THE INFLUENCE OF MALEATION ON POLYMER ADSORPTION AND FIXATION, WOOD SURFACE WETTABILITy, AND INTERFACIAL BONDING STRENGTH IN WOOD-PVC COMPOSITES

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ABSTRACT

The influence of maleation on polymer adsorption and fixation, surface wettability of maleated wood specimens, and interfacial bonding strength of wood-PVC composites was investigated in this study. Two maleated polypropylenes (MAPPs), Epolene E-43 and Epolene G-3015, were used to treat yellow-poplar veneer samples. Retention of coupling agent, graft rate, graft efficiency, static contact angle on treated samples, and shear strength of resultant wood-PVC laminates manufactured under hot-pressing were measured. It was shown that the relationship among graft rate, coupling agent retention, and treating solution concentration for MAPP-treated wood specimens followed a three-dimensional paraboloid model. Graft efficiency decreased with the increase of concentration and retention. The relationship between retention and concentration was linear for G-3015 and polynomial for E-43. Maleation treatment greatly improved the compatibility and interfacial adhesion. The veneer samples treated with these two MAPPs presented different wetting behaviors. For G-3015-treated samples, measured contact angles varied from 115° to 130°, independent of retention, graft rate, and wetting time. For E-43-treated samples, retention, graft rate, and wetting time had a significant influence on the contact angle. Compared with controls made of untreated wood and PVC, shear strength of the maleated wood-PVC laminates increased over 20% on average. There was no direct correlation between measured contact angle and shear strength. Extractives had negative effects on retention. However, they did not significantly influence contact angles and interfacial bonding strength. Monolayer models were proposed to illustrate the bonding structure at the interface.

Keywords: Bonding strength, contact angle, coupling agent, dipping time, extractives, graft rate, laminates, maleation, maleated polypropylene (MAPP), monolayer, PVC, retention, sessile droplet, wettability, yellow-poplar veneer.

INTRODUCTION

Coupling agents played a very important role in improving compatibility and bonding strength between polar wood fibers and non-polar thermoplastics in wood fiber and polymer composites (Chun and Woodhams 1984; Woodhams et al. 1984; Dalvåg et al. 1985). Although exact mechanisms of interfacial bonding between wood and polymer are still unknown.
not fully understood, several hypotheses and schematic models have been proposed to elucidate the interfacial behavior and performance improvement (Chun and Woodhams 1984; Kishi et al. 1988; Maldas et al. 1988; Gatenholm and Felix 1993; Sanadi et al. 1995). The maleation method uses maleic acid (MA) to modify the polymer matrix in the presence of a free radical initiator. The maleated polymer is grafted on to wood fibers by a succinic half-ester bridge. MA can modify a number of polyolefin to form maleated polymers. Maleated polypropylene (MAPP) has been extensively used in wood fiber and polymer composites (Lu et al. 2000). A number of investigations on maleated polypropylene have been done (Maldas et al. 1988; Maldas and Kokta 1989; Felix and Gatenholm 1991; Olsen 1991). However, very limited data are available on the relationship among coupling treatment, surface wettability, and interfacial bonding strength of wood and polymer systems.

Contact angle data have been widely used to evaluate compatibility between wood and polymer at the interface (Felix and Gatenholm 1991; Chen et al. 1995). Non-polar polymers generally have a larger contact angle compared with polar wood. The coupling treatment of wood helps increase contact angle and thus improve the compatibility at the interface. Felix and Gatenholm (1991) reported that the contact angle of cellulose fibers treated with MAPP was in the range of 130° and 140°. There was no significant difference of contact angle between specimens extracted and non-extracted with toluene before coupling treatment. Chen et al. (1995) studied adhesion properties of styrene-lignin graft copolymers using a Cahn dynamic contact angle analyzer. The contact angle data measured with distilled water on grafted lignin were close to those of polystyrene (i.e., 105°), indicating an improved compatibility at the interface. More recently, Matuana and coworkers (1998) used four different coupling agents to treat wood veneer and investigated the wettability of treated wood specimens with a contact angle meter. For wood veneer specimens treated with anhydride-based coupling agents (such as Epolene E-43 and phthalate anhydride), static contact angle of glycerol sessile drops on treated wood specimens was in a range from 100° to 110° (Matuana et al. 1998). However, few investigations have dealt directly with the influence of different coupling agents on the wettability (measured by contact angle) of treated wood and the correlations among contact angle, retention, and graft rate of coupling agents.

Bonding strength provides a direct measure of the interfacial adhesion between wood and thermoplastics. The strength is greatly influenced by properties of wood, polymer, and degree of coupling between them. Several test methods, including pullout, microbond, peel, tension (parallel and perpendicular to the fiber), and planar shear tests, have been used to evaluate interfacial bonding strength of wood and polymer composites. The pullout and microbond tests are usually used to evaluate the bonding strength of a single fiber within thermoplastic matrix (Sanadi et al. 1992; Liu et al. 1994). In these techniques, individual wood fibers are embedded in a plastic matrix. The fibers are pulled out during testing to indicate the interfacial bonding strength. Preparation of proper test specimens is often a difficult task for these tests. Also, it is difficult to test the interfacial bonding strength of very short fibers in the matrix, especially with poor interfaces (Liu et al. 1994). The tension, peel, and planar shear tests are suitable for evaluation of larger specimens. The tension tests (both parallel and perpendicular to the fiber) are the most popular method to evaluate the bonding strength of wood plastic composites (Xanthos 1983; Woodhams et al. 1984; Dalvig et al. 1985; Maldas and Kokta 1989; Krzysik and Youngquist 1991; Olsen 1991; Chow et al. 1996). In peel tests, a 90° peel device is used to separate wood substrate and plastic film with a peeling force (Kolosick et al. 1992). In planar shear tests, the shear stress between laminated planar samples is directly measured under an in-plane shear load. The glue-joint
strength of wood and polypropylene/modified polypropylene laminates was investigated by use of a planar shear test method (Goto et al. 1982). Humphrey (1993) developed an automatic device to bond specimens with adhesives under hot-pressing and to perform a shear strength test sequentially.

Interfacial adhesion in PVC and wood veneer laminates has been studied with a shear testing method (Matuana et al. 1998). It was reported that the interfacial adhesion in PVC and wood veneer laminates was significantly improved when wood veneers were treated with amino-silane, while no improvement was observed for E-43 and other coupling agents (Matuana et al. 1998). Snijder and Bos (2000) investigated the coupling efficiency of nine different MAPPs in agrofiber and polypropylene (PP) composites by injection molding. It was found that the molecular weight of MAPP was a more important parameter than MA content in MAPP for coupling efficiency. The backbone structure of MAPP influenced the interfacial adhesion in resultant composites because of miscibility in the PP matrix (Snijder and Bos 2000). In another paper (Snijder et al. 1997), they reported that the mechanical properties of resultant composites increased with the amount of MAPP, but the effect leveled off or decreased at high MAPP content levels. More recently, MAPP was also used as a coupling agent for kudzu fiber-reinforced polypropylene composites (Kit et al. 2002). Through an extruder, 23% of MAPP (weight percent of the composite) were blended with PP and kudzu fiber. Compared with that of untreated kudzu fiber-polypropylene composites, tensile strength of kudzu fiber-polypropylene composites treated with MAPP increased by 52%.

