

CELLULOSE ESTERS PREPARED BY WOOD ESTERIFICATION

M. V. Efanov

UDC 661.728.82

Trends in the yields and properties of cellulose esters are studied as a function of wood esterification conditions. The yield, total extent of cellulose ester substitution, and degree of conversion depend on the duration and acylation temperature.

Key words: wood esterification, cellulose esters, preparation.

Cellulose isolated from wood or cotton fiber is currently used to produce cellulose esters. Therefore, the development of methods to produce cellulose esters directly from wood is most timely. The isolation of cellulose esters from acetylated wood was attempted long ago. However, the ability to extract cellulose esters from wood in high yield was demonstrated only recently [1, 2].

Recently published studies [3, 4] on the acylation of wood in trifluoroacetic acid (TFAA) and the isolation of cellulose esters using organic solvents are noteworthy. The use of the following solvents was proposed for this [3, 4]: TFAA, CHCl_3 , CH_2Cl_2 , and CH_3OH , which are undesirable from ecological and industrial viewpoints.

We developed an esterification method using a mixture of acetic anhydride and an aliphatic carboxylic acid and wood previously activated by grinding with $\text{Mg}(\text{ClO}_4)_2$. The use of mechanical grinding before esterification can produce highly substituted mixed esters of acetic and butyric acids without using organic solvents in the process.

Using C_3 - C_5 carboxylic acids to esterify wood can increase the solubility of its acylation products in organic solvents (by 80-90% in acetone and CHCl_3) [5] and produce polymers with higher thermal plasticity than wood acetates [11].

An effective method [6] that includes treatment of the whole reaction mixture after esterification with 5-10% peracetic acid was proposed for preparing in high yield cellulose acetates from acylated wood. According to this patent, the production of cellulose esters by this method decreases energy expenditures and environmental contamination and increases the product yield by preserving a part of the hemicellulose. The resulting product contains 65-95% cellulose esters, 5-35% acylated hexosans, and up to 15% pentosans.

A low peracetic acid concentration (5-10%) is insufficient to isolate chemically pure cellulose esters. Increasing the concentration to 15-15.5%, as previously demonstrated [7, 8], can produce a solid that contains only cellulose esters.

Peracetic acid acts as a quantitative oxidant of lignin for delignification of modified wood, which is quite effective for delignification of acetylated wood and produces in high yield cellulose acetates with less than 1% residual lignin [8]. The aromatic ring of lignin is oxidized by a heterolytic mechanism to form benzenedicarboxylic acids, which leads to extensive destruction into water-soluble products and only slightly affects the cellulose [9].

Therefore we studied the effect of wood-esterification conditions on the yield and properties of cellulose esters isolated from the products of its acylation by delignification with peracetic acid.

The IR spectra of cellulose esters isolated from wood esterification products that are produced in 2 and 6 h contain strong bands characteristic of ester vibrations (1740 - 1750 cm^{-1}) and out-of-plane pyranose-ring vibrations (895 - 965 cm^{-1}). The IR spectra of cellulose esters lack absorption bands at 1595 , 1505 , and 1450 cm^{-1} , which are typical of skeletal vibrations of lignin aromatic rings.

This indicates that the principal components of esterified wood are completely separated. This was also confirmed by the low content of residual lignin in acylated cellulose (1.2-1.5% lignin according to Komarov).

Altai State University, Russia, 656099, Barnaul, Dimitrova, 66, fax (3852) 22 54 51. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 68-70, January-February, 2001. Original article submitted November 13, 2000.

