Studies on the Improvement of Cured Two-Stage Phenolics Performance. III. Relation between Conditions of Heat Treatment and Properties of Wood-Flour-Filled Phenolics

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Synopsis

The effect of heat treatment on the properties of cured two-stage phenolics was studied. Samples were compression-molded from the compound that was prepared from novolac, wood flour (100 phr), and hexamethylenetetramine (15 phr). Samples were heat-treated in conditions of four levels for temperature (150°C, 170°C, 190°C, and 210°C) and time (4, 8, 16, and 24 h). The properties of samples heat-treated, such as weight loss, dimensional stability, water absorption after boiling, and flexural properties were measured. The relation between the properties and the conditions of heat treatment was examined statistically. From the results, it was decided that the optimum conditions of heat treatment for practical use were: (i) to decrease water absorption and to heighten electrical resistance, 210°C, 24 h; (ii) to improve flexural properties at room temperature and at 160°C; 170°C, 8 h, and 170–190°C, 24 h, respectively. It was concluded that the decrease of water absorption of moldings was due to the increase of hydrophobic nature of wood flour included in moldings by heat treatment and that the improvement of flexural property of moldings at 160°C was due to an increase of crosslinking density by heat treatment. The reasons for the improvement of the electrical properties by heat treatment were also discussed.

INTRODUCTION

Thermosetting resins are popularly used as engineering plastics, because of their good heat resistance and good mechanical properties. Especially, phenolic resin has been widely used from the field of miscellaneous goods to industrial goods owing to its good moldability, good properties, and economical price.

There are a few papers related to the heat treatment of two-stage phenolic moldings. In two of these papers, the effect of heat treatment on dimensional stability of the moldings was studied,[1,2] and, in the other, the effects of heat aging conditions on properties of moldings were studied.[3] However, it could not be found in these reports that the heat treatment of moldings increased their heat resistance. In the previous papers,[4] it was clarified that the heat resistance of two-stage phenolics were remarkably improved by heating the phenolics over their molding temperature. The heat treatment is a useful process for increasing the performance of phenolics, because the process of heat treatment is simple and the improvement of heat resistance is remarkable. If this process were applied to phenolics, the phenolics could be used economically in various fields which require more heat resistance than

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that of ordinary phenolics, and it would be expected that the application field of phenolic resin moldings became wide.

The object of this paper is to confirm the degree of the improvement of properties of wood-flour-filled phenolic resin moldings by heat treatment and to find the optimum conditions of heat treatment suited for this purpose. The relation between the properties of glass-fiber-filled and whisker-filled phenolic resin moldings and conditions of heat treatment will be shown in the following paper.

EXPERIMENTAL

Reagents and Materials

Hexamethylenetetramine (hexamine) was used after pulverizing the chemical grade reagent. Wood flour and novolac (general purpose novolac) were purchased from Asahi Yukizai Kogyo Co., Ltd.

Molding Compound

The molding compound was prepared by hot roll milling of the mixture of the novolac, the wood flour (100 phr), and hexamine (15 phr) at 90–100°C for 10 min. Then, the molding compounds were kept in an air circulating oven at 100°C until they had the required moldability for compression molding.

To clarify the effect of heat treatment both on weight loss and water absorption of moldings after boiling, the reference molding compound was also prepared by use of heat-treated wood flour instead of the untreated one. The conditions of heat treatment for wood flour will be shown later in the section of heat treatment.

Test Pieces

Two kinds of test pieces were prepared by compression molding from the molding compounds after high frequency dielectric preheating. Molding conditions such as temperature, pressure, and time were: 150°C, 15 N/mm^2, and 5 min, respectively.

One test piece was a disk 100 mm in diameter and 2–3 mm in thickness; the other was a rectangular sample 80 mm in length, 10 mm in width, and about 4 mm in thickness. The former was used for the measurement of electrical properties, weight loss, and water absorption after boiling. The latter was used for the measurement of dimensional change and flexural properties.