It is often believed that bonding strength is influenced by the compatibility between wood and thermoplastics. However, it is not clear whether larger contact angles of wood materials treated with coupling agents would always result in higher interfacial bonding strength of wood and polymer composites (i.e., compatibility determines interfacial bonding). It was reported that an excess of coupling agent at the interface is detrimental to the coupling action and may act as an inhibitor rather than a promoter of adhesion (Maldas and Kokta 1989). However, this phenomenon has not been further studied on compatibility (from chemical coupling) or surface wettability. Most studies on wettability did not include bonding strength. Therefore, it is necessary to further investigate the relationship between wettability and interfacial bonding.

The objectives of this study were to investigate the effects of maleation treatment on polymer adsorption and fixation, wood surface wettability, and interfacial bonding strength of wood-PVC composites, and to examine the correlations among concentration, retention, and graft rate and between surface wettability and interfacial bonding strength.

MATERIALS AND METHODS

Test materials and sample preparation

Two MAPPs (Epolene E-43 and G-3015, Eastman Chemical Company) were used as coupling agent in this study. Epolene E-43 has an average weight molar mass (M_w) of 9,100, and its acid number is between 40 and 55. Epolene G-3015 has a high molecular weight (i.e., 47,000), but has a low acid number (between 12 and 18). E-43 contains more maleic anhydride groups [-CO\(^2\)O-] in its molecular chains than G-3015. Benzoyl peroxide (BPO, Aldrich) was used as initiator, and toluene (Fisher Scientific) was used as solvent for both MAPPs. Clear and rigid polyvinyl chloride (PVC, Curbell Plastics) polymer sheets (508 mm \(\times\) 1,270 mm \(\times\) 0.0762 mm) were purchased commercially. The melting and glass transition temperatures of the PVC are 175°C and 81°C, respectively. The density of the PVC is 1,390 kg/m\(^3\). It has a tensile strength of 55 MPa and a tensile modulus of 2,800 MPa (Delassus and Whiteman 1999).

Sheets of commercial yellow-poplar (Liriodendron tulipifera) veneer (610 mm \(\times\) 610 mm \(\times\) 0.889 mm) were obtained from a wood veneer retailer. The veneer was kept in plastic
bags to prevent large moisture content (MC) changes and potential surface damage. A total of 692 samples (50.8 mm × 25.4 mm × thickness) were cut from the veneer sheets for this study. The 692 samples were randomly divided into two equal groups. Samples in one group were designated for Soxhlet extraction and those in another group were designated as unextracted controls. The samples in both groups were further divided for initiating and coupling treatments as shown in Fig. 1. Prior to the coupling treatment, all veneer samples were conditioned to 5% MC in a conditioning chamber. All samples were numbered and kept in separate plastic bags before testing.

**Soxhlet extraction**

Soxhlet extraction was conducted on the 346 prepared wood veneer samples according to the ASTM standard D1105-96 (ASTM 1998) to reduce the influence of extractives on the coupling process. The wood samples were first extracted with a solution of toluene (52 ml) and ethyl alcohol (68 ml) for 4 h. The samples were then taken out of the solution and rinsed with ethyl alcohol in a Büchner-type filtering funnel. The cleaned samples were placed in the Soxhlet thimble again and underwent the second extraction with 120 ml of ethyl alcohol for 4 h. The extracted wood samples were finally oven-dried at 70°C for 24 h to reach a constant weight. The oven-dry weight of each sample was measured.

To determine graft rate and graft efficiency for MAPP-treated specimens, secondary Soxhlet extraction was conducted after coupling treatment. All treated specimens were continuously extracted with toluene (120 ml) for 24 h. The extracted specimens were then oven-dried at 70°C for 24 h to reach a constant weight. The oven-dry weight of each sample after extraction was measured.

**Initiating experiments with toluene and BPO**

Three completely randomized designs (CRD) factorial experiments were conducted as blank tests to investigate the influence of toluene and BPO on wood specimen weight changes (A—Fig. 1). In the first test (A1—72 samples), the influence of toluene on sample weight loss was investigated. There were two sample types (extracted and unextracted) and six dipping times. In the second (A2—60 samples) and the third (A3—72 samples) tests, the effects of BPO at five concentration levels in toluene solution and at six dipping times on sample weight change were studied, respectively. All these blank tests were done with six replications at each condition.

**Coupling treatments with MAPP**

Coupling treatment with MAPPs followed the procedures developed by Felix and Gatenholm (1991). Three CRD factorial experiments (B—Fig. 1) were conducted for coupling treatment. In the first experiment (B1—200 specimens), the influence of MAPP type, sample condition, MAPP concentration level on retention of MAPP was investigated. Five MAPP concentration levels (i.e., 0—control, 12.5, 25, 50, and 75 g/L) at the same dipping time of 5 min were used to treat extracted and unextracted specimens with two types of coupling agents. The relationship between dipping time and MAPP retention for extracted and unextracted specimens was investigated in the second experiment (B2—144 specimens). Dipping times were 30, 100, 300, 600, 1200, and 2400 s. The concentration of E-43 and G-3015 in coupling agent solution was 25 g/L. In the third experiment (B3—144 specimens), the influence of dipping time in MAPP solution, treating solution concentration level, MAPP type, and BPO on retention of MAPP in wood was investigated. Two coupling agent concentration levels (12.5 and 50 g/L) with and without BPO were used to treat extracted wood specimens. The dipping times were 30, 100, and 300 s.

For each treatment, a specified amount of MAPP pellets, based on the required concentration level, was added into the 150-ml toluene solution in a 600-ml glass beaker. The amount of powder BPO (if added) was cal-
culated based on a weight ratio of 0.5 between BPO and MAPP. The required BPO was weighed and added to the solution. The solution was heated on a hot plate with a magnetic stirrer until it started boiling. The temperature of the solution was kept at 100°C. After all MAPP pellets and BPO powder were dissolved in toluene, the prepared wood samples at each concentration level were placed into the solution for 5 min under continuous stirring with a magnetic stirrer. The treated specimens were then taken out of the beaker and cooled down to room temperature. All treated specimens were finally oven-dried at 70°C for 24 h to reach a constant weight. The oven-dry weight of each sample was re-measured. For determination of graft rate and graft efficiency, 48 treated specimens from the 2 × 2 × 5 CRD experiment (B11—Fig. 1) underwent the secondary Soxhlet extraction for 24 h as mentioned in the above section.

Retention of coupling agent, graft rate, and graft efficiency for treated specimens were calculated as follows:

\[
R_t = \frac{W_t - W_0 - W_{BPO}}{W_0} \times 100\% \quad (1)
\]

\[
Gr = \frac{W_2 - W_0}{W_0} \times 100\% \quad (2)
\]

\[
Ge = \frac{W_2 - W_0}{W_t - W_0 - W_{BPO}} \times 100\% \quad (3)
\]

where,

\(R_t\) = retention of coupling agent in a specimen (%);

\(Gr\) = graft rate of coupling agent in a specimen (%);

\(Ge\) = graft efficiency of coupling agent in a specimen (%);

\(W_0\) = oven-dry sample weight after extraction (g);

\(W_t\) = oven-dry sample weight after coupling treatment (g);

\(W_2\) = oven-dry sample weight after secondary extraction (g).

Fig. 1. Experimental design and sample assignments. For the graft rate measurement (B11), all specimens underwent the secondary extraction with toluene for 24 h.
$W_2 =$ oven-dry sample weight after coupling treatment and secondary extraction (g); and

$W_{BPO} =$ oven-dry weight of residual BPO on a wood sample after initiating experiment (g).

