

A RESEARCH ON DETERMINATION OF OPTIMUM MOLDING CONDITIONS FOR MAKING PHENOLATED WOOD-BASED MOLDING MATERIALS

Mehmet Hakkı Alma

DEPARTMENT OF INDUSTRIAL ENGINEERING OF FORESTRY, FACULTY OF FORESTRY,
UNIVERSITY OF KAHRAMANMARAS SUTCU IMAM, KAHRAMANMARAS, TURKEY

ABSTRACT

Wood powders of birch (*Betula maximowicziana* Regel) species were liquefied into phenol in the presence of hydrochloric acid (HCl). The phenolated wood-based resins thus obtained as well as commercial phenol-formaldehyde resin (as control) were mixed with conventional molding components and molded at various molding conditions. The relationships between several mechanical and physical properties of molding materials obtained from phenolated wood-based resins and molding parameters such as pressure and temperature etc. were investigated. The results showed that the optimum molding pressure and molding temperature were found to be 120 MPa and about 180 °C, respectively, in order to receive comparable mechanical and physical properties of molding materials. Furthermore, the percent of water absorption was remarkably affected by molding temperature while it was not affected by molding temperature.

KEY WORDS: phenolated wood, liquefied wood, phenol, wood powder, molding pressure, molding temperature

INTRODUCTION

Recently, the amount of wood wastes generated has been alarming. The municipal waste stream comprise, essentially, lignocellulosics-based wastes and particularly wood. It was estimated that wood-based wastes were more than about 40 wt% of all the wastes. However, about 9 wt% of the total wood-based wastes was recycled, and the rest of them (about 91 wt%) remained unrecycled (Kitani and Hall 1990).

We are have been burying them in our own residential and commercial discards, which are considered as a waste with no value or a negative value and burning them as fuel in various processes. This is a waste of resources, energy, space, and labor (Inagaki and Philips 1989, Kitani and Hall 1990).

In order to increase the value of the lignocellulosics-based wastes, many trials have been done so far (Hon and Shiraishi 1990). Recently, through liquefaction of wood, wood

components, *i.e.*, cellulose, hemicellulose and lignin, could be brought to low molecular weight compounds with high reactivity (Hon and Shiraishi 1990, Shiraishi et al. 1993, Hon and Shiraishi 1990). As a more recent progress on the liquefaction of the lignocellulosics, the dissolution of chemically modified wood along with untreated wood in neutral solvents, aqueous solvents, organic solvents or solutions has been successfully developed and applied to various composite and engineering materials, *e.g.*, adhesives (Ono and Sudo 1993, Kishi and Shiraishi 1986, Alma et al. 2001), foams (Yao et al. 1999, Alma et al. 1998a), moldings (Alma et al. 1996a, Shiraishi et al. 1993, Alma and Shiraishi 1998b) and carbon fiber (Shiraishi et al. 1993).

So far, wood has been liquefied into phenol in the presence of various acidic catalysts such as sulfuric (Alma et al. 1998), hydrochloric (Alma et al. 1996a and 1996b), phosphoric (Alma et al. 1996c), oxalic (Lin et al. 1994) and phenol sulfonic acid (Trosa and Pizzi 1998), and the liquefied products obtained could become matrix resin for making phenol formaldehyde resin-type (Whitehouse et al. 1967, Knop and Scheib 1979) molding materials with satisfactory mechanical properties (Alma et al. 1996a, Alma et al. 1998b). However, no study has been done on finding optimum conditions for making liquefied/phenolated wood-based molding materials.

The objective of this study was to determine optimum conditions for the production of phenolated wood-based moldings prepared as functions of several parameters.

MATERIAL AND METHODS

Materials

Wood meals (20-80 mesh) of sapwood portion of birch (*Betula maximowicziana* Regel) species were used after drying in a vacuum oven at 60 °C for 24 h. The other chemicals and solvents used were of extra pure or guaranteed reagent grade without further purification.