Heat Treatment

The conditions of heat treatment of moldings determined by preparatory experiments were four levels for temperature (150°C, 170°C, 190°C, and 210°C) and for time (4, 8, 16, and 24 h). Test pieces were kept in an air circulating oven according to predetermined conditions.

When the test pieces were heated from room temperature to 170°C or higher rapidly, sometimes blisters were formed on the surface of the sam-

ples. To avoid the formation of the blisters, the samples were heated gradually, according to following heat schedule: in the case of the heat treatment of 190°C, samples were preheated at 150°C, 1 h, and 170°C, 1 h, respectively, and then heated at 190°C for the predetermined time.

Heat treatment of wood flour was done at 100°C, 120°C, 150°C, 170°C, 190°C, and 210°C, respectively, for 8 h under nitrogen gas flow for the comparative experiment.

Testing Methods

(i) Electrical Properties: Surface and volume resistivity were measured on a High Resistance Meter (Yokogawa-Hewlett-Packard Co.).

(ii) Flexural Properties: The flexural properties were measured on rectangular samples. The span between supports was 60 mm, and the crosshead speed was 1.5 mm/min.

(iii) Boiling Test: Test pieces (disk) were boiled in distilled water for 2 h or 4 h, and then water absorption and electrical properties of the disks were measured.

Measured values of the properties were treated statistically to the conditions of heat treatment, according to the repeated two-way layout method (number of repeats was 3–6). An arrow mark shown in figures represents the region of 95% confidence limit.

RESULTS AND DISCUSSION

A previous report[4] showed that the heat resistance of two-stage phenolic resin moldings was increased by heat treatment, and the effect of the heat treatment on the heat resistance was varied with the conditions of the heat treatment, as shown in Table I.

For the purpose of improving the performance of the moldings, in other words, to put the process of the heat treatment to practical use, it is necessary to know the relation between the heat treatment conditions and the changing behavior of properties of moldings.

Weight Loss. Figure 1 shows that the weight loss of moldings by the heat treatment increases with higher temperature and longer time. It was considered that this weight loss of moldings was mainly due to the thermal

TABLE I
Effect of Heat Treatment on HDT of Moldings from General Purpose Novolac–Hexamine–Wood Flour

Heat treatment temperature[a] (°C)	Weight loss (%)	HDT[b] (°C)
(as molded)	—	158
170	1.24	200
190	2.63	230
210	7.23	>250
230	10.67	>250
250	19.40	>250

[a] Heat treatment time, 8 h at each temperature, respectively.
[b] HDT = heat distortion temperature.

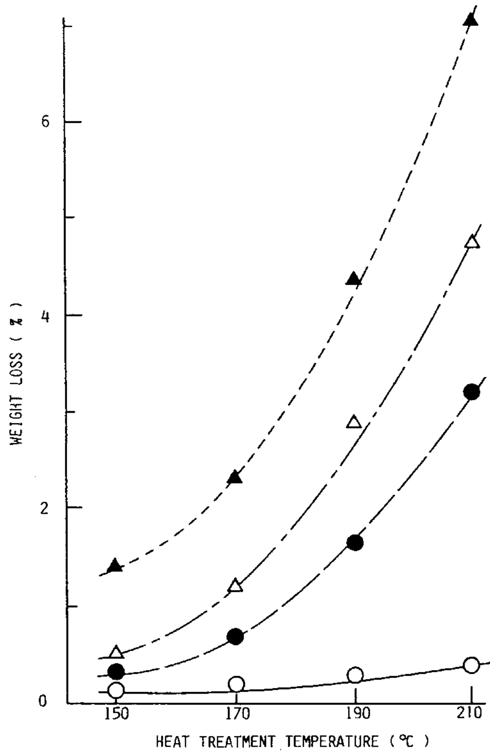

Fig. 1. Weight loss of wood-flour-filled phenolics after heat treatment; heating time (h): (○) 1; (●) 4; (△) 8; (▲) 4.

instability of filler (wood flour) and not to phenolic resin itself. To confirm this consideration, the weight loss of wood flour itself of heating 8 h at various temperatures in nitrogen gas flow and of moldings which contained either the heat-treated wood flour or the untreated wood flour were measured after the heat treatment of the same conditions. The results are shown in Figure 2.