The amount of residual BPO on treated specimens was calculated based on the weight change data from the second blank experiment (A2—Fig. 1).

Contact angle measurement

A Kernco (Model G-1) contact angle meter was used to measure static contact angle of treated and untreated wood veneer samples. The contact angle meter consists of focusing lens, a light source, light prisms and filter slots, a goniometer inserted in the microscope, a cuvette and its adjusting system, and a body and its leveling system. With cuvette positioners, a specimen on the cuvette mounting plate can be moved horizontally and vertically to an appropriate position. The contact angle value is read after adjusting the movable scale of the goniometer to the tangent at the point of contact. The precision of measured angles in the range of $10^\circ$ to $90^\circ$ is within $\pm 1\%$ of the actual reading.

Distilled water was dropped on one specimen surface through a microburette during measurement. The sessile droplet was controlled to be 0.05 ml by a micro adjuster. Three contact angle measurements were taken at each longitudinal edge on each strip (one on each end and one in the center). Twelve contact angle data points were obtained for each treatment. It took 2 to 3 s to complete each contact angle measurement. In this experiment, 44 specimens (including 32 treated and 12 untreated specimens) from the $2 \times 2 \times 5$ CRD factorial experiment with coupling treatment were measured for contact angle data (B12—Fig. 1).

Interfacial bonding strength measurements

Single-lap joints were created using a small-scale bonding machine to evaluate interfacial bonding strength of the wood-PVC system. The machine performs three basic functions: pressing, heating, and cooling. The pressing unit consists of two aluminum platens, two double-acting air cylinders, air pressure regulating valves, and regulated air supply. One platen is mounted on each cylinder. The double-acting cylinders allow opening and closing of the platens during pressing under controlled pressures. The heating unit consists of four 250-Watt cartridge heaters (two in each platen), two Micromega® PID temperature controllers (one controlling each platen), two solid-state relays, and two temperature sensors that provide in-process temperatures to the controllers. A separate control unit for each platen allows controlling each platen temperature within $\pm 1^\circ$C around the set point. The cooling unit for each platen consists of unregulated water supply, water flow control valves, inlet and outlet water-lines (stainless steel tubes) connected directly to the platen. During the cooling process, the heating elements remained on and the water flow rate was adjusted to achieve desired platen temperature.

To create each wood-PVC lap joint, two prepared wood veneer samples were first selected. One line was drawn at the position of 12.7 mm from one end of each sample. One PVC sheet (12.7 by 25.4 by 0.0762 mm) was cut and placed on top of the marked end of one wood sample. The second wood sample was then placed on top of the PVC sheet with its marked end overlapping the PVC sample to create a 12.7-mm-long lap joint with a total bonding area of 323 mm$^2$. The lay-up was secured with two pieces of narrow Scotch tape (one placed on each side). The assembly was then inserted into the gap between the two preheated platens in the bonding machine. It was hot-pressed under a pressure of 0.276 MPa. The pressing cycle for each specimen consisted of a 3-min heating period and a 1-min cooling period under pressure (Fig. 2). The heating temperature was 178°C, which is 3°C higher than the melting temperature of rigid PVC. At the end of the heating period, the press platens were cooled with running tap water to 70°C.
which is about 11°C less than the glass transition temperature of rigid PVC. The press was then opened and the wood-PVC laminate was removed. The laminate was allowed to cool to room temperature. Before the shear test, all manufactured laminates were conditioned to about 5% MC.

Shear tests were conducted with a Model 1125 INSTRON machine according to ASTM standards D3163 and D3165 (ASTM 1993a, b). Two mechanical tensile grips were used to clamp the sample to the loading frame. The span between the two clamps was 50.8 mm. Each sample was tested to failure at a loading speed of 2.54 mm/min. Shear strength (Pa) was calculated as a ratio of the maximum failure load (N) to the bonding area (m²). A total of 108 shear specimens were tested, including 12 untreated specimens used as controls (B13—Fig. 1).

Data analysis

Statistical comparisons based on analysis of variance (ANOVA) were done to test the effects of coupling agent type, initiator, dipping time, concentration, extractives, and their interaction on measured MAPP retention. A regression analysis was performed to establish the correlation between coupling agent retention and concentration of the treating solution (Wozniak and Geaghan 1994). Paraboloid regression models were used to establish a three-dimensional relationship among graft rate, concentration, and retention for MAPP treated specimens.

RESULTS AND DISCUSSION

The extractive composition and the primary color component of yellow-poplar are listed in Table 1. Experimental results on coupling agent retention, graft rate, contact angle, and shear strength of wood-PVC composites are summarized in Table 2. Results of ANOVA for the effects of coupling agent type, concentration levels, dipping time, initiator, Soxhlet extraction, and their interactions on retention are shown in Tables 3 and 4, respectively.
Table 1. Extractive composition in yellow-poplar veneer.

<table>
<thead>
<tr>
<th>Lumber</th>
<th>Physical appearance</th>
<th>Extractives by Soxhlet extraction (mg/g)</th>
<th>Liriodenine (wt%)*</th>
<th>Estimated liriodenine in extractives (%)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapwood</td>
<td>Pale yellow or white</td>
<td>7.37 (6.66)</td>
<td>0.13-0.27</td>
<td>7.98-16.57</td>
</tr>
<tr>
<td>Heartwood</td>
<td>Light or bright yellow</td>
<td>29.43 (6.05)</td>
<td>0.43-0.58</td>
<td>8.04-10.85</td>
</tr>
</tbody>
</table>

- The values in the parentheses are standard deviations.
- *wt% indicates the weight percentage of oven-dried wood specimens.
- **The values are cited from the results by Mutton (1962).
- ***The values are calculated on average according to the data in columns 3 and 5. The average oven-dried weight of wood specimens was 0.551 g.

Adsorption of MAPP on wood surface

Weight losses of wood specimens occurred for specimens treated with toluene, because extractives, including resin acids, fatty acids, waxes, tannins, and coloring matters (Fengel and Wegener 1984), were removed easily from wood under high temperatures by toluene (Fig. 3). For unextracted specimens, sample weight loss increased with increases of dipping time. However, the curve leveled off after dipping time increased beyond 10 min. The weight loss for Soxhlet-extracted specimens was in the range of 0.3-0.4%, independent of dipping time.

As the dipping time increased, BPO was precipitated on the sample surface, which resulted in a weight increase for treated wood specimens. Under short dipping times, weight change was less than 0.5 weight percent of the oven-dried wood specimens (Fig. 4a). For instance, there was little BPO deposition on unextracted and extracted wood specimens when dipping time was less than 5 min. Accordingly, the weight change caused by solvent and BPO can be neglected when dipping time was less than 5 min. However, weight gain resulting from BPO deposition greatly increased under long dipping periods for both extracted and unextracted specimens. The amount of BPO was larger than 1% when dipping time was over 10 min. The weight increase resulting from BPO deposition increased with the increase of BPO concentration in toluene for both extracted and unextracted wood specimens (Fig. 4b). The percentage of weight gain was larger than 1% when the concentration level was larger than 20 g/L. Thus, an adjustment for coupling agent retention was required to reduce the influence of residual BPO. In this study, Fig. 4b was used as a reference to adjust the retention of MAPP.

