

**Esterification of wood with unsaturated
carboxylic acids. I.
Preparation of several wood-esters by
the TFAA method.**

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不飽和カルボン酸による木材のエステル化 (第1報)
TFAA 法による木材エステルの調製

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Résumé

In order to prepare esterified wood which would possess improved properties for many end uses, beech wood meal was treated with carboxylic acids, using the trifluoroacetic anhydride "impelling" method. The esterified wood was examined by several analytical methods.

Monocarboxylic acids reacted with wood in different degrees and more readily than di- and tribasic acids, while removal of very labile trifluoroacetyl groups was incomplete unexpectedly. Different degrees of esterification were well explained in terms of pK_a and steric configuration of acids used. Additional sulfuric acid catalyst brought about increasing esterification in many cases, but weight increase was diminished by its strongly degradative action on wood in some cases. The ordered region of wood was easily destroyed by less esterification, combined with EDA-pre-treatment on wood.

1. Introduction

Cellulose has been esterified with various carboxylic acids for the purpose of production of new plastics and textile fibers, and improvement of textile properties, while chemical modification of wood by acylation has mainly been carried out to improve dimensional stability as a result of decrease in hygroscopicity of wood. A few prepared esters of wood^{1,2)} have been reported. The purpose of the present investigation was to prepare wood esterifi-

ed with unsaturated carboxylic acids, which would possess improved properties for many end uses.

Recently, trifluoroacetic anhydride "impellent" method³⁾ was reported to be applicable for the partial esterification of cotton with retention of the fibrous structure. Furthermore, the method was described to have certain advantages; an esterifying acid need not be in the anhydride form, no additional catalyst is needed, trifluoroacetyl groups are not introduced,³⁾ and trifluoroacetic anhydride may dissolve cellulose.⁴⁾ This procedure was applied to esterification of wood.

2. Experimental

2. 1. Materials

Beech wood meal (*Fagus crenata* BLUME, 42-60 mesh) used in the study was previously extracted with a boiling ethanol-benzene (2 : 1 v/v) mixture for 24 hr. Unsaturated carboxylic acids and trifluoroacetic anhydride (TFAA) were of reagent grade, and summarized in Table 1. Benzene and the other reagents were also of reagent grade.

2. 2. Esterification procedure⁵⁾

In a typical ester preparation, an acid (0.3 g) was mixed with TFAA (0.7 ml) in benzene (10 ml), followed by dissolution of the acid. The mixture stood for 2-3 hr at 30°C (a so-called aging process). Oven-dried wood meal (0.5 g) was then treated by the esterification medium for 24 hr at 30°C. Esterified samples were removed, washed successively in benzene, ethanol and de-ionized water, neutralized in aqueous 5% sodium hydrogen carbonate solution for 2-3 hr at room temperature followed by washing in water again, and then soaked in water for 4-7 days, changing the water every day. These samples were washed in acetone, dried *in vacuo* and finally weighed. Weight increase percent and weight increase percent divided by molecular weight of acids (m mol of acid/100 g of wood) were calculated for the esterified wood, based on the weight of the original wood.

2. 3. Ethylenediamine pre-treatment on wood meal

Wood meal (2 g) was soaked in ethylenediamine (EDA) for 24 hr at room temperature, replaced stepwise by benzene through four benzene-EDA mixture of given ratios.

2. 4. IR absorption spectrophotometry, hygroscopicity measurement and x-ray diffractometry

IR spectra were measured with a Hitachi EPI-G3 spectrophotometer, by the KBr disk technique. Ratios among intensities of absorption bands at 3400 (OH), 2880 (CH), 1740 (C=O), and 1640 (C=C) cm^{-1} were calculated.

Moisture content measurements were made on esterified samples which were previously oven-dried and then conditioned at 65% RH and 20°C, over aqueous saturated solution of sodium nitrite. Moisture contents were expressed in percent increase, based on the dry weight of samples.