In comparison with the amount of weight loss, wood flour itself was the largest, and moldings that contained the heat-treated wood flour were the smallest. Therefore, it has been concluded that most of the amount of weight loss observed on heat treatment was caused by the wood flour filler.

Dimensional Change of Moldings on Heat Treatment. The lengthwise dimension of rectangular test pieces was shrinked by heat treatment: shrinkage changed from 1.3% at 150°C to 2.3% at 210°C. But, on the surface of some test pieces heated at 210°C, small blisters were observed.

Water Absorption (Boiling Test). The heat-treated disks were boiled for 2 h, and then the water absorption of the disks was measured. Figure 3 shows the relation between the water absorption and the heat treatment conditions.

From the relation between the amount of weight loss and the heat treatment conditions, as shown in Figure 1, it was expected that the amount of water absorption also increased with an increase in temperature and time. In contrast with the expectation, however, the amount of water absorption

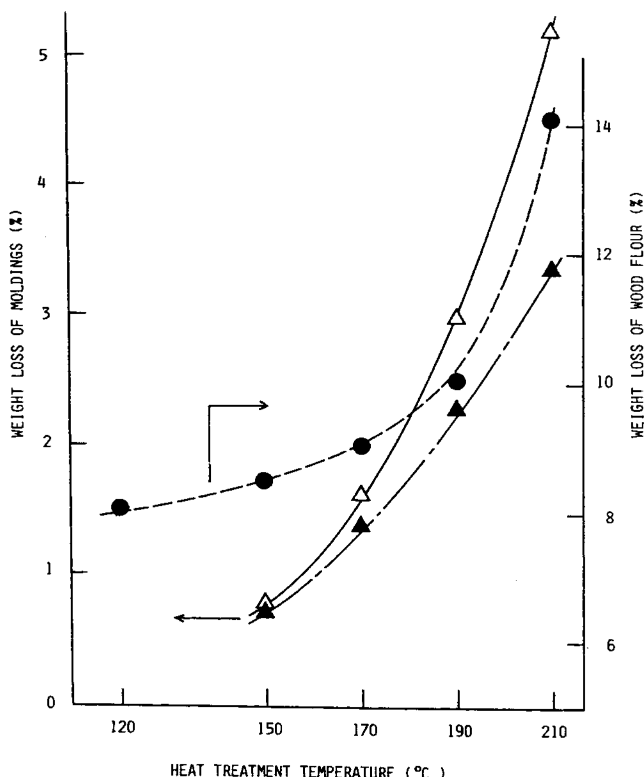

Fig. 2. Weight loss of moldings and of wood flour after heat treatment at various temperatures for 8 h: (△) molding with untreated wood flour; (▲) molding with heat-treated wood flour; (●) wood flour.

has decreased with an increase in temperature and time. This phenomenon means an increase of hydrophobic nature of moldings with the heat treatment.

Uehara and his co-workers[5] reported that the wettability of wood was decreased when it was heated to 150–200°C. From this report, it was considered that the bahavior of water absorption of heat-treated specimens was affected mainly by that of wood flour filler. Therefore, the following experiment was done with comparative test pieces to clarify the reason of the phenomenon.

A different series of test pieces was prepared from molding compounds in which preheat-treated wood flour for 8 h at 120°C, 150°C, 170°C, 190°C, and 210°C, respectively, were formulated. Then, the amount of water absorption of the test pieces was measured after boiling for 2 h and 4 h. The results are shown in Figure 4 [(●) 2 h; (▲) 4 h]. The behavior of the test pieces with untreated ordinary wood flour is also shown in the same figure [(○) 2 h; (△) 4 h].