The initiator, BPO, acted differently on MAPP adsorption at different treating solution concentration levels (Fig. 5). At the low concentration level (i.e., 12.5 g/L), the coupling treatment with BPO did not significantly increase MAPP retention on wood surface. For both MAPPs, the retention level difference between specimens with BPO and without BPO increased with increases of dipping times (Fig. 5a, b). At the high MAPP concentration level (i.e., 50 g/L), the retention level difference increased with increases of dipping times. It reached the maximum value (2 weight percent) at the dipping time of 5 min. Therefore, BPO helped improve the adsorption of MAPP by wood under high concentration levels and long dipping times.

The relationship between dipping time and MAPP retention in wood specimens is shown in Fig. 6. At the concentration level of 25 g/L MAPP, MAPP retention increased with the increase of dipping time. The effect leveled off after dipping time was longer than 20 min (Fig. 6). The retention on extracted specimens was larger than that of unextracted specimens at the same dipping time. At short dipping times, there was no significant retention difference between extracted and unextracted specimens. However, retention on extracted specimens was larger than that of unextracted specimens for long dipping periods. For example, the retention difference between extracted and unextracted specimens was over 1.5% when dipping time was over 10 min.
This implied that extractives in yellow-poplar influenced the adsorption of MAPP on wood specimens. According to the four-way ANOVA (Table 2), the main effects of coupling agent, BPO, and dipping time were significant on adsorption of MAPP at the 5% significance level. The interaction effects between coupling agent and dipping time, between BPO and concentration, and among coupling agent, BPO, and dipping time were also significant. However, other interaction effects were not significant.

The retention of MAPP on wood samples was proportional to the concentration levels in the solution for both coupling agents (Table 2). For G-3015, there was a linear relationship between concentration and retention for unextracted and extracted veneer samples (Fig. 7a). Retention of E-43, however, followed a polynomial relationship with treating solution concentration (Fig. 7b). The E-43 retention was larger than that of G-3015 at low concentration levels, but it was lower than that of G-3015 as the concentration levels increased.

The retention of MAPP on wood samples was related to physical adsorption and graft reaction. For E-43, a larger number of maleic anhydride groups provided more opportunities for graft reaction. This led to a relatively rapid deposition of the coupling agents on wood surfaces through graft polymerization. This graft reaction may be dominant at low concentration levels. However, graft sites on wood surfaces are limited for MAPP even at high treating solution concentrations. Excessive ungrafted or non-reacted maleic anhydride (MA) groups interfered with the graft reaction, thus resulting in a negative retention rate at high concentration levels. For G-3015, there was a relatively constant retention rate throughout the whole concentration range. This shows that yellow-poplar veneer absorbed G-3015 well. Accordingly, maleated polymer with high molecular weight and small acid number can be easily absorbed by wood surfaces. There was about 4 weight percent of extractives on average as determined by Soxhlet extraction.

### Table 2. Experimental results for retention of coupling agent, contact angle data, and shear strength in wood-PVC systems.

<table>
<thead>
<tr>
<th>Coupling agent</th>
<th>Concentration (g/L)</th>
<th>Retention of MAPP (wt%)</th>
<th>Graft rate (wt%)</th>
<th>Initial contact angle (Degree)</th>
<th>Shear strength (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unextracted</td>
<td>Extracted</td>
<td>Unextracted</td>
<td>Extracted</td>
<td>Unextracted</td>
</tr>
<tr>
<td>E-43</td>
<td>0.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>83.8 (10.3)</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>2.16 (0.24)</td>
<td>2.95 (0.15)</td>
<td>2.06 (0.54)</td>
<td>112.6 (3.0)</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>3.64 (0.51)</td>
<td>4.12 (0.94)</td>
<td>2.49 (0.20)</td>
<td>97.5 (2.4)</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>7.14 (1.07)</td>
<td>6.83 (1.08)</td>
<td>3.25 (0.12)</td>
<td>92.1 (2.4)</td>
</tr>
<tr>
<td></td>
<td>75.0</td>
<td>8.05 (1.14)</td>
<td>7.41 (1.16)</td>
<td>1.85 (0.07)</td>
<td>87.1 (2.3)</td>
</tr>
<tr>
<td>G-3015</td>
<td>0.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>83.8 (10.3)</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>1.89 (0.43)</td>
<td>2.17 (0.07)</td>
<td>1.74 (0.34)</td>
<td>120.8 (3.2)</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>3.49 (0.20)</td>
<td>3.64 (0.81)</td>
<td>2.15 (0.35)</td>
<td>121.1 (1.9)</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>6.02 (1.34)</td>
<td>6.35 (1.03)</td>
<td>2.60 (0.70)</td>
<td>122.0 (1.7)</td>
</tr>
<tr>
<td></td>
<td>75.0</td>
<td>9.48 (1.52)</td>
<td>10.54 (1.06)</td>
<td>1.77 (0.57)</td>
<td>122.1 (2.3)</td>
</tr>
</tbody>
</table>

*Unextracted and Extracted indicate non-Soxhlet extracted and Soxhlet extracted before coating.

The values in parentheses are standard deviations.

Weight percentage of oven-dried wood samples.

Moisture content of all specimens was between 4% and 6%.

Contact angle of distilled water on untreated yellow-poplar veneer.
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Table 3. Four-way ANOVA for MAPP adsorption on wood specimens.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F Value</th>
<th>Pr &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>23</td>
<td>962.9673564</td>
<td>41.8681459</td>
<td>61.54</td>
<td>0.0001</td>
</tr>
<tr>
<td>MAPP</td>
<td>1</td>
<td>3.4727565</td>
<td>3.4727565</td>
<td>5.10</td>
<td>0.0257</td>
</tr>
<tr>
<td>BPO</td>
<td>1</td>
<td>64.5665816</td>
<td>64.5665816</td>
<td>94.90</td>
<td>0.0001</td>
</tr>
<tr>
<td>MAPP*BPO</td>
<td>1</td>
<td>0.2452065</td>
<td>0.2452065</td>
<td>0.36</td>
<td>0.5494</td>
</tr>
<tr>
<td>Concentration</td>
<td>1</td>
<td>730.5542275</td>
<td>730.5542275</td>
<td>1073.77</td>
<td>0.0001</td>
</tr>
<tr>
<td>MAPP*Concentration</td>
<td>1</td>
<td>0.0501835</td>
<td>0.0501835</td>
<td>0.07</td>
<td>0.7864</td>
</tr>
<tr>
<td>BPO*Concentration</td>
<td>1</td>
<td>38.0641698</td>
<td>38.0641698</td>
<td>55.95</td>
<td>0.0001</td>
</tr>
<tr>
<td>MAPP<em>BPO</em>Concentration</td>
<td>1</td>
<td>0.3618424</td>
<td>0.3618424</td>
<td>0.53</td>
<td>0.4673</td>
</tr>
<tr>
<td>Time</td>
<td>2</td>
<td>90.2981282</td>
<td>45.1490641</td>
<td>66.36</td>
<td>0.0001</td>
</tr>
<tr>
<td>MAPP*Time</td>
<td>2</td>
<td>11.2037347</td>
<td>5.6018673</td>
<td>8.23</td>
<td>0.0004</td>
</tr>
<tr>
<td>BPO*Time</td>
<td>2</td>
<td>0.5086661</td>
<td>0.2543267</td>
<td>0.37</td>
<td>0.6889</td>
</tr>
<tr>
<td>MAPP<em>BPO</em>Time</td>
<td>2</td>
<td>0.2953047</td>
<td>0.1476523</td>
<td>0.22</td>
<td>0.8052</td>
</tr>
<tr>
<td>Concentration*Time</td>
<td>2</td>
<td>8.5649901</td>
<td>4.2828495</td>
<td>6.29</td>
<td>0.0025</td>
</tr>
<tr>
<td>MAPP<em>Concentration</em>Time</td>
<td>2</td>
<td>11.5708903</td>
<td>5.7854451</td>
<td>8.50</td>
<td>0.0004</td>
</tr>
<tr>
<td>BPO<em>Concentration</em>Time</td>
<td>2</td>
<td>2.7397087</td>
<td>1.3698543</td>
<td>2.01</td>
<td>0.1380</td>
</tr>
<tr>
<td>MAPP<em>BPO</em>Concentration*Time</td>
<td>2</td>
<td>0.470967</td>
<td>0.2354883</td>
<td>0.35</td>
<td>0.7081</td>
</tr>
<tr>
<td>Error</td>
<td>120</td>
<td>81.6434216</td>
<td>0.680361</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* MAPP—Maleated polypropylene; BPO—Benzoyl peroxide; Concentration—Concentration of MAPP; Time—Dipping time.

