Esterification of wood with unsaturated carboxylic acids. II.
Reaction conditions of esterification and properties of the prepared esters of wood.

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不飽和カルボン酸による木材のエステル化 (第2報)
エステル化条件およびエステル化木材の性質について

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Contents

要　　　旨

TFAA法による木材のエステル化の条件を検討した。カルボン酸とTFAAを稀釈剤中で等モル混合し、あらかじめ、30分ほど熟成した後、木材試料に対し大過剰添加すれば良いことが知られた。補助的な硫酸添加はエステル化を促進するが、その使用量には十分な注意を要する。エステル化の速度を両対数グラフに表わすと、屈曲点を持つ直線関係が得られた。温度依存性から算出された見掛けの活性化エネルギーは、Hiller の値より多少小さかった。TFAA法で調製したエステル化木材はASEなどの物性が若干劣化した。

1. Introduction

In order to find new applications, wood has been modified chemically by introduction of various reactive groups, using esterification, etherification and other methods. Authors have recently reported that the TFAA "impelling" method is successfully applicable for esterification of wood with unsaturated carboxylic acids.[1]

This paper describes some reaction conditions of esterification between wood and unsaturated carboxylic acids such as methacrylic acid which has a double bond and whose esters are widely used in graft co-polymerization to cellulose. In addition, several properties of wood specimens esterified are studied in connection with retention of the original wood structure.

2. Experimental

2. 1. Materials

Beech wood meal (*Fagus crenata* BLUME, 42-60 mesh) extracted with benzene-ethanol, and birch wood specimens (*Betula maximowiczii* REGEL, 30 (R) x 30 (T) x 5 (L) mm) were used.

Reagent-grade trifluoroacetic anhydride (TFAA), carboxylic acids and other reagents were used without further purification.

2. 2. Esterification and analyses

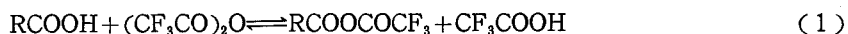A typical ester preparation has been described in the previous paper.[1]

Weight increase percent, IR absorbancy ratio, crystallinity index (Cr. I) and moisture content were obtained according to the methods described previously.[1] Saponification value of the ester was determined by saponification with 0. 1 N alcoholic potassium hydroxide.[2]

Dimensional changes of wood specimens were measured in tangential and radial directions by a screw-micrometer, and volumetric antishrink efficiency (ASE) was calculated.[3]

3. Results and discussions

3. 1. Effect of pre-incubation

Esterification by the TFAA "impelling" method is said to be caused by the acylating activity of the unsymmetrical anhydride which is formed by dissolving a carboxylic acid in TFAA and ionizes to a slight extent into acylium and trifluoroacetate ions, the former being the principal acylating species (Equations 1 and 2).[4]

$$RCOOH + (CF_3CO)_2O \rightleftharpoons RCOOCOCF_3 + CF_3COOH \qquad (1)$$

$$RCOOCOCF_3 \rightleftharpoons RCO^+ + CF_3COO^- \qquad (2)$$

In other words, the mixture of the carboxylic acid and TFAA must be previously incubated to form enough amount of acyl trifluoroacetate, before wood sample is added and esterified. Fig. 1 shows that very short pre-incubation time (aging time) gives even a constant amount of *trans*-crotonyl esters of wood, while about 30 minutes of aging time is necessary for constant formation of methacryl esters. A series of the equilibria (Equations 1 and 2) are thought to be rapidly esterified. Longer aging time may be required for a carboxylic acid of small pK_a, which gave smaller amount of wood-ester,[1] because of unfavourable equilibria for formation of reactive acylium ions. A similar tendency was also obtained by measurements of IR absorbancy ratios and saponification values.

Measurement of IR absorbancy ratio showed that it was advisable to be 1 : 1 for the molar ratio of TFAA to a carboxylic acid (Fig. 2). Although molar ratios of more than 1 : 1 seem to be more effective from weight increase percents and saponification values, these excessive values are caused by the simultaneous formation of both carboxyl and trifluoroacetyl esters, the latter being essentially easy to be removed by washing with water but difficult in the case of esterification of wood.[1]
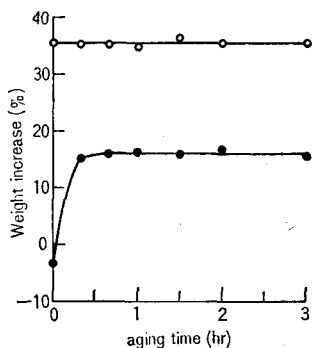
Fig. 1 Effect of aging time of the esterification mixture on *trans*-crotonylation (o) and methacrylation (●), at 30°C
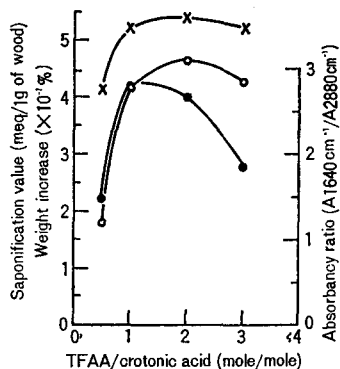