The effect of heat treatment of wood flour on the water absorption of test pieces after 2 h boiling changed with the temperature of heat treatment, that is, the water absorption of test pieces filled with wood flour that was heat-treated above 170°C became less than that of untreated wood flour

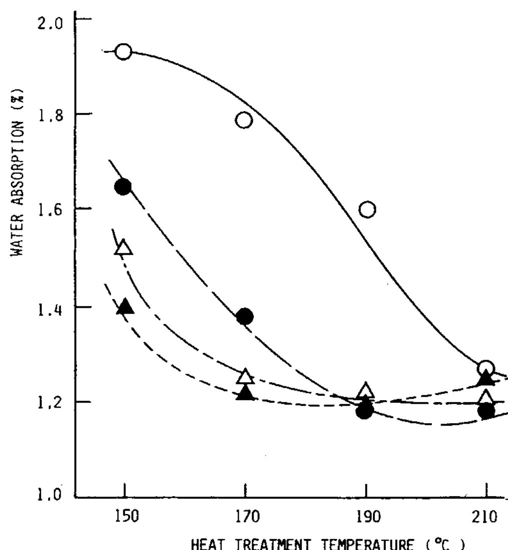

Fig. 3. Water absorption of wood-flour-filled phenolics after heat treatment, 2 h boiling; heat treatment time (h): (○) 1; (●) 4; (△) 8; (▲) 24.

filled sample. The same tendency was also observed in case of 4 h boiling.

Both the samples filled with wood flour preheat-treated as described above and the samples filled with ordinary wood flour were heat-treated in concern with the conditions of heat treatment of wood flour, and then the amount of water absorption of the heat-treated samples was measured after 2 h boiling. These results are also shown in Figure 4 (■, □). Except for the sample that was heat-treated at 150°C, water absorption of samples filled with preheat-treated wood flour was smaller than that of samples filled with ordinary wood flour. It has been considered that the reason for the exceptional behavior at 150°C was as follows: the temperature of heat treatment on wood flour at 150°C was high enough to dry it, but too low to make it hydrophobic, so that the dry wood flour in the samples absorbed much water during the boiling test.

Wood is composed of cellulose, hemicelluloses, and lignin mainly. Cellulose is the main component, and is heat-stable. On the other hand, hemicelluloses and lignin are relatively heat-unstable, and some of them contain carboxyl and hydroxyl groups[6,7] that are strong hydrophilic. It was reported[8] that, by means of infrared spectroscopy of white spruce logs after heat treatment at 200°C for a wide range of time, (i) after 48 h heating in nitrogen atmosphere, the absorbance of 1730 cm^{-1} (carbonyl stretching of ester and carboxyl group) decreased to 65% of the original absorbance of the same sample which was not heated and (ii) after 50 h heating in air, the absorbance of 3350 cm^{-1} (hydroxyl group) decreased to 90% of the original absorbance of the same sample un-heat-treated.

The results described above have led conclusion that the water absorption of wood-flour-filled phenolic moldings decreased by heat treatment above 170°C (Fig. 3), and this decrease of water absorption has been due to the increase of the hydrophobic nature of wood flour by heat treatment; that

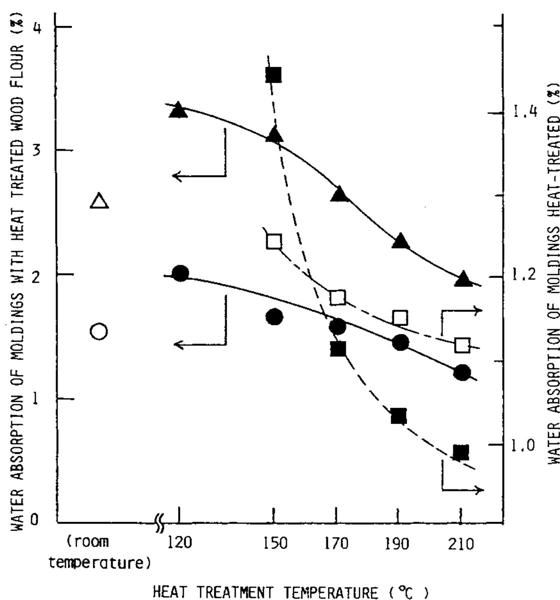

Fig. 4. Water absorption both of molding with wood flour heat-treated at various temperatures and of moldings after heat treatment: moldings with untreated wood flour after 2 h boiling (○) and 4 h boiling (△); moldings with wood flour heat-treated at various temperatures after 2 h boiling (●) and 4 h boiling (▲); heat-treated moldings with untreated wood flour after 2 h boiling (□); heat-treated moldings with heat-treated wood flour after 2 h boiling (■).

is, the increase of the hydrophobic nature of wood flour resulted from the decrease of the amount of carboxyl and hydroxyl groups which were contained in wood.