extraction (Table 1). The ether-soluble extractives (mainly liriodenine) are the primary color element of yellow-poplar (Buchanan and Dickey 1960). The weight percentage of liriodenine in yellow-poplar sapwood and heartwood is about 0.13–0.27% and 0.43–0.58%, respectively (Mutton 1962). Hence, liriodenine accounts for 10–12% of the total extractives on average (Table 1). These extractives had different effects on the adsorption of MAPP on wood veneer for different coupling agents. At low concentration, the retention of E-43 on unextracted veneers was lower than that on extracted veneer. For G-3015, Soxhlet extraction helped improve the coupling agent retention on wood samples (Table 2).

According to the three-way ANOVA (Table 4), the main effects of concentration and Soxhlet extraction were significant on retention of the coupling agent at the 5% significance level. The interaction effects between Soxhlet extraction and coupling agent and between concentration and coupling agent were also significant. The main effect of coupling agent and all other interaction effects were, however, not significant (Table 4). The regression analysis provided excellent fits between coupling agent and treating solution concen-

Table 4. Three-way ANOVA for retention of coupling agent MAPP.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F value</th>
<th>Pr &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>19</td>
<td>1739.2375</td>
<td>91.5388</td>
<td>107.79</td>
<td>0.0001</td>
</tr>
<tr>
<td>MAPP</td>
<td>1</td>
<td>1.6224</td>
<td>1.6224</td>
<td>1.91</td>
<td>0.1708</td>
</tr>
<tr>
<td>Concentration</td>
<td>4</td>
<td>1608.3816</td>
<td>402.0954</td>
<td>473.76</td>
<td>0.0001</td>
</tr>
<tr>
<td>MAPP*Concentration</td>
<td>4</td>
<td>101.5068</td>
<td>25.3767</td>
<td>29.88</td>
<td>0.0001</td>
</tr>
<tr>
<td>Extraction</td>
<td>1</td>
<td>3.6291</td>
<td>3.6291</td>
<td>4.27</td>
<td>0.0420</td>
</tr>
<tr>
<td>MAPP*Extraction</td>
<td>1</td>
<td>4.7609</td>
<td>4.7609</td>
<td>5.61</td>
<td>0.0203</td>
</tr>
<tr>
<td>Concentration*Extraction</td>
<td>4</td>
<td>4.3677</td>
<td>1.0919</td>
<td>1.29</td>
<td>0.2826</td>
</tr>
<tr>
<td>MAPP<em>Concentration</em>Extraction</td>
<td>4</td>
<td>3.6839</td>
<td>0.9210</td>
<td>1.08</td>
<td>0.3699</td>
</tr>
<tr>
<td>Error</td>
<td>80</td>
<td>67.9412</td>
<td>0.8493</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* MAPP—Maleated polypropylene; Concentration—Concentration of MAPP; Extraction—Soxhlet extraction before coating.
Unextracted wood specimens, E-43 had higher graft rate and efficiency than G-3015 at most concentration levels (Fig. 8a, c). It was due to the fact that E-43 has a higher acid number than G-3015 (i.e., E-43 contains more MA groups in its molecular chains), which is helpful for graft reaction. Under the initiator BPO, more graft sites on wood reacted with E-43. However, it was different for extracted wood specimens. G-3015 had higher graft rate and graft efficiency than E-43 at most concentration levels (Fig. 8b, d). Although more hydroxyl groups were exposed on wood surfaces after Soxhlet extraction, the electrostatic blocking effect (Tanaka et al. 1999) significantly resisted the graft reaction for E-43. It was also attributed to the inhibitor effect of coupling agent at high concentration (Maldas and Kokta 1989; Lu et al. 2000). The relationships of retention with graft rate and graft efficiency were similar to those of concentration with graft rate and graft efficiency (Fig. 9).

The relationship among graft rate, concentration, and retention followed paraboloid regression models for both MAPPs (Fig. 10). The shapes of distributions with these three factors for E-43 and G-3015 were similar. Graft rate was proportional to concentration and retention of MAPP at low concentration and low retention levels and reached its maximum value, and then decreased at high concentration and high retention levels. Graft rate had a parabolic relationship with concentration and retention for both MAPPs. Retention had a linear relationship with G-3015 and polynomial with E-43. The curved surfaces for extracted wood specimens had a smaller curvature than that for unextracted specimens. All these features are illustrated with the two-dimensional relationships between retention and concentration, between graft rate and concentration, and between graft rate and retention, respectively (Figs. 7, 8, and 9). The paraboloid models used in this study provided excellent fits among graft rate, concentration, and MAPP retention for treated wood specimens (Fig. 10 and Table 6).

Wettability

For untreated wood veneers, both extracted and unextracted specimens showed a similar wetting behavior (Table 7 and Fig. 11). After being dropped on a wood surface, water droplets spread and penetrated into a porous wood surface. Thus, contact angles gradually decreased with the increase of wetting time until wood surface was completely wetted. Compared with unextracted samples, extracted yellow-poplar had a smaller initial contact angle,
FIG. 4. Effect of BPO solution on weight change of treated wood specimens at a) different dipping time (The concentration level of BPO was 30 g/L in toluene solution) and b) different concentration levels (Dipping time was 5 min).
FIG. 5. Effect of BPO and dipping time on retention for extracted wood specimens treated with different MAPPs. 
a) E-43 and b) G-3015.
but the contact angle was almost the same at 60 s. Extracted specimens had a smaller difference between the initial contact angle and the contact angle at 60 s than unextracted samples. Also, initial contact angles on extracted yellow-poplar had smaller standard deviations than that on unextracted samples. This behavior indicated that wood surface chemical composition and structure (e.g., polarity and roughness) influenced the wettability of yellow-poplar veneer.

Compared with untreated specimens, samples treated with MAPP had more uniform contact angles with smaller standard deviations (Table 7). Since the rough and void wood surfaces were covered with a thin and uniform polymer film, wetting variations caused by extractives, annual rings, heartwood and sapwood, grain orientations, and other macroscopic characters of wood were decreased. Accordingly, extractives did not have significant influence on initial contact angles and dynamic contact angles for MAPP treated specimens (Table 7). This agreed with the results reported by Felix and Gatenholm (1991).

