SURFACE AND INTERFACIAL CHARACTERIZATION OF WOOD-PVC COMPOSITE: IMAGING MORPHOLOGY AND WETTING BEHAVIOR[1]

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ABSTRACT

An imaging technique was used to investigate wetting behavior of wood-PVC composites in this study. Two-dimensional and time-dependent profiles of water droplets on maleated wood surface and wood-PVC interface were observed. Experimental results indicated that coupling agents Epolene E-43 (a maleated polypropylene copolymer with low molecular weight)- and polyethylene-maleic anhydride (PEMA)-treated veneers had a hydrophilic surface, whereas the coupling agent Epolene G-3015 (a maleated polypropylene copolymer with high molecular weight)-treated veneer had a hydrophobic surface. For E-43- and PEMA-treated veneers, a water droplet had an elliptical shape after initial contact with the wood surface. However, a sessile droplet on G-3015-treated specimens was closer to a circular shape. During wetting, contact angle changes on E-43- and PEMA-treated specimens were larger than those on G-3015-treated specimens. Contact angles on maleated specimens with heat treatment and maleated interphases were almost independent of wetting time. Initial contact angle was influenced by coupling agent type, acid number, and retention and directions of wood grains. Initial contact angle decreased with increase of E-43 retention, but it was proportional to PEMA retention. However, it was independent of G-3015 retention. Wettability of fractured wood-PVC interface was similar to that of maleated wood surface with heat treatment. Thus, the interfacial characteristics of wood-PVC interface can be simulated with maleated wood surface with heat treatment.

Keywords: Composites, imaging analysis, maleation, wetting behavior, wood-PVC interface.

INTRODUCTION

Wettability is an essential property to wood adhesion (Gray 1962). Wettability of wood materials is usually evaluated with contact angle, which provides an adverse measure of wettability (Zisman 1976). Wetting quality of wood is influenced by many factors including wood macro characteristics (e.g., porosity, surface roughness, wood surface polarity, pH value, moisture content, grain orientation, and extractives), surface quality of wood (e.g., virgin, aging, and contamination), processing temperature, and properties of adhesives (e.g., acidity, rheology, and viscosity) (Bryant 1968; Lee and Luner 1972; Jordan and Wellons 1977; Scheikl and Dunky 1998).

There are several kinds of devices for static contact angle measurements. For a traditional device, the contact angle data were manually measured with a microscope eyepiece combined with a separate protractor or goniometer (Freeman 1959; Herczeg 1965). Since the late 1970s, static contact angle analyzers (such as Kernco -

G-1, Krüss G1/G40, Rame-Hart, Zeiss) have been equipped with an inserted goniometer in the microscope eyepiece. These improved optical apparatuses are relatively easy to use and accurately measure static contact angles on the wood surface. The profile of sessile drops on wood surfaces can be captured with a camera attached to the microscope. However, it is difficult to use this optical technique for determining dynamic contact angle data on surfaces with high polarity, because the measurement of contact angle is usually accomplished in several seconds and lagged to the actual contact angle (Lu et al. 2002).

In the early 1970s, Elliott and Ford (1972) proposed a photography technique for dynamic contact angle measurements. This photography technique was later successfully combined with a microscope for convenient observation of liquid droplets on a substrate (Jordan and Wellons 1977). Skinner and colleagues (1989) applied two sets of microscopes and video cameras horizontally and vertically arranged to observe the instantaneous time-elapsed profiles of a droplet on a subject in three dimensions. Kalnins et al. (1988) used a video camera to record dynamic contact angle data to a video tape.

The operation with these early devices was laborious because most contact angle data were manually measured. The limitation for dynamic contact angle measurement was reduced by using a computer in combination with a video camera (Scheikl and Dunky 1996). A CCD (charged couple device) type video camera connected to a computer was directly equipped on a Krüss G1/G40 contact angle meter. The image of a droplet on a specimen was captured with the video camera and processed by the computer during measurements. A number of publications on dynamic contact angles are attributed to the applications of these techniques (Skinner et al. 1989; Scheikl and Dunky 1998; Shi and Gardner 2001).