TABLE 1. Degree of Cellulose Conversion (α_i) from Aspen Wood Esterification as a Function of Duration (τ , h) and Temperature*

| τ , h | Temperature, °C | | | | | |
|------------|-------------------------|--------------------------|-------------------------|--------------------------|-------------------------|--------------------------|
| | 80 | | 100 | | 120 | |
| | $\alpha_{\text{acet.}}$ | $\alpha_{\text{butyr.}}$ | $\alpha_{\text{acet.}}$ | $\alpha_{\text{butyr.}}$ | $\alpha_{\text{acet.}}$ | $\alpha_{\text{butyr.}}$ |
| 2 | 0.19 | 0.01 | 0.25 | 0.03 | 0.26 | 0.03 |
| 4 | 0.24 | 0.03 | 0.29 | 0.04 | 0.31 | 0.05 |
| 6 | 0.30 | 0.03 | 0.36 | 0.05 | 0.38 | 0.07 |
| 8 | 0.34 | 0.05 | 0.44 | 0.06 | 0.49 | 0.08 |

*Grinding for 15 min in a ball mill with 10^{-3} moles $\text{Mg}(\text{ClO}_4)_2$, mole ratio WOH:AA:BA = 1:1:1

TABLE 2. Yield (W, %) and Extent of Substitution (ES_{tot}) of Cellulose Esters as a Function of Duration (τ , h), and Temperature of Wood Esterification

| τ , h | Temperature, °C | W, % | ES_{tot} |
|------------|-----------------|------|--------------------------|
| 2 | 80 | 39.8 | 0.55 |
| 4 | 80 | 40.1 | 0.78 |
| 6 | 80 | 42.3 | 1.07 |
| 2 | 100 | 40.4 | 0.84 |
| 4 | 100 | 43.7 | 0.99 |
| 6 | 100 | 45.3 | 1.26 |
| 2 | 120 | 42.9 | 0.91 |
| 4 | 120 | 45.6 | 1.12 |
| 6 | 120 | 47.2 | 1.38 |

The conversion of cellulose from wood esterification was estimated from the degree of conversion of cellulose (α_{acet} , α_{butyr}), calculated from the content of bound acyls in its esters (Table 1).

The total degree of cellulose conversion (α) after 2 h from the start of the reaction is 20, 28, and 29% at acylation temperatures 80, 100, and 120°C, respectively. Increasing the duration of the esterification reaction in the temperature range increases smoothly the content of bound acyl groups in the cellulose esters and, therefore, the degree of conversion.

The yield and properties of cellulose esters isolated from esterified wood should depend on the acylation conditions. Such factors as temperature and duration of the esterification and the composition of the acylating mixture also affect the yield and extent of substitution of the esters.

Increasing the temperature and duration of wood esterification increases the yield of cellulose esters (Table 2) because the extent of esterification increases. This is consistent with the increased degree of cellulose conversion in it (Table 1) and, therefore, the extent of substitution of cellulose acetic-butyric ester (Table 2).

Table 3 contains data for the yield and extent of substitution (ES) of cellulose esters isolated from wood esterification products at different mole ratios of acylating agents.

The results suggest that increasing the amount of acylating agent per mole of wood hydroxyls increases the yield and ES of cellulose esters (Table 3). The increased degree of cellulose conversion when acylated in the wood also explains this.

The ES of cellulose by acetic and butyric acids is different. We demonstrated previously [5] using GLC and PMR spectroscopy that the acylating agents for wood esterification by an acetic anhydride—butyric acid mixture are acetic and mixed acetic—butyric anhydrides.

The ES by acetic acid for all mole ratios of reagents (1:1:1-1:10:10) is greater than that by butyric acid. This can be explained by the higher reactivity of acetic anhydride compared with the mixed anhydride, the concentration of which becomes significant only if the reaction proceeds for more than 2 h.

TABLE 3. Yield (W, %) and ES of Cellulose Esters Isolated from Acylated Wood as a Function of Duration (τ , h) and Amount of Acylating Mixture

| τ , h | Mole ratio OH:AA:BA | W, % | ES _{tot} | ES _{AA} | ES _{BA} |
|------------|------------------------|------|-------------------|------------------|------------------|
| 2 | 1:3:3 | 42.2 | 0.45 | 0.40 | 0.05 |
| 6 | 1:3:3 | 45.6 | 2.25 | 2.00 | 0.25 |
| 2 | 1:10:10 | 44.9 | 1.49 | 1.39 | 0.10 |
| 6 | 1:10:10 | 47.6 | 2.03 | 1.64 | 0.39 |

