

Preparation and crosslinking of oligoesterified woods based on maleic anhydride and allyl glycidyl ether

H. Matsuda, M. Ueda and H. Mori, Kagawa-ken, Japan

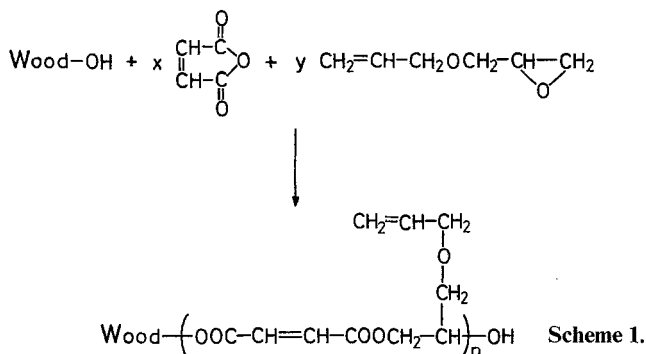
Summary. Oligoesterification of wood was investigated by alternately adding esterification reactions of wood with maleic anhydride and allyl glycidyl ether. The products obtained consisted of acetone-insoluble and soluble parts. The insoluble parts were novel oligoesterified woods with oligoester chains having polymerizable double bonds. The oligoester chain length showed a tendency to decrease with increase in wood content in feed. The soluble parts were free oligoesters which were not linked with the wood matrix. The products (the oligoesterified wood-containing mixtures), when subjected to hot-pressing in the presence of a peroxide, gave plasticized crosslinked wood boards whose surfaces are smooth, glossy, and plasticlike. In this case, the free oligoesters which were hardening worked as a plasticizer for the wood components and were combined, by the crosslinking, with the oligoesterified woods, resulting in the formation of the network structure. The crosslinked wood boards exhibited outstanding properties in heat distortion temperature ($> 165^{\circ}\text{C}$) and compressive strength (ca. 1,600–2,300 kg/cm²).

Introduction

Previously we have reported that dicarboxylic acid anhydrides such as maleic anhydride (MA), succinic anhydride, etc. add to wood by addition reaction (esterification), even in the absence of solvent, to produce esterified woods bearing carboxyl groups (Matsuda et al. 1984; Matsuda 1987). The esterified woods, when subjected to an addition reaction (esterification) with phenyl glycidyl ether (PGE), gave PGE-adducted esterified woods (Matsuda, Ueda 1985 a; Matsuda 1987). Other epoxides such as allyl glycidyl ether (AGE) and glycidyl methacrylate also react with the esterified woods (Matsuda, Ueda 1985 b; Matsuda 1987).

When the PGE-adducted esterified woods were allowed to react with a mixture of the anhydride and PGE, alternately adding esterification reactions occurred, to produce oligoesterified woods (Matsuda, Ueda 1985 a; Matsuda 1987). Similarly, when the carboxyl group-bearing esterified woods were subjected to the addition reactions with the epoxide and the anhydride step by step alternately, oligoesterified woods having oligoester chains with various chain length were obtained (Matsuda, Ueda 1985 b; Matsuda 1987). In the detailed studies on the preparation of the oligoesterified woods, mainly PGE was used as the epoxide.

However, detailed studies on oligoesterified woods with oligoester chains having polymerizable double bonds have not been reported so far. Such oligoesterified woods are of interest in that they will be crosslinked at high temperatures and under high pressures, accompanying plasticization of the wood components. Further, it is considered to be more advantageous to prepare the oligoesterified woods without the process of isolating the intermediate esterified wood. In the present study, preparation of novel crosslinkable oligoesterified woods was investigated by the oligoesterification reaction of wood with MA and AGE without isolating the intermediate esterified wood, as shown by Scheme 1. The oligoesteri-



fied woods obtained were subjected to crosslinking reaction accompanying the plasticization of the wood components, to obtain novel plasticized crosslinked woods. Further, main properties of the crosslinked woods were discussed.

Experimental

Materials

The wood sample used was wood meal (100–200 mesh) of red pine (*Pinus densiflora* Sieb. et Zucc.). It was subjected to Soxhlet extraction with ethanol–benzene (1 : 2) for 8 h, and then with acetone for 8 h. Before use, it was thoroughly dried at 120 °C. MA and AGE of special grade were used as received.

