	37.3	30.7	2.04
	0.5	29.2	23.4	1.97
	1	34.1	27.2	1.97
	2	36.2	28.7	1.91
	4	38.4	32.1	2.08

^a Reaction temperature, 25°C; pyridine/anhydride mole ratio, 1:1; chloral/cellulose ratio, 5:1 (v/w).

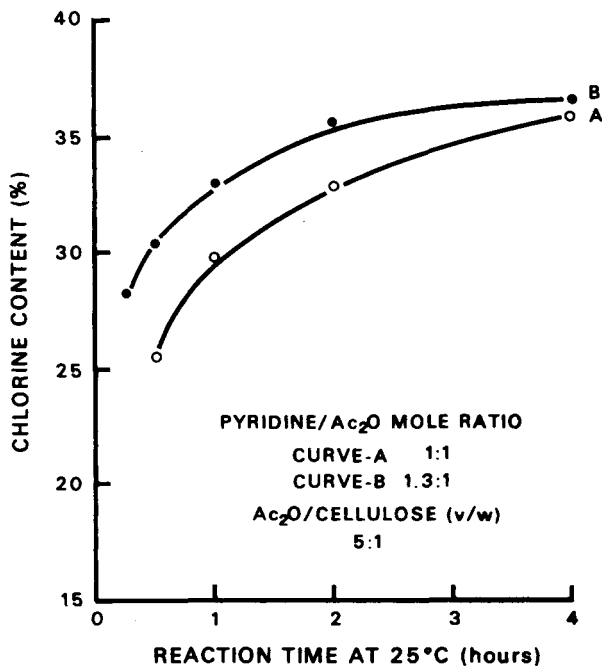


Fig. 7. Effect of pyridine/acetic anhydride mole ratio on the rate of chlorination at 25°C.

and 2.5 ml pyridine. Before acetylation, enough pyridine was added to give an equimolar ratio of pyridine to acetic anhydride. It may be seen that at all anhydride/cellulose ratios, the mole ratio of acetyl to chloral in the products was approximately 2. It is known that diacyl type of esters are formed in the reaction of aldehydes with anhydrides, using either

TABLE II
Composition of a Few Modified Cellulose Acetate Derivatives^a

Sample no.	Acetic anhydride/cellulose ratio (v/w)	Acetylation time, hr	Chlorine, %	Acetyl, %	Carbon, %	Hydrogen, %
1	3:1	1	22.6	20.0	34.5	4.11
2	7:1	0.5	29.2	23.4	32.7	3.51
3	3:1	4	34.8	27.3	31.6	3.22

^a Reaction temperature, 25°C; pyridine/anhydride mole ratio, 1:1; chloral/cellulose ratio, 5:1 (v/w).

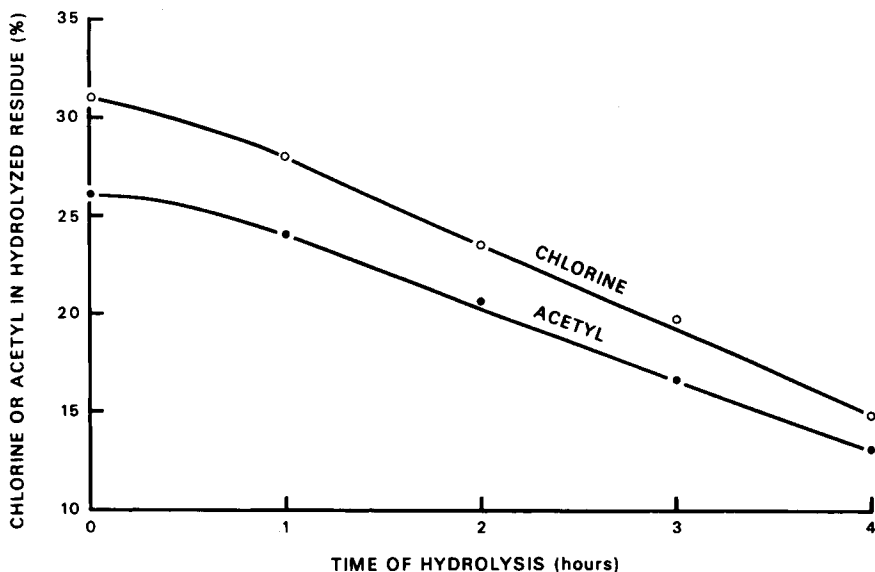


Fig. 8. Rate of hydrolysis of modified acetate in 12% hydrochloric acid at 50°C.

sulfuric acid or pyridine as catalyst at room temperature.¹⁰ However, it is difficult to see how such a compound could react with cellulose. A more likely explanation for the observed results would be the formation of mixed cellulose acetate and acetate of hemiacetal. This would be consistent with the reported yields of products and with the differential hydrolysis curves shown in Figure 9. However, it is obvious that until the reaction mixture and the hydrolysis products are examined, one can only speculate as to the exact composition of those derivatives.