X-ray diffractometer traces were taken on a Rygaku Denki (Geiger Flex 2011 B) goniometer using nickel-filtered copper radiation between the angles 5 and 35° (2θ). Wood meal (0.2 g) was pressed to a pellet under a pressure of 2.03 ton/cm² for 1 min.⁶⁾ Crystallinity index (Cr. I) was determined according to the method of Segal et al.⁷⁾

3. Results and Discussion

3. 1. Preparation of wood-esters

Using several carboxylic acids shown in Table 1, esterifications of the original (untreated) beech wood meal extracted previously with a ethanol-benzene mixture were carried out under fixed conditions which might not be suitable for all of the acids used; for examples, a molar ratio of TFAA to a carboxyl group was not considered carefully, while it is advisable for the ratio to be about 1 : 1.⁸⁾

As hydrophobic ester linkages take the place of hydrophilic hydroxyl groups, esterification of wood will generally cause decrease in moisture content, if there is no introduction of unreacted hydrophilic acid or bulky ester groups which give rise to decrystallization and new accessible hydroxyl groups in wood. Moisture contents of all esterified wood were lower than that of the original wood (10-11%), as shown in Fig. 1. Weight increase percent corresponded also to saponification value of each esterified wood. These facts suggest that weight increase, in the present study, is due to formation of ester linkages rather than deposition of unreacted acids; that is, wood is well esterified by the TFAA method. However, weight increase may not indicate the correct degree of esterification, since absorption bands at 1780, 1160, 775 and 745 cm⁻¹ in some esterified wood (Fig. 2) show remain of trifluoroacetic ester which is said to be much less stable than normal carboxylic acid esters and easily removed.⁹⁾ Complexity of wood seems to cause difficult and incomplete

Table 1 Partial esters of beech wood meal esterified with unsaturated mono- and dicarboxylic acids

Acid	Weight increase (%)	Wt. inc. Mol. Wt. x 10 ⁻³	Acid	Weight increase (%)	Wt. inc. Mol. Wt. x 10 ⁻³
Acrylic	9.37	130	Fumalic	0.95	8
Vinylacetic	23.54	273	Maleic	0.34	3
Methacrylic	5.13	60	Mesaconic	3.96	31
<i>trans</i> -Crotonic	33.92	394	Citraconic	0.13	1
Tiglic	30.64	306	Itaconic	- 0.23	- 2
β -Methylcrotonic	18.25	183	Phthalic	- 0.48	- 3
Sorbic	59.59	532	Adipic	11.32	78
10-Undecylenic	25.95	141	Citric	2.88	15
Linoleic	8.57	32	Acetic	26.71	445
Elaidic	27.20	96	Stearic	10.74	38

Beech wood meal 0.5g, carboxylic acid 0.3g, TFAA 0.7ml, and benzene 10ml; at 30°C, for 24 hr.

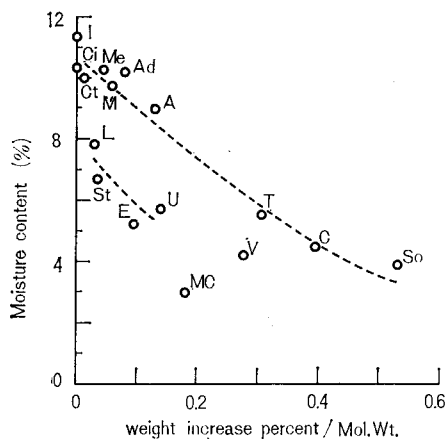


Fig. 1 Moisture contents of the wood meal esterified in different degrees with the following acids; acrylic (A), vinylacetic (V), methacrylic (M), *trans*-crotonic (C), tiglic (T), β -methylcrotonic (MC), sorbic (So), itaconic (I), mesaconic (Me), citraconic (Ci), 10-undecylenic (U), linoleic (L), elaidic (E), stearic (St), adipic (Ad) and citric (Ct)

Fig. 1 shows that higher hydrophobicity (*i. e.*, lower moisture content) was given by acids of long chain length (lower line in Fig. 1) rather than shorter analogues (upper line) because of the increasingly hydrophobic nature of acids with increasing chain length. Moisture content was not changed by esterification with adipic acid. Campbell and Francis⁸⁾ obtained similar results, explained by formation of diester cross linkages not always giving rise to diminishing moisture content for cellulose esterified with diacids of short chain length, but which may be simply due to formation of the monoester of these dibasic acid. The finding that two repeated experiments gave dissimilar weight increase of 18.25 and 71.51%, in the case of esterification of wood with β -methylcrotonic acid, suggests dissolution of the esterified wood into the reaction medium followed by weight-loss, since the cellulose-ester is soluble in benzene.