Oligoesterification reaction

In a 5 l separable flask equipped with a stirrer, a dropping funnel, and a condenser were placed fixed amounts of the wood meal and MA, and the content was stirred at 120 °C for 1 h. Next, a quantity of AGE such as to give a desired weight ratio of the reaction system was gradually added with stirring over 15 min. Then, the mixture was stirred at the same temperature for a given time, to obtain the product.

During the reaction, samples were taken for analyses of acid and epoxide. After the reaction, a part (17–19 g) of the product was subjected to Soxhlet extraction with acetone for 6 h for separation of acetone-soluble and insoluble parts.

Also, reaction of wood with MA was conducted as follows: A mixture of the wood meal and MA at a fixed weight ratio was stirred at 120 °C for a given time. After the reaction, a large quantity of acetone was added, and the mixture was filtered to isolate the product. The product was washed with acetone and then further subjected to Soxhlet extraction with acetone for 6 h to remove unreacted MA completely, and was dried.

Crosslinking reaction accompanying plasticization of wood

To the oligoesterified wood-containing mixture, 2 wt-% of dicumyl peroxide (DCP) was added, and the mixture was kneaded with a mixing roll thoroughly. Then, 97 or 194 g of the mixture was placed in a mold and the mold was placed in a hot-press (of 30.3 cm ram-diameter) equipped with electrically heated plates. The mixture in the mold was hot-pressed at 150 °C, 275 kg/cm² for 30 min, to obtain the plasticized crosslinked wood board of 23 × 8.6 × 0.37 cm or 23 × 8.6 × 0.7 cm.

Determinations

Acid value was determined as follows: About 0.1 g of sample was weighed accurately into a flask and about 10 ml of acetone was added. Next, 10 ml of 0.1 N HCl was added by pipet, and further 100 ml of distilled water was added. It was titrated with 0.1 N KOH using phenolphthalein (PhPh) as indicator. Acid value was calculated using the equation shown in the previous article (Matsuda 1987).

When the progress of reaction was followed, acid value was determined not only in the aqueous medium but also in nonaqueous medium. Acid value determined in nonaqueous medium will be denoted by NA acid value: About 0.1 g of sample was weighed accurately into a flask and about 10 ml of acetone was added. Next, 10 ml of 0.1 N KOH-methanol was added by pipet. After standing for 5 min, 10 ml of 0.11 N HCl was added and then 100 ml of distilled water was added. It was titrated with 0.1 N KOH using PhPh indicator. NA acid value was calculated using the following equation:

$$\text{NA acid value (eq/kg)} = \frac{(V' - L) \times f'}{W'}$$

where V' = amount (ml) of 0.1 N KOH aqueous solution used in titration; L = amount (ml) of 0.1 N KOH aqueous solution used for neutralizing mixed solution of 10 ml of 0.1 N KOH methanol solution – 10 ml of 0.11 N HCl aqueous solution; f' = factor of 0.1 N KOH aqueous solution; W' = weight (g) of sample.

The acid values shown in this article, unless NA is added to acid value as NA acid value, mean those determined in the aqueous medium.

Epoxide value (E) was determined, referring to the HBr method (Fisch, Hofmann 1961), as follows: About 0.1 g of sample was weighed accurately into a

flask and about 10 ml of chloroform was added. Further, 7 ml of 0.1 N HBr glacial acetic acid solution was added and the mixture was allowed to stand for 30 min. Next, 10 ml of 0.1 N solution of PGE in monochlorobenzene was added by pipet. It was back-titrated with 0.1 N HBr glacial acetic acid solution using crystal violet as indicator. Since the original wood sample consumed a constant, small quantity of HBr, correction was made for this factor. E was calculated using the following equation:

$$E \text{ (eq/kg)} = \frac{(7.0 + V - B) \times f}{W} - C$$

where V = amount (ml) of 0.1 N HBr glacial acetic acid solution used in titration; B = amount (ml) of 0.1 N HBr glacial acetic acid solution used for titrating 10 ml of 0.1 N solution of PGE in monochlorobenzene; f = factor of 0.1 N HBr glacial acetic acid solution; W = weight (g) of sample; C = correction value (eq/kg) for the original wood sample.