The initial contact angles on specimens treated with E-43 were smaller than those treated with G-3015. For specimens treated with E-43, initial contact angles decreased with increases of E-43 retention for both extracted and unextracted specimens (Fig. 11a, b). Similar to the case of untreated specimens, contact angles on unextracted specimens had a large drop (about 60°) in 60 s, while there was a smaller drop (about 50°) on extracted specimens over the same wetting period. As a result, specimens treated with E-43 had a wetting behavior similar to untreated wood.

For G-3015, measured contact angles on treated samples were independent of the retention levels of the coupling agent. The contact angles were 122° on average for both extracted and unextracted samples. Wood samples treated with G-3015 showed good compatibility with PVC even at low concentrations. Water droplets did not spread on treated wood surfaces and did not wet them. For both extracted and unextracted specimens, there were little changes on initial contact angle at each retention level after the wetting time increased to 60 s (Fig. 11a, b). Therefore, veneers treated with G-3015 acted more like thermoplastics.

For specimens treated with E-43, initial contact angles were reduced to less than 110° in 2 to 3 s, and the contact angle drop increased with the increase of E-43 retention, especially at the high retention levels (Fig. 11a, b). However, G-3015-treated specimens had stable contact angles. In 60 s, contact angles on G-3015-treated specimens decreased only by 3–5° on average (Table 7). Hence, water droplets had a low wetting speed on G-3015-treated specimens, while they had a high wetting speed on E-43-treated specimens, which was related to the surface polarity of treated specimens. Increases of E-43 retention resulted in the wetting acceleration on treated specimens. However, the wetting speed on G-3015-treated specimens was almost constant and independent of G-3015 retention. Compared with the results by Felix and Gatenholm (1991), measured initial contact angles on E-43-treated specimens might be less than actual contact angles. Initial contact angles on spec-
FIG. 7. Retention of MAPP on treated yellow-poplar veneer samples. a) Wood specimens were not Soxhlet-extracted before coupling treatment and b) Wood specimens were Soxhlet-extracted before coupling treatment. Dipping time was 5 min.
TABLE 5. Relationship between concentration and retention of coupling agent.\(^3\)

<table>
<thead>
<tr>
<th>MAPP</th>
<th>Extraction before coating</th>
<th>Regression for MAPP retention(^a)</th>
<th>R-value</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-43</td>
<td>Unextracted</td>
<td>Rt(%) = -0.1083 + 0.1926C - 0.0011C(^2)</td>
<td>0.996</td>
<td>0.3893</td>
</tr>
<tr>
<td></td>
<td>Extracted</td>
<td>Rt(%) = 0.1744 + 0.2056C - 0.0014C(^2)</td>
<td>0.996</td>
<td>0.3893</td>
</tr>
<tr>
<td>C-3015</td>
<td>Unextracted</td>
<td>Rt(%) = 0.12602C</td>
<td>0.999</td>
<td>0.2630</td>
</tr>
<tr>
<td></td>
<td>Extracted</td>
<td>Rt(%) = 0.1377C</td>
<td>0.998</td>
<td>0.3780</td>
</tr>
</tbody>
</table>

\(^a\) Dipping time was 5 min.
\(^b\) Rt = Retention of coupling agent, wt% and C = Concentration of coupling agent, g/L.

imens treated with E-43 would be independent of the retention level, similar to the case of G-3015.

After removing the ungrafted MAPP from wood by secondary Soxhlet extraction, initial contact angles were over 120° on average and independent of graft rate for E-43- and G-3015-treated specimens (Table 7). For G-3015-treated specimens, the contact angles at 60 s were over 120° on average and independent of graft rate. In the case of E-43, however, contact angles at 60 s decreased with the increase of graft rate (Fig. 11c, d). Therefore, grafted E-43 contained ungrafted MA groups in its molecular chains and the amount of ungrafted MA groups increased with the increase of graft rate. Some ungrafted MA groups may exist as the free MA groups in the succinic

![Graphs a, b, c, d](image)

**Fig. 8.** Relationships of concentration with graft rate and graft efficiency of MAPP. The dipping time was 5 min.
half-ester structure (Kishi et al. 1988; Felix and Gatenholm 1991).

In summary, samples treated with E-43 and G-3015 had different wetting behaviors. Contact angles on E-43-treated veneer samples decreased with increases of retention and wetting time; whereas contact angles on G-3015-treated specimens were independent of retention and wetting time (Table 7). The hydrolyzed products of ungrafted MA groups in E-43, double or single carboxylic acids, were released and freely exposed on the wood surface. Thus, these hydrolyzed products increased the surface energy of wetted wood specimens. The polarity of treated specimens increased with E-43 retention and led to a large contact angle drop in a short time. Veneer samples treated with G-3015, however, had fewer polar surfaces because there are fewer MA groups in its molecular chains and some ungrafted MA groups may be buried in its larger molecular chains after coating. Therefore, these different wetting behaviors of MAPP treated specimens were mainly related to the acid number of MAPP, the amount of ungrafted or non-reacted MA groups on wood surface, and the polarity of treated specimens.

**Interfacial bonding strength**

Shear strength of all resultant wood-PVC laminates made of wood treated with both coupling agents increased with increase of coupling agent retention for both extracted and unextracted wood samples (Fig. 12). Thus, both maleated polypropylenes provided excel-
lent improvement on interfacial bonding strength of resultant wood-PVC laminates compared with those without coupling treatment. With Soxhlet extraction, the maximum shear strength of wood-PVC laminates treated with E-43 and G-3015 was 3.71 MPa and 3.85 MPa, respectively. Without Soxhlet extraction, the shear strength of the composites treated with E-43 and G-3015 was 3.57 MPa and 3.85 MPa, respectively. Shear strength of untreated wood-PVC composites was 3.14 MPa for extracted samples and 2.98 MPa for unextracted samples (Table 2 and Fig. 12). Compared with untreated wood-PVC laminates, there was an 18.2% (extracted) and 20.8% (unextracted) increase in shear strength for E-43-treated lam-

TABLE 6. Relationship among graft rate, concentration, and retention of coupling agent.

<table>
<thead>
<tr>
<th>MAPP</th>
<th>Extraction before coating</th>
<th>Regression for MAPP graft ratea</th>
<th>R-value</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-43</td>
<td>Unextracted</td>
<td>( Gr(%) = 0.3096 + 0.0422C + 0.6986Rt - 0.0007C^2 - 0.0472Rt^2 )</td>
<td>0.877</td>
<td>0.4694</td>
</tr>
<tr>
<td></td>
<td>Extracted</td>
<td>( Gr(%) = 0.0545 - 0.0018C + 0.8079Rt + 0.0001C^2 - 0.0510Rt^2 )</td>
<td>0.959</td>
<td>0.2470</td>
</tr>
<tr>
<td>G-3015</td>
<td>Unextracted</td>
<td>( Gr(%) = 0.0746 - 0.0107C + 0.9713Rt - 0.0001C^2 - 0.0674Rt^2 )</td>
<td>0.920</td>
<td>0.3400</td>
</tr>
<tr>
<td></td>
<td>Extracted</td>
<td>( Gr(%) = 0.03026 - 0.0048C + 0.8677Rt - 0.0003C^2 - 0.0409Rt^2 )</td>
<td>0.887</td>
<td>0.4631</td>
</tr>
</tbody>
</table>

Table 6: Relationship among graft rate, concentration, and retention of coupling agent.