TABLE 4. Effect of Carboxylic Acid on Yield (W, %) and ES of Cellulose Esters

| Carboxylic acid | W, % | ES _{tot} | Solubility in acetone, % |
|-----------------|------|-------------------|--------------------------|
| Propionic | 41.4 | 1.84 | 79 |
| Butyric | 45.3 | 1.26 | 65 |
| Valerianic | 48.4 | 0.97 | 57 |

For a 1:10:10 mole ratio of reagents and various esterification times (2 and 6 h), when the concentration of mixed anhydride is sufficiently high, the amount of added butyric acid increases whereas the total ES slightly decreases (Table 3).

Increasing the length of the added acyl radical smoothly increases the yield of cellulose esters (Table 4). The acylation rate apparently decreases with increasing molecular weight of the carboxylic acid used for wood esterification. This is due to the less favorable steric factors. Thus, the total ES of cellulose esters decreases (Table 4). Therefore, the duration of wood esterification must be increased in order to achieve the limiting ES of cellulose esters.

Thus, the production of mixed cellulose esters from wood by a unique method without previous isolation of the cellulose and without using organic solvents is shown to be possible in principle. Cellulose esters can be isolated from modified wood in 90-95% of the theoretical yield with ES 0.5-2.2.

The resulting cellulose esters are soluble to 57-79% in acetone and can be used to form films and thermoplastic binders for laminated composites.

EXPERIMENTAL

Acetic—butyric of esters aspen-wood were produced by the literature method [5] at 80-120°C in 2-8 h with preliminary mechanical treatment of air-dried sawdust together with a catalyst $[\text{Mg}(\text{ClO}_4)_2]$ in a ball mill at various mole ratios $\text{OH}:(\text{CH}_3\text{CO})_2\text{O}:\text{C}_3\text{H}_7\text{CO}_2\text{H}$. Cellulose esters were isolated from the products by the literature method [8] proposed for cellulose acetates.

Acylated wood (5 g) in a flask with a reflux condenser was treated over 5 h with peracetic acid (15.5%) at 100°C. The solid was filtered off, washed with hot water until the washings were neutral, washed with ethanol—acetone (100 mL, 1:1), and dried in air to constant weight. The yield was determined from the ratio to the mass of acylated wood.

The content of bound acyls in the isolated cellulose esters was determined by GLC and saponification of the acylated derivative with alcoholic NaOH [9].

IR spectra of cellulose esters in KBr (1.5%) were recorded under nitrogen on a Bruker W200 instrument.

REFERENCES

1. D. G. Barkalow, R. M. Rowell, and R. A. Young, in: *Polym. Mater. Sci. Engr.*, Proc. ACS Div. Polym. Mater., Washington, D.C. (1987), Vol. 57, p. 52.

2. R. M. Rowell and R. A. Young, in: Abstracts of Papers of the 194th ACS National Meeting, New Orleans (1987), p. 1061.
3. M. M. Chemeris, N. P. Mus'ko, B. N. Salin, et al., *Lesn. Zh. (Archangel)*, 84 (1998).
4. M. M. Chemeris, N. P. Mus'ko, O. L. Malikova, et al., *Lesn. Zh. (Archangel)*, 89 (1998).
5. M. V. Efanov, Candidate Dissertation in Chemical Sciences, Krasnoyarsk (1999).
6. R. P. Taylor and D. B. Abson, USA Pat. No. 3554775, MPK S 08 V 3/06, Publ. 12/01/1971.
7. D. E. Turksne, I. O. Ozolinya, and K. P. Shval'be, *Tr. Latv. SKh. Akad.*, No. 65, Elgava (1972), p. 51.
8. D. E. Turksne, *Wood Modification* [in Russian], Elgava (1977), p. 32.
9. V. M. Nikitin, *Theoretical Principles of Delignification* [in Russian], Moscow (1981).
10. M. Girardin and M. Metche, *J. Chromatogr.*, **46**, 155 (1983).
11. M. V. Efanov, L. A. Pershina, and A. G. Klepikov, *Plast. Massy*, No. 7, 41 (2000).