There was no degradation during the acetylation reaction, the D.P. remaining unchanged at 800.

Table II shows the elementary composition of a few derivatives obtained by treating the cellulose dissolved in the DMF-chloral-pyridine mixture with various ratios of acetic anhydride at room temperature.

Figure 8 shows the rate of hydrolysis in 12% hydrochloric acid at 50°C of a derivative having an initial chlorine content of 31.0% and an initial

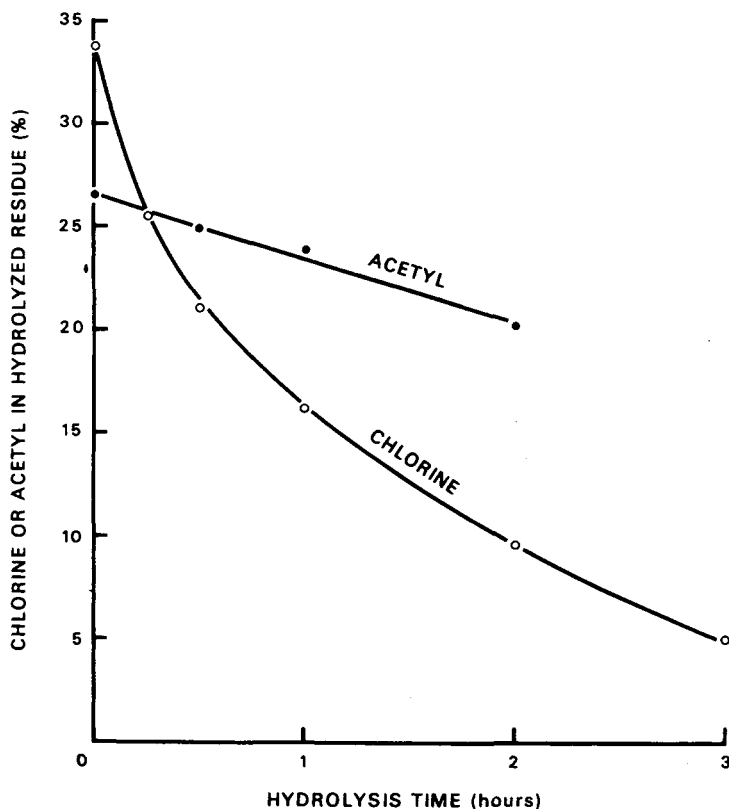


Fig. 9. Rate of hydrolysis of modified acetate in 0.5% ammonium hydroxide at 25°C.

acetyl content of 26.0%. The resistance to acid hydrolysis was appreciable. In this respect, these derivatives behaved much like commercial cellulose acetates. The hydrolyzed derivatives contained acetyl and chloral in the same mole ratios as the initial derivatives (i.e., approximately 2:1).

Figure 9 shows that these derivatives were very sensitive to hydrolysis in dilute base (0.5% ammonium hydroxide) at room temperature. The chlorine content decreased much more rapidly than the acetyl content, as opposed to what was observed in acid, indicating a preferential removal of chloral in dilute base. The acetyl content also showed a rapid decrease compared to a commercial diacetate which showed hardly any deacetylation under similar conditions. This was not surprising, however, since the nature of the substituent groups in these cellulose derivatives was bound to affect their rates of hydrolysis.

Figure 10 shows an infrared spectrum of a derivative prepared by acetylation at 25°C for 1 hr at an anhydride/cellulose ratio of 5:1 (v/w), a chloral/cellulose ratio of 5:1 (v/w), and with an equimolar mixture of pyridine and anhydride. The derivative contained 35.3% chlorine and 29.2% acetyl. The spectrum was similar to that of a commercial diacetate except for an intense absorption band at 800 cm^{-1} . The equilibrium moisture content of

TABLE III
 Dielectric Properties of Films^a

Frequency, Hz	Permittivity	a.c. Conductivity, mho/cm
Cellulose Diacetate Film ^b		
10 ²	3.58	2.34×10^{-12}
10 ³	3.51	2.80×10^{-11}
10 ⁴	3.44	3.50×10^{-10}
10 ⁵	3.35	3.81×10^{-9}
Modified Cellulose Acetate Film ^c		
10 ²	3.82	1.50×10^{-12}
10 ³	3.81	1.87×10^{-11}
10 ⁴	3.77	2.54×10^{-10}
10 ⁵	3.70	3.32×10^{-9}

^a Measurements made on vacuum-dried samples at 20°C.