Fig. 2 Effect of molar ratio of TFAA to *trans*-crotonic acid in the esterification mixture
wt. inc. (o) absorb. ratio (●) saponif. value (x)

3. 2. Several reaction conditions

Trifluoroacetic acid formed according to the equation 1 is thought to act as the catalyst in the present method. Moreover, increasing addition of sulfuric acid as another acid-catalyst brought about increasing esterification, as shown by the saponification value in Fig. 3. Weight increase measurement indicated, however, that excessive sulfuric acid afforded smaller amount of products than that of starting materials, as the mineral acid had strong hydrolytic ability on cellulosic materials, which has been widely applied to quantitative lignin analysis,[5] cellobiose synthesis[6] and so on. A similar result was also obtained for *trans*-crotonylation. Thus, curves in Fig. 3 show the most suitable quantity of sulfuric acid to produce the greatest yield of esters. In most cases, sulfuric acid is not advisable or else must be used as little as possible, although the mineral acid is an effective and useful catalyst for the esterification with strong carboxylic acids.

Fig. 4 shows the effect of the ratio of wood to the esterification mixture (molar ratio,
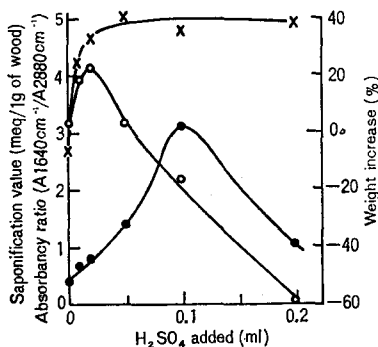

Fig. 3 Effect of the additional sulfuric acid-catalyst on methacrylation
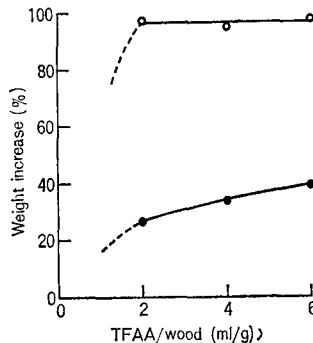Same symbols used as in Fig. 2

Fig. 4 Effect of ratio of TFAA (or a carboxylic acid) to wood on β-methylcrotonylation (o) and acetylation (●)

1 : 1) of a caboxylic acid and TFAA. Considering that the used beech wood contains about 25 % lignin (by the Klason method[5]), one gram of wood has about 14 mmol of reactive hydroxyl groups which are equivalent to 1. 9 ml of TFAA, 1. 4 g of β-methylcrotonic acid or 0. 84 ml of acetic acid. Increasing esterification was obviously brought about by increasing excess of the medium. In the case of β-methylcrotonic acid, a slight excess of the medium theoretically required gave efficiently the wood-ester whose DS (degree of substitution) was 2. 56. On the other hand, DS of the acetylated wood were 1. 37, 1. 75 and 2. 00, respectively. These DS values were calculated from the weight increase percent (W. I.), using the following equation; assuming that no degradation occurs during the esterification,

$$DS = \frac{M_g \times (W. I.)}{(100 - L)(M_a - 18)}$$

L is lignin content in wood sample (25 % for beech wood used), and M_a and M_g are molecular weights of carboxylic acids and anhydroglucose units of cellulose, respectively.

Reaction rates of esterification of wood with some of carboxylic acids are shown in Fig. 5, on a log scale. A refractive point, showing a probable change of reaction mechanism, appeared on the lines of esterification of the ethylenediamine (EDA)-untreated wood. Weight increases of 20, 18 and 16 % at the point correspond to similar DS values of 0. 64, 0. 59 and 0. 64 for *trans*-crotonylation, methacrylation and acrylation, respectively, calculated from the equation 3 and 25 % lignin content. Assuming that amorphous materials are at first esterified throughout and subsequent acylation of crystalline cellulose sets in, and that maximum theoretical DS of the amorphous materials is 3 or 2, the above DS will show that the crystalline cellulose content of holocellulose in wood is about 80 or 70 %. In the range of the measurements, β-methylcrotonylation was too fast to estimate the crystallinity. Unusual decrease of acrylation may be due to degradation of wood substance with the additional sulfuric acid. On the other hand, no refractive point is shown on two lines of esterification of the EDA-treated wood, which is known to have different crystalline structure
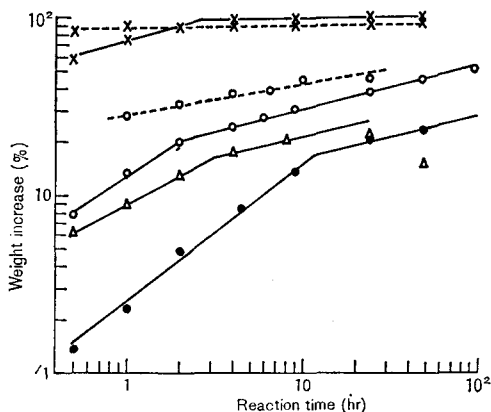

Fig. 5 Reaction rates of esterification with *trans*-crotonic (○), methacrylic (●), acrylic (△) and β-methylcrotonic (x) acid, at 30°C wood ; ——untreated ······EDA-treated
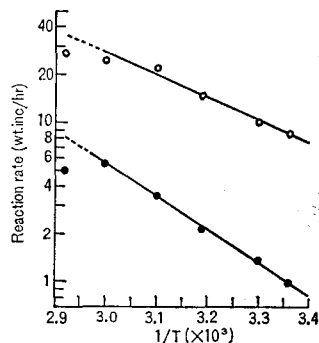
Fig. 6 Temperature dependence of reaction rates for *trans*-crotonylation (○) and methacrylation (●)

from that of the original wood.