Scanning electron micrograph (SEM) was taken using a scanning electron microscope JSM-T 100 (Nihon Denshi Co.).

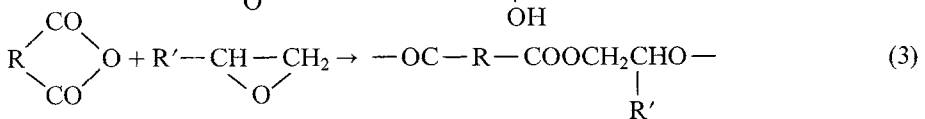
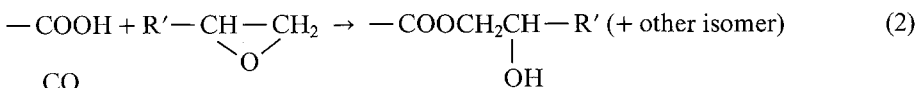
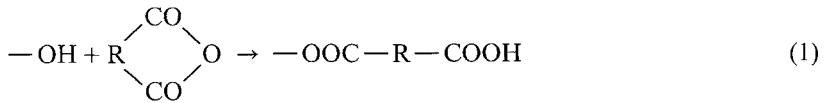
Tensile strength was determined according to ASTM D 638-68, by using a Shimadzu Autograph IS-5000.

Furthermore, the following determinations were conducted by the same methods as described in the previous article (Matsuda 1987): Saponification value; weight increase; monoester and diester contents; infrared (IR) spectra; flexural, compressive, and impact strengths; Rockwell hardness; heat distortion temperature (HDT); water resistance.

Results and discussion

Oligoesterification reaction

In the oligoesterification of wood in this work, the following main reactions of the functional groups are considered:



First, the reaction of hydroxyl groups of wood with MA, that is, reaction (1), should occur, to produce esterified wood bearing carboxyl groups. The carboxyl groups are starting points for chain extension. That is, to the carboxyl group, AGE adds to form a new hydroxyl group, as shown by reaction (2). Next, the reaction of

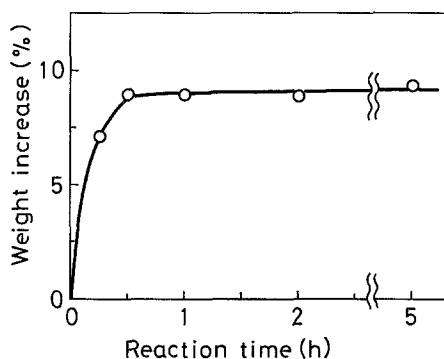


Fig. 1. Effect of reaction time on weight increase of esterified wood obtained for reaction of wood with MA at 120 °C. Feed weight ratio of wood : MA = 100 : 26.5

the hydroxyl group so produced with MA, that is, again reaction (1), occurs. Thus, these addition reactions are considered to repeat alternately, leading to the formation of oligoesterified woods (Scheme 1). Isomers are considered in the product, depending on the position of ring opening of the epoxy ring. The structure of the product in Scheme 1 is an idealized one. Meanwhile, since the concentration of MA is high in the initial stages of the reaction, the reaction of MA with AGE (Fischer 1963), that is, reaction (3) is considered possible. However, this reaction results in structurally analogous free oligoester chains which are not linked with the wood matrix. In addition, active hydrogens contained in trace amounts of impurities existing in the reaction mixture would initiate the alternately adding esterification reactions. Also in this case, similar free oligoester chains are formed.

In order to make the reaction system as favorable as possible for the oligoesterification which results in oligoester chains linked with the wood matrix, it is necessary that concentration of the starting points, that is, the carboxyl groups in the esterified wood, be as high as possible. In addition, when the amount of the starting points is known, it is possible to estimate apparent oligoester chain length from the starting points amount and weight increase of produced oligoesterified wood. Therefore, it is considered to be desirable that conversion of the initial wood – MA reaction reaches a maximum conversion attainable before AGE is added to the reaction system. Figure 1 shows, as a typical example, the wood – MA reaction at 120 °C in terms of the effect of reaction time on weight increase of produced esterified wood. The feed weight ratio of wood : MA was 100 : 26.5. The weight increase reached a maximum value attainable after 30 min. Also at other feed ratios examined, the maximum value was attained within 1 h.