Both saturated and unsaturated monocarboxylic acids reacted readily with wood in the presence of TFAA "impellent", but the degree of esterification with di- and tribasic acids was very low, except for adipic acid (Table 1). In the work of Campbell et al.,⁸⁾ similar low reactivities of dibasic acids in the range C₂ to C₅ were observed. As dibasic acids used in this study are considered to have a main-chain length of four carbon atoms, the result is consistent with the finding described by Campbell et al. Moreover, the facts were explained in terms of less dissolution of acids in benzene containing TFAA, decomposition of acids by TFAA, and preferred formation of intramolecular cyclic anhydride. Although dibasic acids were less reactive, the last interpretation seems to explain satisfactorily that *trans*-type acids such as fumaric and mesaconic acids, which were less soluble in the esterification medium, reacted more readily with wood than *cis*-type acids such as maleic and citraconic

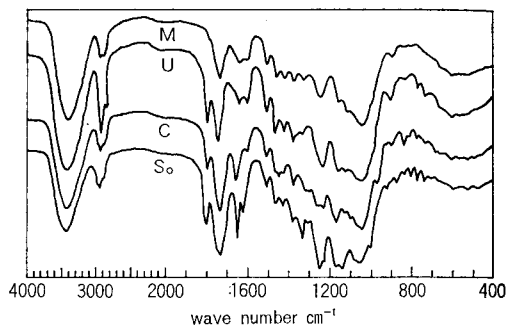


Fig. 2 Infrared spectra of the original wood esterified with methacrylic (M), *trans*-crotonic (C), sorbic (So) and 10-undecylenic (U) acids

removal of trifluoroacetyl groups, even if it is soaked in water for 7 days. Hence, weight increase percent will not always express correctly the extent of esterification for esterified wood, but is thought to indicate it approximately.

acids, which were completely dissolved in the medium, and also than acids such as phthalic and itaconic acids which would be able to form stable intramolecular cyclic anhydrides.

On rearranging the data of various cellulose-esters prepared by Hamalainen et al.³⁾ in pK_a of each acid, acyl contents of these esters were found to depend on their pK_a ; that is, they were large for weak acids and small for strong acids. The acylating properties of solution of weak acids in TFAA are generally attributed to acyl ion (RCO^+) derived from ionization of the unsymmetrical anhydride which is preferentially formed by interaction of TFAA with acids, and the ionization is accelerated by general acid catalyst, TFAA present in these systems being important in this respect.¹⁰⁾ Thus, acidity of each acid is thought to affect equilibrium between TFAA and acids. Fig. 3 gives relationship between pK_a and extents of esterification,

expressed in the ratio of intensities of absorption bands of carboxyl and hydroxyl groups, for acids of similar molecular structure. Reactivity is found to depend on pK_a rather than molecular size, as cited above. It seems also to be effective and important for esterification with acrylic acid analogues that the carboxyl group is joined to one of the unsaturated carbon atoms, and methyl groups to the other. A similar result was described by Matsuzaki and Miyata, who esterified cellulose with a mixture of acetic anhydride and unsaturated carboxylic acids in the presence of sulfuric acid catalyst.¹¹⁾ Again, low reactivities of dibasic acids can reasonably be explained by their small pK_a ; dibasic acids employed were stronger than the other monobasic acids.

That sulfuric acid as an additional catalyst brought increasing esterification, in the cases of acrylic, methacrylic and adipic acids (Table 2), is in agreement with recommended

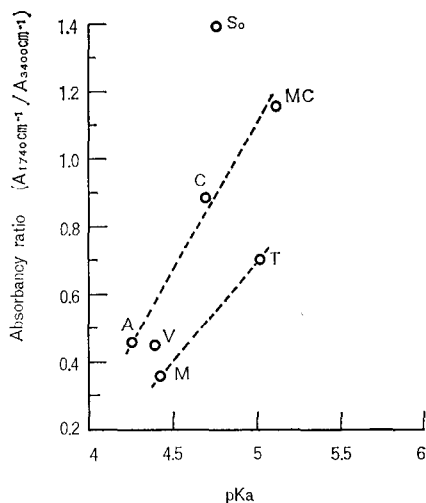


Fig. 3 Relation between the ratio of intensity of the IR band at 1740 (CO) cm^{-1} to that at 3400 (OH) cm^{-1} for esterified wood and pK_a of acrylic acid analogs

Same symbols as in Fig. 1

Table 2 Esterification of wood with unsaturated carboxylic acids in the presence of sulfuric acid

Acid	Weight increase (%)	Wt. inc. Mol. Wt. $\times 10^{-3}$	Acid	Weight increase (%)	Wt. inc. Mol. Wt. $\times 10^{-3}$
Acrylic	21, 21	294	Fumalic	- 0, 32	- 3
Methacrylic	18, 51	215	Maleic	0, 06	1
<i>trans</i> -Crotonic	- 72, 26	- 839	Mesaconic	8, 05	62
Adipic	13, 08	90	Citraconic	- 0, 94	- 7
			Phthalic	- 2, 88	- 17