The effect of temperature on acylation is illustrated in Fig. 6, where the logarithm of the reaction rate, in terms of weight increase percent per hour, is plotted against the reciplocal of the absolute temperature. In the range of these measurements, the rate of *trans*-crotonylation is obviously larger than that of methacrylation. Apparent activation energies (E_a) calculated from the slopes of the straight lines in Fig. 6 were 6.33 and 9.43 kcal/mole for *trans*-crotonylation and methacrylation, respectively. On the 0.1 % sulfuric acid-catalyzed acetylation of the primary and secondary hydroxyl groups of the partially acetylated cellulose in homogeneous solution, Hiller[7] has obtained E_a of 10.3 and 13.4 kcal/mole, respectively, which are pointed out to be reasonable comparing with those of acetylation of simpler alcohols. He has also reported 11.0 and 24.6 kcal/mole for the uncatalyzed acetylation of the same samples. Considering both the proportion of crystalline cellulose in wood and the calculated maximum amount of the esterified holocellulose from weight increase, the similar but somewhat smaller values are thought to be those of esterification of amorphous cellulose or hemicellulose which are present as a more homogeneously soluted state in the reaction medium. Deviation in the higher temperature range of the *trans*-crotonylation may be caused by the use of average weight increase per initial one hour or else by a change of a reaction mechanism.

3.3. Properties of esterified wood specimens

Although a reaction condition was not the most suitable for each acid but fixed, weight increase in wood specimen was smaller than that in wood meal[1], on esterification, except vinylacetylation[9]. More reduced weight increases of the specimens were obtained especially for acids of high molecular weight such as elaidic and 10-undecylenic acid. In the case of esterification of the specimen, steric effects are necessary to be considered additionally.

Several properties of esters of specimens are given in Table 1. The β-methylcrotonyla-

Table 1 Some properties of birch wood specimens esterified with various carboxylic acids

Wood[a] esterified	Weight[b] increase (%)	DS[c]	Moisture content (%)	Cr. I	ASE	Volume[b] increase (%)
Original	0	0	10.83	60.7	0	0
Acetyl	26.03	1.26	5.26	24.5	−111	5.9
Acryl	4.77	0.18	9.52	57.8	− 57.8	− 2.8
Methacryl	4.76	0.14	9.09	58.4	− 68.8	− 2.3
trans-Crotonyl	30.75	0.92	4.91	38.5	− 10.4	19.7
Vinylacetyl	29.30	0.87	4.80	44.9	15.7	16.5
Tiglyl	29.51	0.73	5.35	42.3	− 2.2	17.0
β-Methylcrotonyl	—	—	—	−25.4	—	—
Sorbyl	29.65	0.64	5.61	6.9	6.0	29.6
10-Undecylenyl	15.10	0.18	6.73	51.0	− 9.1	5.5
Elaidyl	2.90	0.02	9.97	61.8	− 41.7	−3.0

a) esterified with wood 5g, acid 3g, TFAA 7ml and benzene 50ml, at 30°C for 24hr
b) percentage increase in oven-dry weight or volume on esterification
c) calculated from the equation 3 and 20% lignin content

tion proceeded readily, specimens were degraded, and a part of the ester produced were dissolved in the reaction medium. In the table, esterification seems to have brought about a increase in oven-dry volume[8] and decrease in Cr. I and moisture content.[8] Undecylenyl ester gave smaller moisture content, as suggested in the previous paper.[1] Small Cr. I of the sorbyl ester may be caused by a preferential and inhomogeneous esterification in the surface area of the wood specimen. On the other hand, ASE measurement did not show a definite tendency. However, limited esterification with acrylic, methacrylic and elaidic acid afforded remarkable decrease in ASE and negative values of oven-dry volume, in spite of a little change of Cr. I and moisture content. This result is undesirable for retention of the original wood structure.

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Résumé

Several reaction conditions for the esterification of wood by the TFAA method were investigated. The results showed conclusively that wood could be esterified satisfactorily with an excess of an esterification mixture which contained nearly equimolar amounts of a carboxylic acid and TFAA in benzene as diluent and was preliminarily incubated for about 30 minutes. The additional sulfuric acid-catalyst gave a greater degree of esterification. The curves of the esterification rates, on a log scale, had refractive points which would show a change in the reaction mechanisms related to the crystalline structure of the wood. The apparent activation energies were also calculated from the slopes of the lines of the temperature-dependence of the reaction rates. This esterification method caused, however, an unfavourable reduction in the antishrink efficiency.