“Guaranteed reagent grade” phenol and a 36.5% aqueous HCl solution (catalyst) were used for the phenolation of the wood. Hexamethylene tetraamine (HMTA) (curing agent), zinc stearate (lubricating agent), and Ca(OH)₂ (accelerating agent) were used as molding components. Commercial novolak resin (Novolak, HP-700 NK), which was used as a control for all the tests, and wood flour (filler) were obtained from Hitachi Chemical Co. Ltd., Japan.

Phenolation of wood

Wood meals (5 g), phenol (5-20 g), and 36.5% aqueous HCl (0.05-6 g) catalyst were mixed together in a stainless steel autoclave. The autoclave was dipped into an oil bath, and liquefaction was conducted at a temperature of 150 °C for 2 hours using HCl catalyst concentrations (1.0 and 2.0%, based on the weight of phenol) and phenol/wood ratios (3, and 4, w/w).

The production of phenolated wood was carried out according to Fig. 1. As shown in the figure, after the liquefaction, black liquid obtained in the tube was diluted with about 250 mL of methanol and filtrated with a glass-fiber filter (Toyo GA-100) (1 μm particle-retainable). The methanol-insoluble part, thus collected, was dried in an oven at 105 ± 2 °C for 24 h and weighed for the determination of the methanol-insoluble part, while methanol-soluble fraction was neutralized with MgO. And then, the neutralized solution was once again filtered with the glass-fiber to remove the salt produced during the neutralization. Subsequently, methanol, and free phenol were removed from the methanol-soluble fraction by distillation under reduced pressure at 50 and 180 °C, respectively.

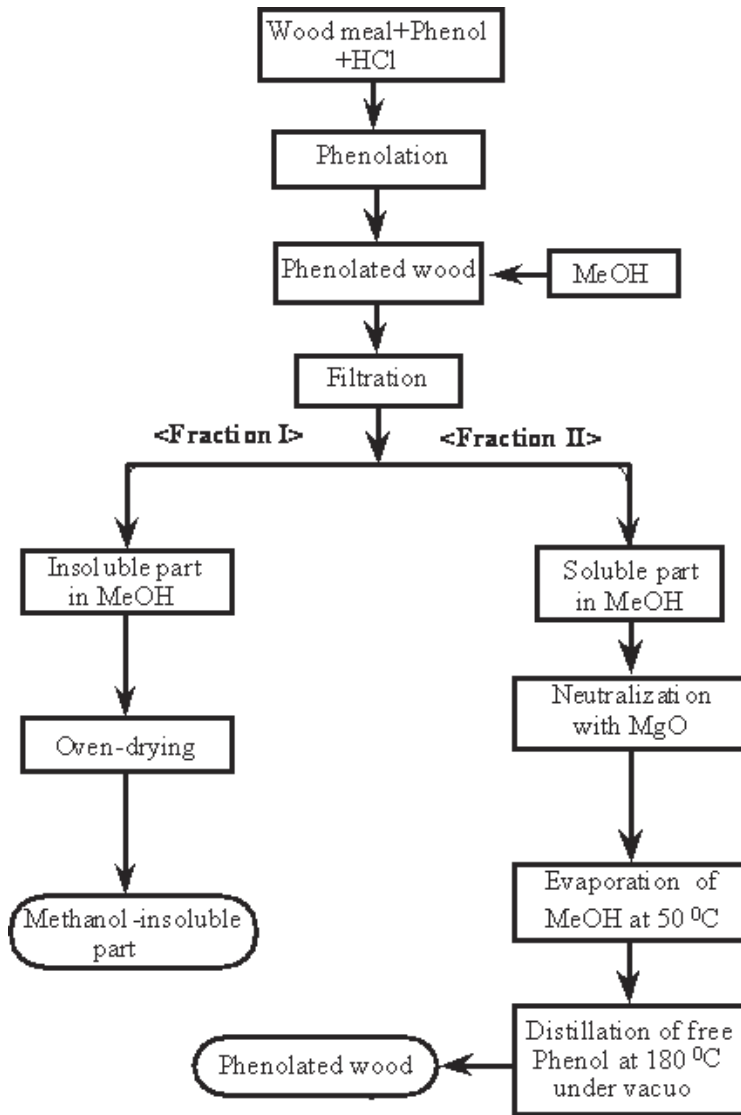


Fig. 1: Scheme for the production of phenolated wood

The obtained phenolated wood resin was ground into powder, and then examined for determination optimum preparation conditions for making phenol-formaldehyde type resin moldings.