---

**Fig. 10.** Relationship among graft rate, concentration, and retention of MAPP. a) E-43/Unextracted, b) G-3015/Unextracted, c) E-43/Extracted, and d) G-3015/Extracted. The dipping time was 5 min.
Table 7. Contact angle of distilled water on modified wood specimens with different treatments.

<table>
<thead>
<tr>
<th>MAPP</th>
<th>Soxhlet extraction before coupling treatment</th>
<th>Retention of MAPP (wt%)*</th>
<th>Graft rate (wt%)*</th>
<th>Contact angle (Degree)</th>
<th>After coupling treatment</th>
<th>After secondary Soxhlet extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0 second</td>
<td>60 seconds</td>
</tr>
<tr>
<td>E-43</td>
<td>Unextracted</td>
<td>0</td>
<td>0</td>
<td>83.8 (10.3)</td>
<td>56.6 (13.2)</td>
<td>38.3 (10.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.16 (0.24)</td>
<td>2.06 (0.54)</td>
<td>112.6 (3.0)</td>
<td>50.4 (7.6)</td>
<td>125.1 (2.2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.64 (0.51)</td>
<td>2.49 (0.20)</td>
<td>97.5 (2.4)</td>
<td>30.9 (3.4)</td>
<td>111.1 (1.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.14 (1.07)</td>
<td>3.25 (0.12)</td>
<td>92.1 (2.4)</td>
<td>29.0 (4.4)</td>
<td>119.5 (3.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.05 (1.14)</td>
<td>1.85 (0.07)</td>
<td>87.1 (2.3)</td>
<td>27.5 (6.8)</td>
<td>122.6 (2.3)</td>
</tr>
<tr>
<td>Extracted</td>
<td></td>
<td>0</td>
<td>0</td>
<td>63.6 (6.3)</td>
<td>56.0 (8.2)</td>
<td>63.6 (6.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.95 (0.15)</td>
<td>1.96 (0.24)</td>
<td>102.4 (2.6)</td>
<td>55.9 (8.1)</td>
<td>125.0 (2.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.12 (0.94)</td>
<td>2.42 (0.21)</td>
<td>94.9 (2.6)</td>
<td>44.3 (3.8)</td>
<td>126.0 (1.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.83 (1.08)</td>
<td>2.86 (0.36)</td>
<td>85.0 (5.2)</td>
<td>34.9 (4.3)</td>
<td>122.9 (3.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.41 (1.16)</td>
<td>2.75 (0.21)</td>
<td>79.1 (3.6)</td>
<td>34.0 (5.6)</td>
<td>121.9 (4.6)</td>
</tr>
<tr>
<td>G-3015</td>
<td>Unextracted</td>
<td>0</td>
<td>0</td>
<td>83.8 (10.3)</td>
<td>56.6 (13.2)</td>
<td>83.8 (10.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.89 (0.43)</td>
<td>1.74 (0.34)</td>
<td>120.8 (3.2)</td>
<td>116.9 (4.9)</td>
<td>129.6 (0.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.49 (0.20)</td>
<td>2.15 (0.35)</td>
<td>121.1 (1.9)</td>
<td>117.6 (2.1)</td>
<td>128.5 (0.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.02 (1.34)</td>
<td>2.60 (0.70)</td>
<td>122.0 (1.7)</td>
<td>119.0 (1.4)</td>
<td>129.1 (1.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.48 (1.52)</td>
<td>1.77 (0.57)</td>
<td>122.1 (2.3)</td>
<td>120.1 (2.5)</td>
<td>125.0 (2.4)</td>
</tr>
<tr>
<td>Extracted</td>
<td></td>
<td>0</td>
<td>0</td>
<td>63.6 (6.3)</td>
<td>56.0 (8.2)</td>
<td>63.6 (6.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.17 (0.07)</td>
<td>2.06 (0.18)</td>
<td>124.0 (2.6)</td>
<td>121.1 (2.6)</td>
<td>123.1 (3.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.64 (0.81)</td>
<td>2.63 (0.35)</td>
<td>122.1 (1.6)</td>
<td>118.6 (1.3)</td>
<td>123.1 (2.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.35 (1.03)</td>
<td>3.08 (0.78)</td>
<td>123.0 (2.1)</td>
<td>119.0 (2.2)</td>
<td>123.6 (3.1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.54 (1.06)</td>
<td>2.74 (0.62)</td>
<td>123.3 (2.9)</td>
<td>119.1 (3.3)</td>
<td>125.1 (3.2)</td>
</tr>
</tbody>
</table>

*The values in parentheses are standard deviation.

† Weight percentage of the oven-dried wood specimen.

* All MAPP treated specimens were extracted with toluene for 24 h.

 indicates the interfacial structure with high MAPP retention (>6%). In model I, over 90 weight percent of MAPP molecular chains were grafted on the wood surface. In model II, however, less than 30 weight percent of MAPP were grafted on wood and most MAPP molecules were physically fixed on the wood surface (Fig. 9).

For Model I, the interfacial area consists of four interphases, including wood-polymer, wood-MAPP, polymer-MAPP, and wood-MAPP-polymer interphases (Fig. 13a). In Model I, the monolayer is decrepit and randomly distributed. For Model II, there are three interphases except the wood-polymer interphase because wood and PVC are completely separated with a continuous and compact microfilm, monolayers (Fig. 13b). Within a monolayer and between monolayers of these two models, the primary bonding force includes secondary bonding (such as van der Waals’s forces and hydrogen bonding) and
polymer chain entanglement. At the interface between wood and coupling agent, some MAPP may penetrate into wood by capillary action, thus resulting in mechanical interlocking. Esterification links, hydrogen bonding, and polymer chain entanglement also exist at this interface. Secondary bonding and polymer chain entanglement may be dominant between PVC film and the monolayer(s). The monolayer(s) may form esterification links with PVC under an initiator during hot-pressing. The succinic half-ester links at the interface are possibly limited in an area within one or two monolayers close to wood surface and PVC film. Also, wood and PVC would be cross-linked by MAPP molecules across these monolayers (Fig. 13).

For G-3015, the monolayer(s) close to the wood surface has a switch-like structure with a head-tail configuration (Sanadi et al. 1995). In this structure, one side of these MAPP molecules was grafted on the wood surface like an anchor. On the other side, these long flexible molecular chains would be helpful to form entanglement with other MAPP molecular chains. The morphological structure of E-43 may form a brush-like interface at the monolayer(s) close to the wood surface (Gatenholm and Felix 1993). This brush-like structure may restrict the mobility of grafted MAPP and offer a compact contact between MAPP and the polymer matrix at the wood-coupling agent interphase, thus effectively improving the interfacial adhesion.