^b Film density, 1.18 g/cm³.

^c Film density, 1.31 g/cm³.

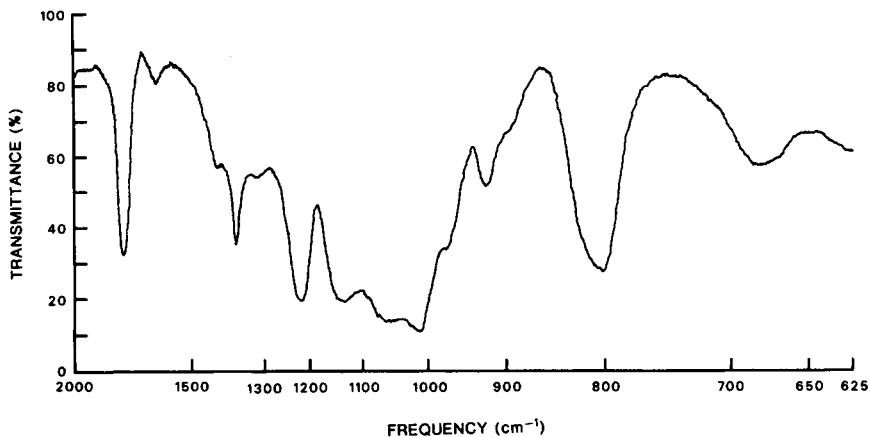


Fig. 10. Infrared spectrum of modified acetate containing 29.8% chlorine and 23.4% acetyl.

the same derivative at 95% relative humidity was 3.1% compared to 8.3% and 11.4% for cellulose tri- and diacetate, respectively. These derivatives therefore, have very low water sorption.

The dielectric properties of cellulose diacetate films (38.1% acetyl) and those of a film with 33.1% chlorine and 29.1% acetyl made from the modified cellulose acetate are shown in Table III. The permittivity values were corrected to an arbitrary unit density for comparison purposes. The modified acetate having higher permittivity and lower conductivity would obviously be a superior capacitor or insulating material.

Differential thermal analyses performed on cellulose diacetate and on the modified cellulose acetate (35.5% chlorine, 29.2% acetyl) are shown in Figures 11 and 12, respectively. The modified acetate clearly displayed

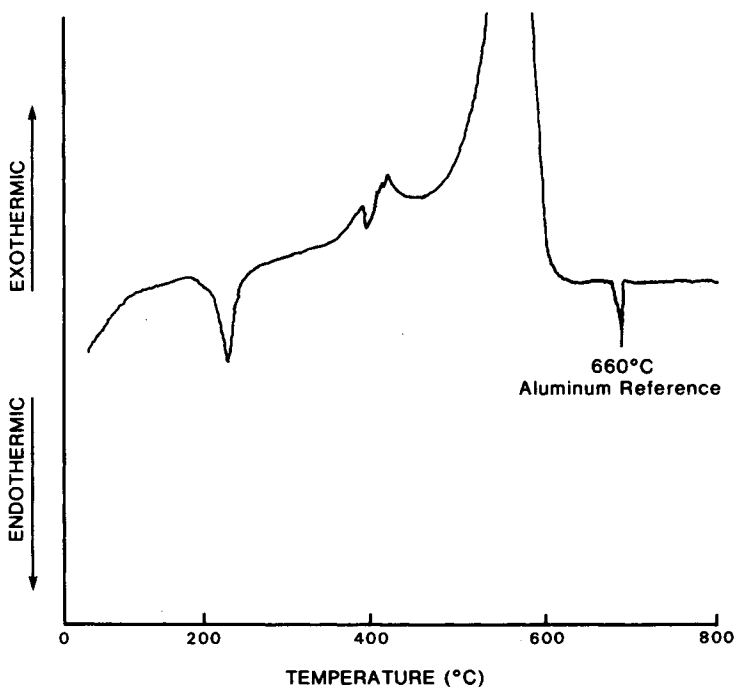


Fig. 11. Differential thermal analysis curve of cellulose diacetate (2.3-mg sample, 38.1% acetyl) heated in nitrogen atmosphere at 10°C/min.