Beech wood meal 0.5g, carboxylic acid 0.3g, TFAA 0.7ml, H_2SO_4 0.01ml, and benzene 10ml; at 30°C, for 24 hr.

addition of strong acid, together with the monochloroacetic anhydride "impellent"¹⁰⁾. Unusually large decrease in the weight of wood esterified with *trans*-crotonic acid, in the presence of additional sulfuric acid, is considered to be due to degradation of cellulose and hemicellulose components by sulfuric acid, followed by dissolution of the esterified sugar into the reaction medium, since it is easily soluble in benzene. The mild nature of TFAA and the great value of the TFAA method seem to be clearly shown in Tables 1 and 2, comparing very little degradation by TFAA with remarkable decrease by sulfuric acid.

3. 2. Effect of EDA-pre-treatment on wood

The fine structure of cellulose has long been considered to be the overriding factor in determining chemical reactivity, since reaction takes place most readily in the region of low, three-dimensional, molecular order.¹²⁾ Therefore, decrystallization of wood is hoped to bring about increasing ester-formation. However, saponification values in the present work were 2.32, 4.32, 4.63 and 2.95 meq/g for the untreated wood, and 0.50, 2.98, 3.95 and 1.96 meq/g for the EDA-treated wood, on esterifying with methacrylic, crotonic, sorbic and 10-undecylenic acids, respectively. The EDA-treatment did not always lead to increasing esterification, even if loss of acetyl groups (about 2 meq/g) of the untreated wood by the pre-treatment is taken into account. A similar tendency was clarified by measuring intensities of absorption bands of unsaturated carbons (1640 cm^{-1}). This unexpected result is explained in the term of insufficient solvent-replacement. In other words, remaining EDA suppressed the esterification reaction, since a basic substance inhibits the important acid-catalyzed ionization cited above.

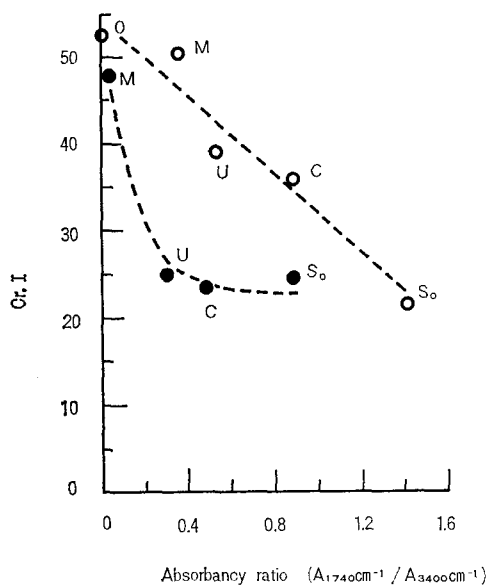


Fig. 4 Crystallinity indices of the original (O) and EDA-treated (●) wood meal, esterified with four acids

Same symbols as in Fig. 1

A little esterification of the EDA-treated wood showed remarkable decrease in its Cr. I, but increasing ester-formation gave gradually diminishing Cr. I for the untreated wood (Fig. 4). EDA-swollen wood almost completely reverts back to the original cellulose I structure after soaking in water and polar solvents, but only a little in nonpolar solvents such as chloroform and benzene.¹³⁾ In the present study, wood which was treated with EDA which was then replaced by benzene is considered to have been in EDA-cellulose complex structure, that is, in a loose arrangement than original cellulose I. During the subsequent esterification process, polar acids in the reaction medium would, however, be able to remove the diamine from the complex in the swollen wood, and easily penetrate in place of the diamine into the original ordered region. Hence, the reaction in the crystalline

region would proceed more readily in the treated wood than in the untreated. Regeneration to cellulose I by soaking in water after the reaction would be inhibited by introduction of new ester groups into the original crystalline region, because of their bulky effects and different electrostatic properties to OH groups. On the other hand, the gradual decrease in Cr. I for the original wood seems to be caused by simply overlapping peaks of non-esterified crystalline cellulose and esterified amorphous cellulose on the x-ray diffractogram, or by slow esterification in the ordered region.