The amount of phenol combined with liquefied wood (combined phenol) was calculated by the following equation:

$$CP = \frac{W_T - (W_0 - W_1)}{(W_0 - W_1)} \times 100 \quad [\%] \quad (1)$$

where, CP is the percent combined phenol, W_T is the total weight of the phenolated wood (g) obtained after condensation, W_0 is the oven-dry weight of wood powder (g) and W_1 is the oven-dry weight of methanol-insoluble part (g).

Preparation of the moldings

The oven-dried phenolated wood (37.7%) was dissolved in acetone and mixed with HMTA (9.4%), zinc stearate (1.0%), $\text{Ca}(\text{OH})_2$ (2.4%), and wood flour (49.5%). After mixing thoroughly, the mixture was oven-dried at 70 °C for 1 h to remove acetone, and then ground in a mortar to make a fine powder.

For the measurement of mechanical properties, the powder of phenolated wood resin so obtained was compression molded into test specimens in a die with a dimension of 80 x 10 x 4 mm. The molding conditions were as follows: molding temperature, 150, 170, 190 and 210 °C, molding pressure, 40, 80, 120, 160 and 190 MPa, time, 5 (mainly), 10, 15, 20, 25 and 30 min and cooling under a slight pressure.

Mechanical properties

Mechanical properties, including the modulus of rupture (MOR) and the modulus of elasticity (MOE), were measured according to JIS (Japanese Industrial Standard) K 7203. The specimen's dimensions were measured to the nearest 0.01 mm. The tests were performed on a Shimadzu Autograph DCS R-500 universal testing machine. Load-deflection curves were recorded automatically on an x-y chart. Prior to the test, the samples were conditioned at 20 ± 2 °C and $60 \pm 5\%$ RH (relative humidity) for two weeks. The MOR and MOE were calculated from the load-deflection curves.

Physical properties

Some molding samples were first oven dried at 60 °C under vacuum, and the dried samples were dipped into distilled water. Their weight gains due to water absorption were measured every fifteen days. The percent weight gains were calculated on the basis of oven-dry weight and stated as percent of water absorption.

Solvent extraction

The molding samples prepared at various molding durations (5, 10, 15, 20, 25 and 30 min) were cut into small pieces (10 x 10 x 4 mm) and were extracted with acetone for 32 h by using soxhlet equipment.

RESULTS AND DISCUSSION

Fig. 2 shows relationship between molding pressure and MORs of the phenolated wood-based molding materials along with those of commercial phenol formaldehyde resin the so-called "Novolak." As one can easily see from this figure, molding pressure is one of the important factors influencing MOR values of the phenolated wood-based molding materials along with those of novolak-based ones. The MOR values of the molding materials from phenolated wood-based resin increase with increasing molding pressure from about 40 MPa to 120 MPa unlike those of commercial novolak resin-based ones and then decrease with further increment. The optimum molding pressure is determined to be 120 MPa for receiving sufficient MOR values.

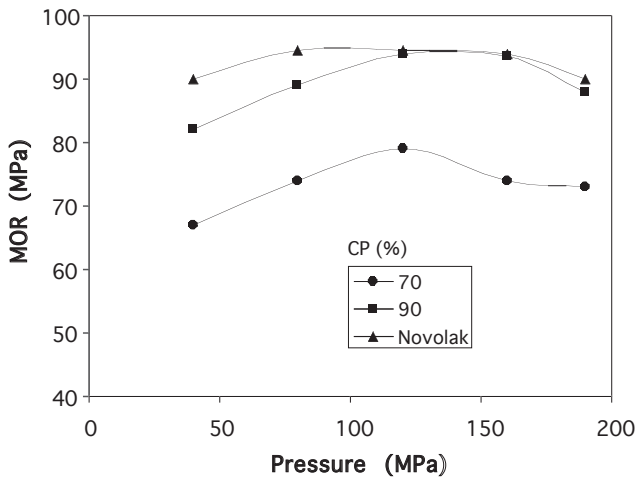


Fig. 2: Relationship between molding pressure and MORs of the phenolated wood-based molding materials along with those of commercial phenol formaldehyde resin (Novolak). Temperature: 170 °C, Time: 5 min.