Table 1 shows the wood – MA reactions at 120 °C at various feed weight ratios. The content of monoester derived from MA is obtained from acid value, and that of diester from difference between the acid value and saponification value (Matsuda 1987). Sum of the monoester content and the diester content is referred to as ester content. After 1 h, the conversions of MA were ca. 29–37% and the weight increases agreed well with the monoester and the ester contents. These values remained unchanged with further increase in reaction time. The close agreements between the monoester and the ester contents indicate that MA has added to the wood in the form of monoester. The feed weight ratios of wood : MA in Table 1 correspond to those without AGE in the wood – MA – AGE systems which will be shown later

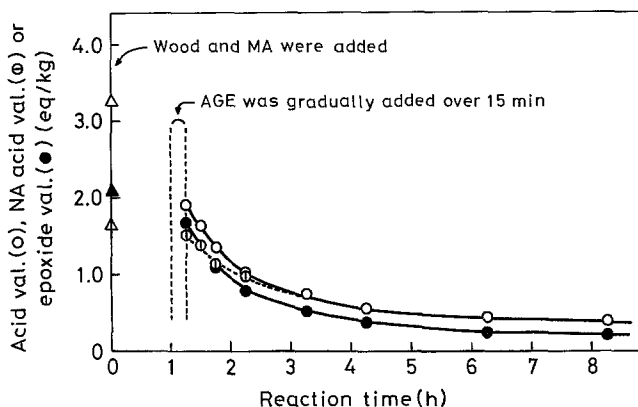


Fig. 2. Oligoesterification reaction of wood with MA and AGE at 120 °C. Feed weight ratio of wood:MA:AGE=100:26.5:40.1. Mole ratio of MA:AGE=1:1.3. (Δ), (\diamond), and (\bullet) are initial acid value, NA acid value, and epoxide value, respectively, which were calculated on the assumption that wood, MA, and AGE were mixed at a time at the beginning of the reaction

Table 1. Reactions of wood with MA at 120 °C at various feed weight ratios

Feed weight ratio of wood : MA	After 1 h			
	Weight increase %	Monoester content %	Ester content %	Conversion of MA %
100:48.6	14.2	14.9	15.0	29.2
100:39.8	13.6	14.3	13.6	34.2
100:32.6	11.4	12.0	12.4	35.0
100:26.5	9.1	9.1	9.4	34.3
100:21.4	7.8	8.6	8.3	36.4
100:17.0	6.3	6.3	7.0	37.0
100:13.3	4.8	6.0	6.1	36.2

(in Table 2). In the practical oligoesterification, the initial wood – MA reaction was conducted for 1 h before AGE was added. In this case, no further reaction of remaining hydroxyl groups in the original wood with MA is believed to occur after the addition of AGE.

Figure 2 shows, as a typical example, the oligoesterification reaction of wood with MA and AGE at 120 °C. Since preliminary experiments disclosed that a temperature of 120 °C gave a convenient rate, the reactions were carried out at 120 °C in this work. After 1 h of the initial wood – MA reaction, AGE was gradually added over 15 min. At the end of the addition, the acid value and the epoxide value were considerably lower than their calculated initial values. This indicates that the reaction proceeded rapidly during the addition. The acid values are due to carboxyl groups and further to those produced by hydrolysis of anhydride groups in the determination. The NA acid values are due to the carboxyl and the anhydride

groups. The difference between the acid value and the NA acid value corresponds to concentration of the anhydride groups. The greater decrease (from the calculated initial value) of acid value than that of NA acid value at the end of the addition of AGE suggests that anhydride groups preferentially entered into the reaction at the initial stages of the reaction. With increase in reaction time, acid value and epoxide value decreased and conversions reached nearly maximum conversions attainable after 7–8 h. Anhydride groups were almost consumed after about 3 h, suggesting that the progress of the reaction in the latter stages is due mainly to reaction (2). The decrease of epoxide value was slightly greater than that of acid value, even with a slight excess of AGE over MA in feed. This shows that etherification of epoxide occurred to a slight degree under the catalytic influence of the anhydride and the carboxylic acid (Fisch, Hofmann 1954).