Electrical Properties. The surface (○) and volume resistivity (●) of samples were changed with the conditions of heat treatment as shown in Figure 5. These properties of the heat-treated samples after 2 h boiling are also shown in the same figure (△, ▲).

The volume resistivity of samples has increased with an increase in temperature and time of heat treatment, while the surface resistivity was not affected remarkably. However, the both resistivities of samples boiled for 2 h have become higher with higher temperature and longer time of heat treatment.

The reasons for the improvement of the properties by heat treatment are as follows: (i) hydrophilic nature of the filler that was contained in samples decreased with the heat treatment; (ii) concentration of the ion carriers such as water, ammonia, and amine compounds in the samples was decreased by the heat treatment due to their volatilization[9]; (iii) the kind of cross linkage was changed from methylene amine bond containing hydrophilic nitrogen atom to methylene bond.[9]

Flexural Properties. Figure 6 shows the flexural strength of heat-treated samples as a function of heat treatment temperature and time. This figure shows that a maximum value of the flexural strength appears in each heating time, and the value is the largest at the heating time of 8 h.

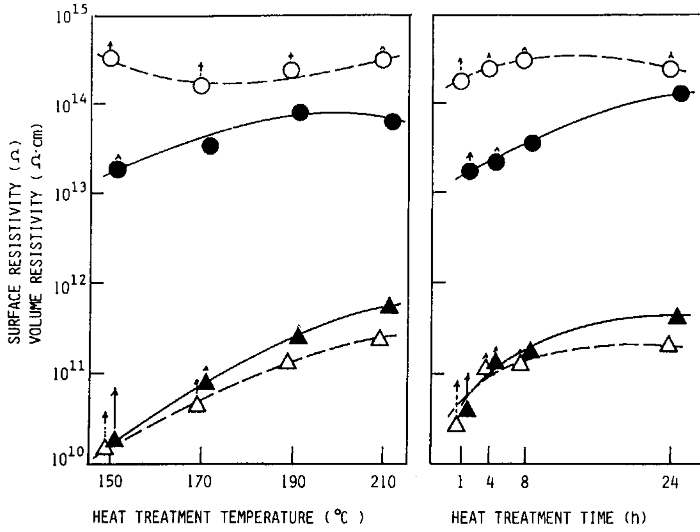

Fig. 5. Electrical properties of wood-flour-filled phenolics after heat treatment: (○) surface resistivity; (△) surface resistivity after 2 h boiling; (●) volume resistivity; (▲) volume resistivity after 2 h boiling.

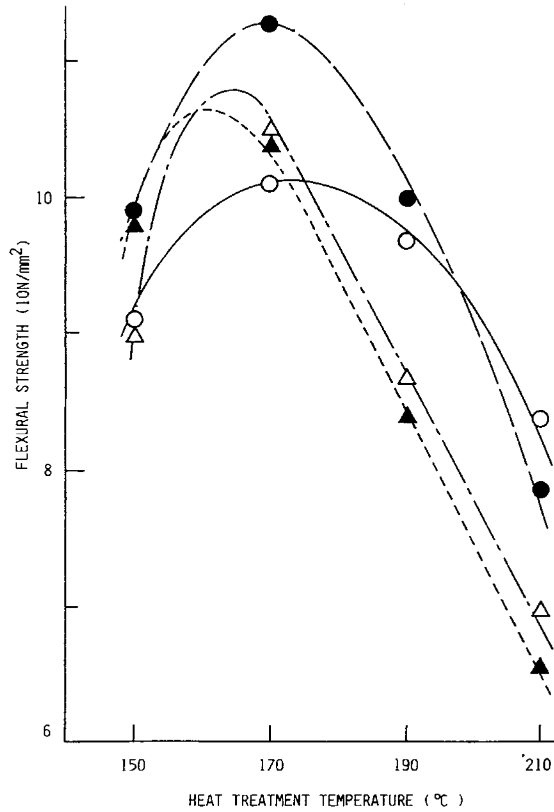

Fig. 6. Flexural strength of wood-flour-filled phenolics after heat treatment; heat treatment time (h): (○) 4; (●) 8; (△) 16; (▲) 24.