It is also important to notify that on the surface of the molding materials obtained at the extreme pressures (40 and 190 MPa), some defects are observed. Moreover, the MOR values go up when increasing the amount of combined phenol in the phenolated wood-based resin. The molding materials made from phenolated wood resin with combined phenol of 90% have similar MOR values to novolak resin-based ones at 190 MPa. However, so as to provide satisfactory flexural strength (MOR), the phenolated wood resin-based molding materials need higher molding pressure as compared to novolak resin-based ones.

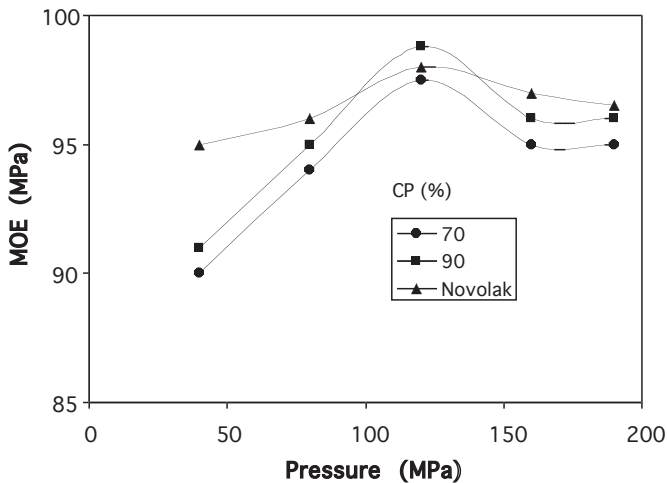


Fig. 3: Relationship between molding pressure and MOEs of the phenolated wood-based molding materials along with those of commercial phenol formaldehyde resin (Novolak resin). Temperature: 170 °C, Time: 5 min.

Fig. 3 depicts relationship between molding pressure and MOEs of the phenolated wood-based molding materials along with those of novolak resin-based ones. As shown in this figure, molding pressure is one of the important parameters on the MOE values of the phenolated wood-based molding materials along with those of novolak resin-based ones. The MOE values of the molding material from phenolated wood-based resin increase when increasing molding pressure from about 40 MPa to 120 MPa like those of novolak resin-based ones and then go down with further increment. The optimum of molding pressure is about 120 MPa.

Moreover, the MOE values rise when increasing the amount of combined phenol in the phenolated wood-based resin. The molding materials made from phenolated wood resin with combined phenol of 90% have somewhat greater MOE values than novolak resin-based ones at 190 MPa. However, in order to get sufficient MOE values, the phenolated wood resin-based molding materials require higher molding pressure as compared to novolak resin-based ones.

Fig. 4 demonstrates relationship between molding temperature and the MORs of the phenolated wood-based molding materials along with those of novolak resin-based ones. As indicated in this figure, molding temperature is one of the effective parameters on the MOR values of the phenolated wood-based molding materials and those of novolak resin-based ones. The MOR values of the molding materials from phenolated wood-based resin increase with increasing molding temperature from about 150°C to 190°C unlike those of novolak resin-based ones and then decrease with further increment. The optimum molding temperature is about 180°C to achieve sufficient MOR values.