In Table 2 are shown the results of the oligoesterification reactions carried out at various feed weight ratios. It was found that the products consisted of acetone-insoluble and soluble parts. The insoluble parts were oligoesterified woods; they showed, in the IR spectra, a sharp absorption band at $1,720\text{ cm}^{-1}$ due to ester linkage. The soluble parts which were viscous liquids were free oligoesters not linked with the wood matrix, and were found to have molecular weights of 210–400 (as determined by gel permeation chromatography). The formation of the free oligoesters is considered due to the side reactions described above.

Table 3 shows the analytical data of the products. The insoluble parts exhibited weight increases (based on original wood) of ca. 14–66%, which decreased with increase in the wood content in feed. The weight increases correspond to the amount of oligoester chains linked with the wood matrix. In addition, the insoluble and soluble parts exhibited slight residual acid values, indicating that they contain small amounts of residual terminal carboxyl groups. Meanwhile, residual epoxide values of the soluble parts were extremely low, suggesting that most of unreacted AGE molecules have been removed away during condensation under reduced pressure of acetone solution of the soluble part after the Soxhlet extraction. In Table 3 are also shown apparent average chain lengths of the oligoester chains linked with the wood matrix. That is, the values of n in the oligoester chain in Scheme 1 have been estimated to be 1.4–2.1. The chain length showed a tendency to decrease with increase in the wood content in feed.

Crosslinking accompanying plasticization of wood

The insoluble parts, that is, the oligoesterified woods did not show good thermo-plastic properties. Similarly, when the products which had not been separated into the insoluble and the soluble parts, that is, the oligoesterified wood-containing mixtures were subjected to hot-pressing, a great part of the soluble part exuded from the system and sufficient plasticization of the wood components was not observed. On the other hand, in the case of the mixtures into which a catalytic amount of DCP had been added, both at high temperatures and under high pressures, the wood components plasticized to give reddish or yellowish brown, crosslinked wood boards whose surfaces are smooth, glossy, and plasticlike. In this case, the exudation of the soluble parts was not observed, indicating that the free

Table 2. Oligoesterification reactions of wood with MA and AGE^a at various feed weight ratios

Feed weight ratio of wood: MA: AGE	Wood content in feed	Initial acid value ^b	Initial epoxide value ^b	Final acid value	Final epoxide value	Product	
	%	eq/kg	eq/kg	eq/kg	eq/kg	Code	Insoluble part ^c % Soluble part ^d %
100:48.6:73.6	45	4.462	2.902	0.398	0.188	OEW(45)	74.6 22.8
100:39.8:60.2	50	4.059	2.637	0.327	0.218	OEW(50)	77.4 19.3
100:32.6:49.3	55	3.653	2.373	0.449	0.221	OEW(55)	79.6 17.8
100:26.5:40.1	60	3.247	2.110	0.373	0.240	OEW(60)	80.1 17.1
100:21.4:32.4	65	2.841	1.846	0.474	0.252	OEW(65)	82.3 15.2
100:17.0:25.8	70	2.431	1.584	0.465	0.260	OEW(70)	83.3 14.8
100:13.3:20.1	75	2.030	1.319	0.456	0.322	OEW(75)	85.7 11.6

^a Reaction condition = 120 °C for 7.25 h after initial wood - MA reaction at 120 °C for 1 h

^b Calculated values at starting point. They were calculated on the assumption that wood, MA, and AGE were mixed at a time at the beginning of the reaction

^c Acetone-insoluble part

^d Acetone-soluble part

Table 3. Analyses of products (oligoesterified wood-containing mixtures) obtained in Table 2