The temperature at the maximum strength in each heating time was lowered with an increase in the heating time.

The flexural modulus also increases with an increase in the heating temperature and time in the same manner as the flexural strength.

From these results, it has been concluded that the optimum conditions of heat treatment improving both the flexural strength and modulus was 170°C for 8 h.

It was suggested that the improvement of flexural properties by heat treatment were: (i) increase of cross linking density[9]; (ii) relaxation of internal stress of moldings. The decrease of flexural strength after reaching the maximum value was possibly due to the deterioration of the moldings, namely, crazings which were caused by volatilization of low molecular weight compounds, and which formed on the surface of moldings.

As a tool of the evaluation of heat resistance, heat distortion temperature, and flexural properties of moldings under high temperature are generally used. In this paper, the flexural properties at 160°C have been measured to evaluate the degree of the improvement of heat resistance of moldings by heat treatment. The results derived from statistically treated data are shown in Figure 7.

Since the flexural strength and modulus of the as-molded sample at 160°C were 55 N/mm^2 and 3800 N/mm^2 respectively, it has been recognized that the heat treatment of moldings much improved the flexural properties at 160°C. In the relation between flexural properties and the temperature of heat treatment, the flexural strength at 160°C reached maximum value in the range of 170–190°C, and the modulus became the maximum at 190°C. As for heat treatment time, flexural properties increased with an increase in time; thus the maximum properties were reached at the heating time of 24 h.

The results described above have indicated that the optimum heat treatment conditions to improve the flexural properties under high temperature were from 170°C for temperature and 24 h for treating time. It has been

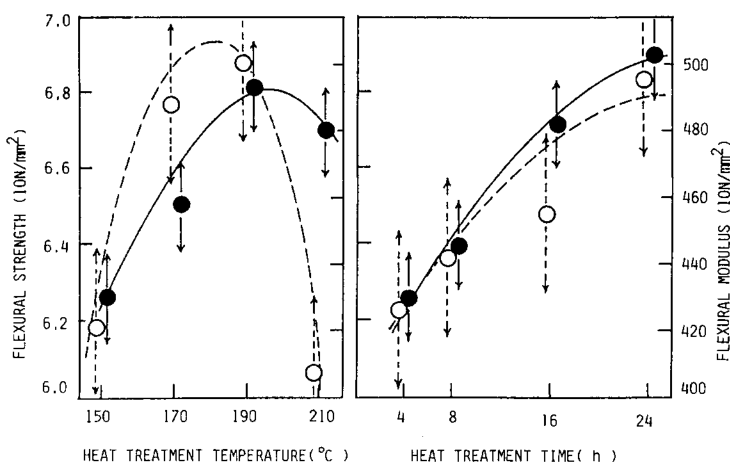

Fig. 7. Flexural properties at 160°C of wood-flour-filled phenolics after heat treatment: (○) flexural strength; (●) flexural modulus.

concluded that the improvement of heat resistance was mainly caused by some change of type of cross linkage as well as the increase of the cross linking density.[9]

CONCLUSIONS

It has become clear that the properties of wood-flour-filled two-stage phenolic resin moldings such as water absorption, electrical resistance, and flexural strength and modulus were improved by heat treatment under a temperature higher than that of their molding process.

Optimum conditions of heat treatment suitable for practical use of moldings have been decided as far as showing these experimental conditions: (i) water absorption and electrical resistance, 210°C, 24 h; (ii) flexural properties at room temperature, 170°C, 8 h; (iii) flexural properties at 160°C, 170–190°C, 24 h.

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