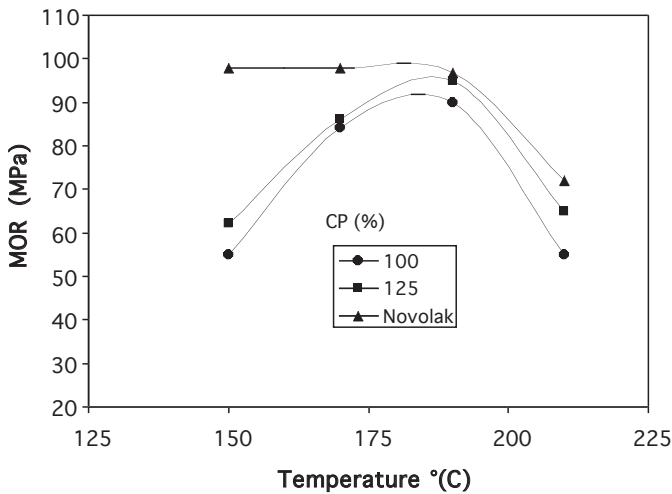


Fig. 4: Relationship between molding temperature and MORs of the phenolated wood-based molding materials along with those of commercial phenol formaldehyde resin (Novolak resin). Molding pressure: 120 MPa, Time: 5 min.

It is also interesting to say that on the surface of the molding materials obtained at the extreme temperatures (150 and 210°C), some crack lines are observed. Moreover, the MOR values go up when rising the amount of combined phenol in the phenolated wood-based resin. The molding materials from phenolated wood resin with combined phenol of about 125% have

similar MOR values to novolak resin-based ones at about 180°C. However, for getting good the MOR, the phenolated wood resin-based molding materials require higher molding pressure in comparison to novolak resin-based ones.

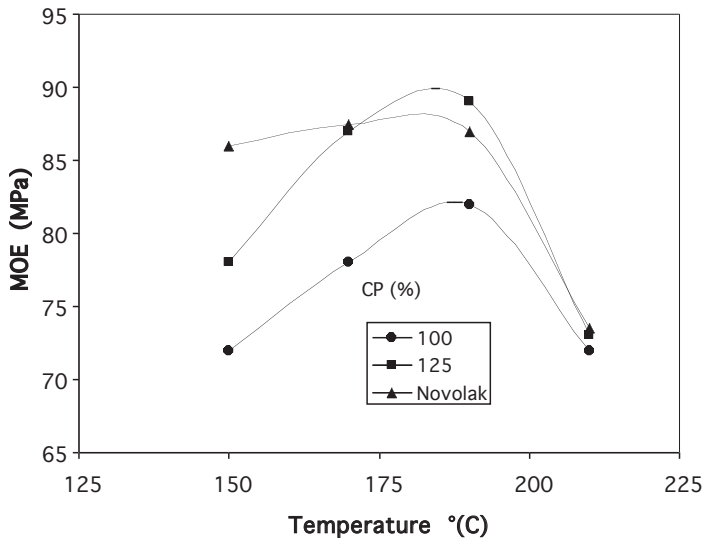


Fig. 5: Relationship between molding temperature and MOEs of the phenolated wood-based molding materials along with those of commercial phenol formaldehyde resin (Novolak). Molding pressure: 120 MPa, Time: 5 min.

Fig. 5 indicates relationship between molding temperature and MOEs of the phenolated wood-based molding materials along with those of commercial phenol formaldehyde resin the so-called “Novolak.” It is obvious from Fig. 5 that molding temperature is effective factor on the MOE values of the phenolated wood-based molding materials along with those of Novolak resin-based ones. The MOE values of the molding materials from phenolated wood-based resin increase with increasing molding temperature from about 150°C to 190°C in contrast to those of novolak resin-based ones and then decrease with further increment. The optimum molding pressure is determined to be about 180°C.

Moreover, the MOE values go up when increasing the amount of combined phenol in the phenolated wood-based resin. The molding materials made from phenolated wood resin with combined phenol of about 125% have somewhat greater MOE values than those made from novolak resin at about 180°C. However, in order to receive sufficient MOE values, the phenolated wood resin-based molding materials need higher molding temperature when compared to novolak resin-based ones.

Fig. 6 illustrates the effect of molding pressure on the percent of water absorption as a function of various dipping times. As can be depicted in this figure, percent of water absorption increases with increasing time from 5 days to about 35 days and then levels off with further increment for all the molding pressures applied. It is also clear from the same figure that the lowest percent of water absorption is obtained for the molding pressure of 160 MPa, and the highest one is for 40 MPa as expected. The molding pressures of 80 and 120 MPa result in almost the same water absorption trend.