Product	Acid value eq/kg	Epoxide value eq/kg	Acetone-insoluble part ^a		Weight increase ^b %	Acetone-soluble part		n ^c in oligoester chain in Scheme 1
			Acid value eq/kg	Epoxide value eq/kg		Acid value eq/kg	Epoxide value eq/kg	
OEW(45)	0.398	0.188	0.257	0.081	65.8	0.587	0.020	2.1
OEW(50)	0.327	0.218	0.261	0.004	54.8	0.550	0.139	1.9
OEW(55)	0.449	0.221	0.381	0	44.7	0.606	0.044	1.8
OEW(60)	0.373	0.240	0.271	0	33.5	0.641	0.065	1.7
OEW(65)	0.474	0.252	0.356	0	26.6	0.593	0.012	1.6
OEW(70)	0.465	0.260	0.373	0	19.0	0.642	0.140	1.4
OEW(75)	0.456	0.322	0.349	0	14.3	0.987	0.018	1.4

^a Separated oligoesterified wood

^b Weight increase based on original wood

^c Obtained from weight increase of acetone-insoluble part and weight increase after 1 h in the reaction of wood with MA in Table 1

oligoester chains were combined, by the crosslinking, with the oligoesterified woods, resulting in the formation of the network structure. It is advantageous that the free oligoesters which were hardening worked as a plasticizer for the wood components.

Figure 3 shows IR spectra of the system of OEW(60). In the spectrum (a) before hot-pressing, absorption bands at $1,640\text{ cm}^{-1}$ characteristic of the allylic and the maleic double bonds, and at 930 cm^{-1} due to the allylic double bond are noteworthy. Meanwhile, in the spectrum (b) after hot-pressing at $150\text{ }^{\circ}\text{C}$, 275 kg/cm^2 for 30 min, the former band has decreased considerably and the latter band has almost disappeared. The remaining band at $1,640\text{ cm}^{-1}$ is due mainly to the maleic

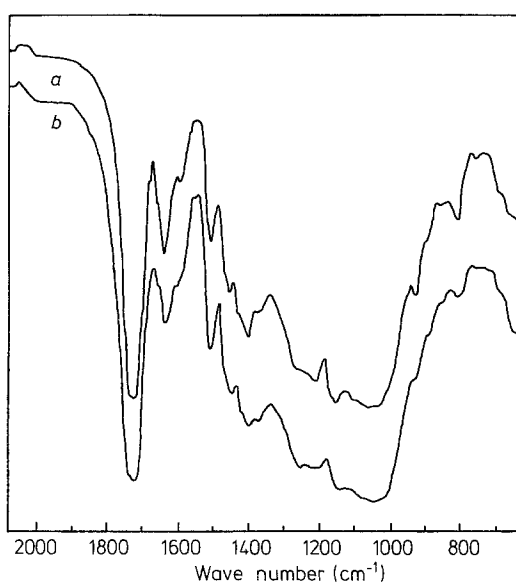


Fig. 3a and b. IR spectra of system of OEW(60). **a** Before hot-pressing. **b** Hot-pressed at $150\text{ }^{\circ}\text{C}$ for 30 min, under a pressure of 275 kg/cm^2 . The system contained 2 wt-% of DCP

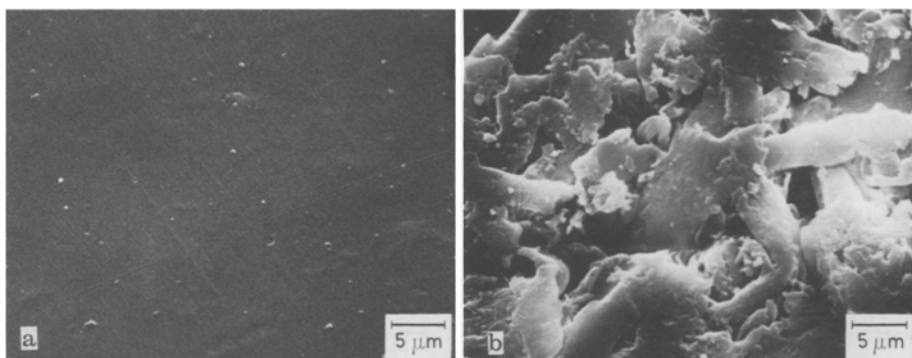


Fig. 4a and b. Scanning electron micrographs (SEM) of **a** crosslinked wood board obtained by hot-pressing of OEW(60) system and **b** board obtained by hot-pressing of untreated wood meal. Hot-press condition = $150\text{ }^{\circ}\text{C}$, 275 kg/cm^2 , 30 min