Compared with wood fiber, wood veneer is smooth and continuous. The monolayers easily produce a microfilm on wood surface. This microfilm fills the gaps between wood and thermoplastics and decreases the contact distance between the wood-coupling agent interphase and between the polymer-coupling agent interphase, thus effectively transferring
FIG. 12. Shear strength of yellow-poplar and PVC composites treated with MAPP a) Non-Soxhlet extracted before coupling treatment and b) Soxhlet extracted before coupling treatment.
stresses at the interface. The microfilm thickness, $\delta$ (\(\mu m\)), is calculated with the following equation (Khroulev 1965):

$$\delta = \frac{Q}{\rho}$$  \hspace{1cm} (4)

where $Q$ is the quantity of adhesive in g/m\(^2\), and $\rho$ is the density of adhesive solution in kg/m\(^3\). For phenolic formaldehyde (PF) resins with about 40% solid content, the PF quantity was 250–300 g/m\(^2\) in order to achieve the optimum bonding strength on wood. Accordingly, the optimum microfilm thickness for PF was estimated to be 200–250 \(\mu m\) (Khroulev 1965). In this study, MAPP solution has a low solid content (<10%) and it contained a very small amount of water (<1%). The average density of MAPP solution was 910 kg/m\(^3\). Referenced to PF, the optimum coating quantity for MAPP was estimated to be 50–70 g/m\(^2\). Based on the above equation, the Khroulev thickness of MAPP was estimated to be 60–80 \(\mu m\). At low retentions (e.g., 1–2%), the MAPP microfilm thickness was about 10 \(\mu m\), while it was about 40 \(\mu m\) at high retentions (e.g., 9–10%). As a result, the MAPP microfilm thickness was close to the Khroulev value at high retention. However, the thickness at low retention was only one fourth of that at high retention.

It was reported that E-43 was not effective in improving interfacial bonding strength in wood veneer and PVC laminates (Matuana et al. 1998). Based on the above-proposed mono-layer models, MAPP at low retention levels formed a decretive and thin microfilm (much less than the Khroulev thickness) on the wood surface and could not significantly improve the interfacial adhesion. According to our experimental results, the shear strength of wood-PVC laminates treated with MAPP was lower or close to that of wood-PVC laminates when MAPP retention was less than 5%. However, there was a significant improvement on interfacial adhesion when MAPP retention levels were larger than 5% (Fig. 12). The interface
between PVC and smooth wood veneer seemed to be less sensitive to retention levels and graft rate of MAPP than the interface between PVC and relatively rough wood fiber. Therefore, even at high MAPP retention levels (e.g., 10%), shear strength of resultant wood-PVC laminates was still increasing as the retention levels increased.

Acid number significantly influenced the graft reaction of MAPP with wood components. It directly affected bonding strength of resultant composites. In general, MAPP with a larger acid number is helpful to improve interfacial bonding strength and compatibility (Olsen 1991). Although the molecular weight of E-43 is smaller than that of G-3015, the shear strength of wood veneer and PVC laminates treated by E-43 was higher than or close to that of G-3015 when MAPP retention levels were less than 5% (Fig. 12). At low retention, E-43 had more MA groups grafted by esterification links and even generated more cross-linking sites at the interface than G-3015. As a result, a low molecular weight coupling agent can compete with a high molecular weight coupling agent at low retention levels.

Extractives did not significantly influence shear strength of resultant wood-PVC laminate composites (Table 2 and Fig. 12). Liriodenine in extractives may interfere with the graft reaction between MA groups of MAPP and hydroxyl groups of cellulose and lignin. Since carboxylic acid products from liriodenine by oxidation might react with MA groups of MAPP during coupling treatment (Buchanan and Dickey 1960; Taylor 1961), this reaction would reduce the number of MA groups and coupling effect of MAPP. However, the amount of liriodenine was so small that it did not interfere with the graft reaction. As shown in Fig. 12, the shear strength of wood and PVC laminate composites with extraction was close to those without extraction at most retention levels. Therefore, shear strength of resultant laminate composites was not so sensitive to extractives in yellow-poplar veneer.

Wettability versus interfacial bonding strength

In this study, wettability was evaluated based on measured contact angle data. According to the experimental results, it appears that there is no obvious relationship between contact angles of treated wood samples and bonding strength of resultant composites (Table 2). For example, shear strength increased with increases of coupling agent retention. However, contact angle values on treated veneer were almost identical at all G-3015 retention levels. For E-43, contact angle values seemed to decrease with the increase of coupling agent retention, but the shear strength increased.

Larger contact angle values on treated veneer samples did not necessarily result in higher bonding strength of the resultant laminates. For example, the contact angle values of wood samples treated with G-3015 were as large as 120° at low concentration levels (Table 7), which means that the treated wood samples were compatible to PVC. However, the shear strength of wood-PVC composites was close to and even less than that of untreated wood composites. Shear strength of E-43-treated composites at low retention levels (e.g., 2–4%) was smaller than that at high levels (e.g., 7–8%), even though treated wood samples at low retention levels were less polar than that at high levels (Table 2). As a result, large contact angles (or good surface compatibility between treated wood and thermoplastics) did not necessarily ensure improvement of bonding strength at the interface.

SUMMARY AND CONCLUSIONS

During coupling treatment, adsorption and fixation of MAPP were influenced by many factors such as solvent, initiator, dipping time, concentration, extractives and extraction, acid number, and molecular weight of MAPP. Adsorption and fixation of MAPP influenced the wettability of treated wood specimens and finally influenced the compatibility and bonding strength at the interface in wood and PVC.
laminates. Based on the above discussions, the following conclusions can be drawn.

1) Retention of coupling agent on wood samples increased with the increase of coupling solution concentration. The shape of the retention and concentration curves varied with coupling agents. For G-3015, the relationship between retention and concentration was linear. However, a polynomial pattern was followed for E-43.

2) The relationship among graft rate, concentration, and retention of MAPP followed three-dimensional paraboloid models. Graft efficiency decreased with the increase of concentration and retention. This indicates that there was a limit to graft MAPP on wood surface. At low concentration levels and low retention, coupling agent molecules were mainly fixed on wood by esterification. At high concentration levels, however, most coupling agent molecules were deposited on wood by physical adsorption (such as capillary adsorption), accompanied with graft polymerization.

3) Wettability of MAPP-treated wood specimens was mainly influenced by the acid number of MAPP, the amount of ungrafted or non-reacted MA groups, and the surface polarity. Coupling treatment with G-3015 led to large and stable contact angles (115–130°), independent of wetting time, retention, and graft rate. Contact angles of wood samples treated with E-43 decreased with the increase of E-43 retention and wetting time, due to the deposit of ungrafted or non-reacted MA groups on wood surface. After removing the ungrafted E-43, contact angles decreased with the increase of graft rate and wetting time because many hydrolyzed products of ungrafted MA groups (double or single carboxylic acids) in the grafted E-43 molecular chains were released and freely exposed on wood surfaces during wetting.

4) Adhesion took place within monolayers formed by MAPP and between these monolayers and the adherends (wood and PVC). Interfacial bonding consisted of covalent bonding, secondary bonding (such as hydrogen bonding and van der Waals’s forces), polymer molecular entanglement, and mechanical interlocking. Esterification was limited on the monolayer(s) close to wood surface and PVC film. All these bonding forms may concurrently exist across the interface.

5) Shear strength of the resultant composites increased with the increase of MAPP retention in the wood. Increases of graft rate improved the coupling performance of MAPP at the interface. However, shear strength seemed not so sensitive to the change of graft rate at high retention levels. The acid number of MAPP had a significant influence on interfacial bonding of wood-PVC composites. There was no direct correlation between measured contact angle and shear strength.

6) Wood extractives had negative effects on MAPP retention in most cases. Soxhlet extraction helped improve retention of G-3015. However, it only worked at low concentration levels for E-43. Extractives did not significantly influence contact angles on MAPP-treated specimens and interfacial bonding strength of resultant wood and PVC composites.

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