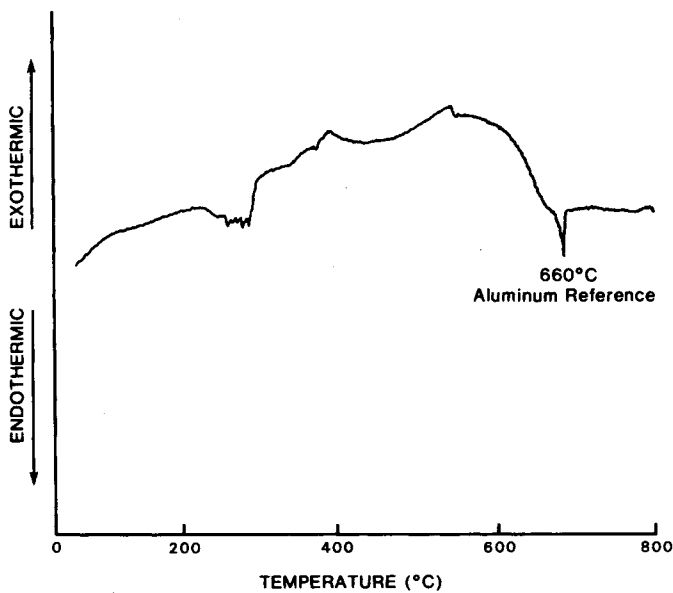


Fig. 12. Differential thermal analysis curve of modified cellulose acetate (2.3-mg sample, 35.3% chlorine, 29.2% acetyl) heated in nitrogen atmosphere at 10°C/min.

a different thermal behavior. The endotherm at about 230°C in the cellulose diacetate was absent in the modified sample. Instead, an ill-defined endotherm appeared in the latter at a somewhat higher temperature. The huge exotherm starting at about 500°C in the diacetate was absent in the modified acetate.

Effect of Reaction Medium on Derivative Composition

When DMF was replaced by methylene chloride as the reaction medium and the reaction carried out as outlined above using pyridine as the catalyst, a product containing 7.08% chlorine and 14.6% acetyl was obtained. When sulfuric acid was used as the catalyst and acetylation was carried out in methylene chloride, a product was obtained containing 40.8% acetyl and 3.43% chlorine. If perchloric acid was used as the catalyst, the product contained 38.3% acetyl and 2.25% chlorine. Obviously, the reaction medium had a profound effect on product composition.

CONCLUSIONS

New cellulose derivatives are formed when cellulose dissolved in a mixture of DMF and chloral containing small amounts of pyridine as catalyst is treated with a mixture of acetic anhydride and pyridine. These new derivatives appear to be modified cellulose acetates which may be made into films having good dielectric properties and which are strongly hydrophobic.

The authors wish to thank Dr. A. Venkateswaran for the conductance and permittivity measurements, Dr. D. P. C. Fung for the differential thermal analyses, and G. Leblanc who carried out the acetyl analyses.

References

1. J. Nakao and S. Yamazaki, Jap. Pat. 7,107,468 (February 24, 1971).
2. L. A. Tepteleva, *Khim. Tekhnol. Proizvod. Tsellyul.*, 318 (1971).
3. M. B. Schostleva, L. A. Tepteleva, and F. A. Kriutchkov, *Khim. Tekhnol. Proizvod. Tsellyul.*, 303 (1968).
4. D. C. White, *Mikrochim. Acta*, **3**, 449 (1961).
5. J. W. P. Lin and C. Schuerch, *J. Polym. Sci. A-1*, **10**, 2045 (1972).
6. A. Donetzhuber, *Svensk Papperstidn.*, **63**, 447 (1960).
7. A. Venkateswaran, *Wood Sci.*, **4**, 248 (1972).
8. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, 2nd ed., Wiley, New York, 1958, p. 331.
9. E. Ott and H. M. Spurlin, Eds., in *High Polymers*, vol. 5, *Cellulose and Cellulose Derivatives*, 2nd ed., Interscience, New York, 1954, p. 771.
10. W. J. Hickinbottom, *Reactions of Organic Compounds*, 3rd ed., 1957, p. 240.

Received February 4, 1974

Revised March 19, 1974