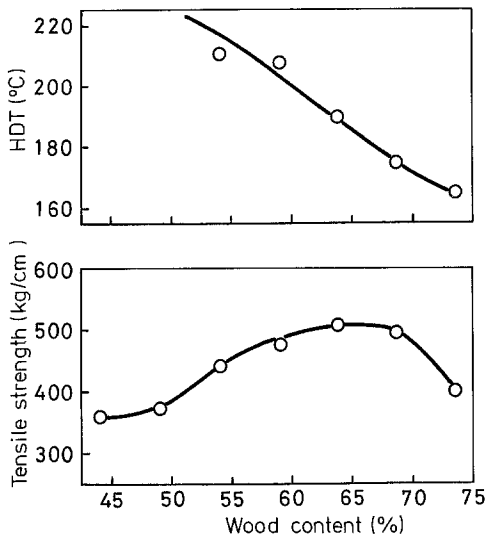


Fig. 5. Effect of wood content on HDT and tensile strength for plasticlike cross-linked wood boards from oligoesterified wood-containing mixtures

double bond. Thus, the crosslinking is considered due largely to polymerization of the allylic double bands; however, also, copolymerization of the allylic and the maleic double bonds would have occurred to some extent (Fischer 1963; Urushido et al. 1980). No further decrease of the remaining band was observed with further increase in hot-pressing time. Therefore, applying the above hot-press condition, a series of plasticlike (plasticized) crosslinked wood boards were prepared.

Figure 4 shows SEM of the crosslinked wood board obtained by the hot-pressing of the OEW(60) system and of the board obtained by the hot-pressing of untreated wood meal. In the former board, the wood texture has disappeared, indicating the thermal melting of the wood components. Meanwhile, in the latter board, the wood texture is clearly seen.

Properties

Figures 5–7 show physical properties of a series of the plasticlike crosslinked wood boards from the oligoesterified wood-containing mixtures in Table 3. In Figure 7, water resistance is also shown. They exhibited HDT above 165 °C, which increased with decrease in wood content. It should be noted that the HDT values were above 220 °C at wood contents of 45–50% (220 °C is a limit of the determination by the testing machine). These values are much higher than those of plasticlike crosslinked wood boards from the carboxyl group-bearing esterified woods and bisphenol A diglycidyl ether (BADG) (Matsuda, Ueda 1985c; Matsuda 1987), probably due to higher crosslinking density of the former boards. Further, the values are generally higher than those (165–168 °C) of crosslinked polyesters from AGE and MA (Fischer 1963).

Tensile strength ranged from 360 to 510 kg/cm², showing a peak at a wood content of 65%. Flexural and impact strengths were little influenced by wood

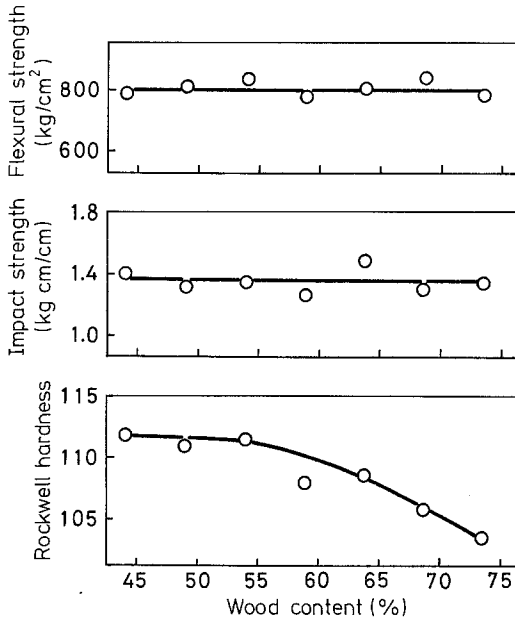


Fig. 6. Effect of wood content on flexural and impact strengths, and Rockwell hardness for plasticlike crosslinked wood boards from oligoesterified wood-containing mixtures