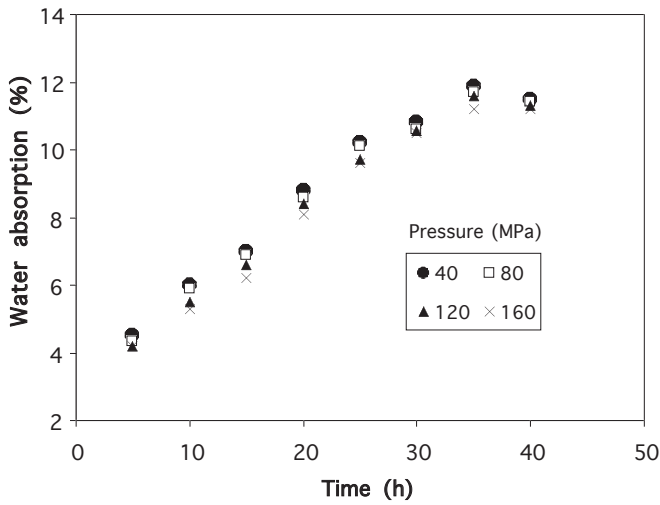


Fig. 6: The effect of molding pressure on the percent water absorption as a function of dipping time. Molding temperature: 170 °C, Time: 5 min.

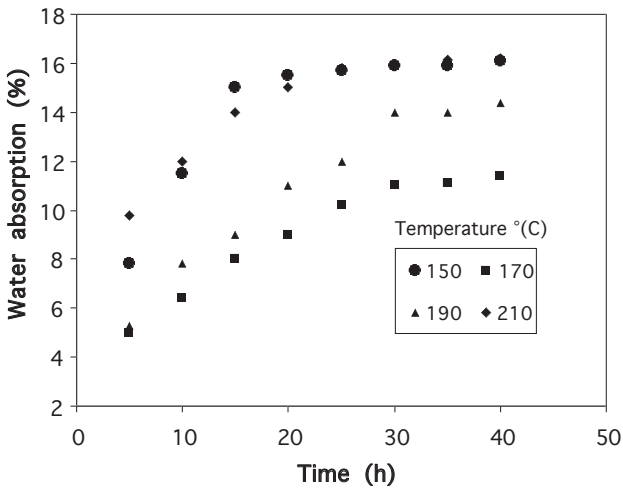


Fig. 7: The effect of molding temperature on the percent water absorption as a function of dipping time. Molding pressure: 120 MPa, Time: 5 min.

Fig. 7 shows the effect of molding temperature on the percent of water absorption as a function of various dipping times. It is evident from this figure that the percent of water absorption rises when increasing time from 5 days to about 20 days for the molding temperatures of 150 and 210 °C while the percent of water absorption goes up with increasing time from 5 days to about 30 days for the other temperatures, i.e., 170 and 190 °C. And then, this trend

becomes constant with further increment in time. It is also clear from the same figure that the lowest percent of water absorption is obtained for molding temperature of 170 °C, and the highest is for 150 and 210 °C as expected, which gives almost the same water absorption rates. This may result, most probably, from some defects due to insufficient curing and excess curing when using molding temperatures of 150 and 210 °C, respectively.

Tab. 1 lists the ratio of acetone extraction for the phenolated wood-based molding samples as a function of molding times. As can be seen from this table, above the molding time of 2 min, the ratio of acetone extraction is almost the same. The optimum molding time is found to be about 5 min.

Tab. 1: The ratio of acetone extraction for the phenolated wood-based molding samples as a function of molding time

Molding time (min)	Extraction ratio (%)
2	5.40
5	0.24
10	0.23
15	0.24
20	0.23
25	0.25
30	0.24

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PROF. DR. MEHMET HAKKI ALMA
 DEPARTMENT OF INDUSTRIAL ENGINEERING OF FORESTRY
 FACULTY OF FORESTRY
 UNIVERSITY OF KAHRAMANMARAS SUTCU IMAM
 KAHRAMANMARAS
 46060 TURKEY
 TEL: +90-344-223-7666, ++905336632884
 FAX: +90-344-221-7244, ++905336632884, ++344 2217244
 E-mail: alma@ksu.edu.tr