The degree of decrease in moisture content of the untreated wood was larger than that of the EDA-treated one, when they were esterified (Fig. 5). Submicroscopic structure and chemical composition of wood usually determine the amount of moisture absorbed. Thus, moisture content will be increased by decrystallization (increasing amorphous region), but be reduced by exchanging hydrophilic OH groups for hydrophobic ester linkages (increase in the degree of esterification). The degree of esterification, restricted to the expression of change in chemical composition, will affect moisture content of both EDA- and untreated wood in the same manner. Therefore, a smaller degree of decrease in moisture content of the EDA-treated wood is considered to be mainly due to changes in submicroscopic structure, that is, decrystallization of wood. These results suggest that more disordered wood will be prepared by less esterification in this TFAA method, combined with the EDA-treatment and subsequent solvent-replacement.

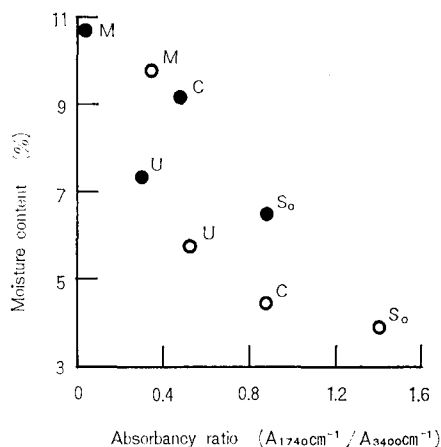


Fig. 5 Moisture contents of the esterified wood which were employed in Fig. 4

Same symbols as in Fig. 4

References

- 1) H. Tarkow, A. J. Stamm and E. C. O. Frickson : Acetylated wood, U.S. Dept. Agric. Circ., No. 1593 (1955)
- 2) R. Popper und M. Bariska : Die Azylierung des Holzes, *Holz Roh Werkstoff*, **30**, 289 (1972)
- 3) C. Hamalainen, R. H. Wade and E. M. Buras, Jr. : Fibrous cellulose esters by trifluoroacetic anhydride method, *Text. Res. J.*, **27**, 168 (1957)
- 4) O. Nakao : New method for dissolving cellulose and/or cellulose graft copolymer, *Fiber Sci. Ind.*, **4**, 128 (1971)
- 5) M. D. Cruz-Lagrange, C. Hamalainen and A. S. Cooper, Jr. : Preparation and evaluation of selected aliphatic acid esters of cotton fiber, *Amer. Dyest. Rep.*, **51**, 428 (1962)
- 6) N. Shiraishi, T. Yokota, T. Kimura and K. Sumizawa : The interaction of wood with organic solvents, *Mokuzai Gakkaishi*, **18**, 215 (1972)
- 7) L. Segal, J. J. Creely, A. E. Martin, Jr. and C. M. Conrad : An empirical method for estimating the degree of crystallinity of native cellulose using the x-ray diffractometer, *Text. Res. J.*, **29**, 786 (1959)
- 8) H. J. Campbell and T. Francis : The cross-linking of cotton cellulose by aliphatic dicarboxylic acids, *Text. Res. J.*, **35**, 260 (1965)
- 9) E. J. Broune, M. Stacey, J. C. Tatlow and J. M. Tedder : Studies on trifluoroacetic acid, *J.*

Chem. Soc., **1949**, 2976

- 10) J. M. Tedder : The use of trifluoroacetic anhydride and related compounds in organic synthesis, *Chem. Rev.*, **55**, 787 (1955)
- 11) K. Matsuzaki and T. Miyata : Reactions of cellulose with α, β -unsaturated carboxylic acids-acetic anhydride mixture, *Kogyo Kagaku Zasshi*, **70**, 770 (1967)
- 12) D. M. Jones : Structure and some reactions of cellulose, *Adv. Carb. Chem.* **19**, 219 (1964)
- 13) L. Loeb and L. Segal : Studies of the ethylenediamine-cellulose complex, *J. Polym. Sci.*, **15**, 343 (1955)

要 旨

無水トリフルオロ酢酸法を用いて、木材の不飽和カルボン酸エステルを調製し、木材の改質を試みた。エステル化木材を赤外線吸収、X線回折、吸湿およびけん化法で検討し、次の結果を得た。

1) エステル化度は酸の種類により大きい差異があった。これは主として酸の pK_a で説明されたが、分子構造（アクリル酸系列でのメチル基とカルボキシル基の相互位置、二塩基酸でのシスとトランス配置など）も影響した。2) 反応後、トリフルオロ酢酸を除くことは意外に困難であった。3) 硫酸の少量添加はエステル化を促進したが、木材の分解ももたらした。4) 木材をエチレンジアミンで前処理すると、わずかのエステル化で木材の非晶化が行なえる結果も示された。