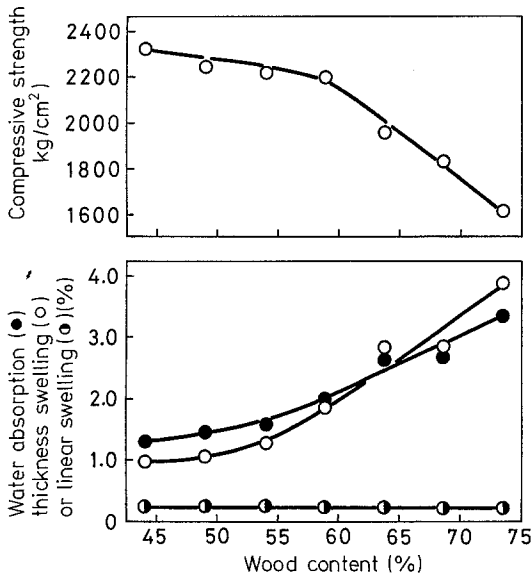


Fig. 7. Effect of wood content on compressive strength and water resistance for plasticlike crosslinked wood boards from oligoesterified wood-containing mixtures

content, remaining around 800 kg/cm^2 and around $1.4 \text{ kg} \cdot \text{cm/cm}$, respectively. Rockwell hardness showed values in the range of ca. 104–112, and had a tendency to decrease with increase in wood content. Compressive strength increased with decrease in wood content and, at wood contents of 45–60%, exhibited values of ca. 2,200–2,300 kg/cm^2 , which are considerably higher than those of the boards from the esterified woods and BADG (Matsuda, Ueda 1985c; Matsuda 1987).

As for water resistance, linear swelling was not affected by wood content, showing almost constant values of ca. 0.2%; however, water absorption and thickness swelling ranged from ca. 1.3 to 3.3%, and from ca. 0.9 to 3.9%, respectively, and increased with increase in wood content, due to the increase in the remaining hydrophilic hydroxyl groups in the wood matrix.

References

- Fisch, W.; Hofmann, W. 1954: Über den Härtungsmechanismus der Äthoxylharze. *J. Polym. Sci.* 12: 497–502
- Fisch, W.; Hofmann, W. 1961: Chemischer Aufbau von gehärteten Epoxyharzen III. Mitteilung über Chemie der Epoxyharze. *Makromol. Chem.* 8: 44–46
- Fischer, R. F. 1963: Crosslinked polyesters from allyl glycidyl ether and maleic anhydride. *J. Appl. Polym. Sci.* 7: 1451–1469
- Matsuda, H.; Ueda, M.; Murakami, K. 1984: Preparation and utilization of esterified woods bearing carboxyl groups II. Esterification of wood with dicarboxylic acid anhydrides in the absence of solvent. *Mokuzai Gakkaishi* 30: 1003–1010
- Matsuda, H.; Ueda, M. 1985a: Preparation and utilization of esterified woods bearing carboxyl groups V. Addition reaction of esterified woods with epoxide and oligoesterification of the adducts obtained. *Mokuzai Gakkaishi* 31: 267–273
- Matsuda, H.; Ueda, M. 1985b: Preparation and utilization of esterified woods bearing carboxyl groups VI. Stepwise alternately adding esterification reaction of esterified woods with epoxides and dicarboxylic acid anhydrides. *Mokuzai Gakkaishi* 31: 468–474
- Matsuda, H.; Ueda, M. 1985c: Preparation and utilization of esterified woods bearing carboxyl groups VIII. Crosslinking of esterified woods with bisepoxide and properties of crosslinked woods. *Mokuzai Gakkaishi* 31: 903–911
- Matsuda, H. 1987: Preparation and utilization of esterified woods bearing carboxyl groups. *Wood Sci. Technol.* 21: 75–88
- Urushido, K.; Matsumoto, A.; Oiwa, M. 1980: Polymerization of allyl esters of unsaturated acids I. Cyclopolymerization of methyl allyl maleate. *J. Polym. Sci. Polym. Chem. Ed.* 16: 1081–1091

(Received January 9, 1987)

Dr. Hideaki Matsuda
Dr. Minoru Ueda, and Hideki Mori
Research Laboratory
Okura Industrial Co., Ltd.
1515 Nakatsu-cho, Marugame
Kagawa-ken 763, Japan