Static contact angle measurement techniques have been extensively used to characterize water repellency, weathering, and durability of solid wood (Nussbaum 1999), bondability and adhesion of wood composites (Chen 1972; Hse 1972; Jordan and Wellons 1977), gluability of preservative-treated wood materials (Zhang et al. 1997), adsorption, printing, and recycling of paper products (Oye and Okayama 1989), coatability of wood materials for paints (Feist 1977; Kleive 1986), and surface energy and wettability for wood and wood products (Lee and Luner 1972; Hodgson and Berg 1988). Recently, contact angle measurement methods have been applied to evaluate compatibility of chemically modified wood fibers in wood-polymer composites (Felix and Gatenholm 1991; Chen et al. 1995).

Although a number of researches on wettability and interfacial bonding of wood-polymer composites have been published (Felix and Gatenholm 1991; Matuana et al. 1998; Lu et al. 2002), there are few reports on characteristics of wettability at the wood-polymer interface. This was due to the difficulty in separating individual wood fibers from the polymer matrix in wood-polymer composites (Liu et al. 1994). To overcome these obstacles, wood-polymer laminates can be used as a substitute because interfacial layers in the laminates can be more easily separated and used for contact angle analysis. The study is a new approach to determine surface and interfacial characterization (e.g., wettability) in wood-polymer composites. This simulation method may help reveal the wetting behavior at the interface in wood-polymer composites.

The objective of this work was to investigate wetting behavior (i.e., static contact angle and water droplet morphology) of maleated wood surface and wood-polymer interface as a function of time and maleation treatments. The interfacial wettability characteristics were determined with maleated wood surface after heat treatment; and with wood-PVC interfaces.

MATERIALS AND METHODS

Test materials and sample preparations

Two maleated polypropylene (MAPP) copolymers (Epolenes E-43 and G-3015, Eastman Chemical Company) and one copolymer of maleic anhydride and ethylene, polyethylene-

maleic anhydride (PEMA, Polysciences, Inc.) were used in this study. The properties of these coupling agents are listed in Table 1. Benzoyl peroxide (BPO, Aldrich) was used as an initiator. Toluene (Fisher Scientific) was used as a solvent for both MAPPs and *n*-butanol (Fisher Scientific) for PEMA. Polyvinyl chloride (PVC) sheets (508 mm × 1270 mm × 0.0508 mm) were purchased from Curbell Plastics Company, Phoenix, AZ.

Sheets of commercial yellow-poplar (*Liriodendron tulipifera*) and red oak (*Quercus rubra*) veneers (610 mm × 610 mm) were obtained from Columbia Forest Products Inc., Newport, VT. The nominal thickness for red oak and yellow-poplar was 0.76 and 0.91 mm, respectively. The deviation of veneer thickness for both species was 0.127 mm. A total of 124 samples (50.8 mm × 25.4 mm × thickness) were cut from the veneer sheets for this study. Prior to coupling treatment, all veneer samples were conditioned to 5% MC in a conditioning chamber. All samples were numbered and kept in separate bags before testing.

Soxhlet extraction

Soxhlet extraction was conducted on all wood specimens according to the ASTM standard D1105-96 (ASTM 1998) to reduce the influence of extractives on chemical coupling. The wood samples were first extracted with a 120-ml mixing solution of toluene and ethyl alcohol for 4 h. They sequentially underwent the second extraction with 120 ml ethyl alcohol for 4 h. The extracted wood specimens were finally oven-dried at 70°C for 24 h to reach a constant weight. The oven-dried weight of each sample was measured and reported in the literature (Lu et al. 2002).

Surface treatments and interphase preparations

Four kinds of surfaces from modified wood materials and wood-PVC composites were prepared for the wettability evaluation. They consisted of surfaces with coupling treatment (**S1**), surfaces with heat treatment (**S2**), PVC-coupling interphase (**S3**), and wood-coupling interphase (**S4**). For the last three kinds of surfaces, post treatments (e.g., heat treatment and tensile test) were performed after coupling treatment.

During coupling treatment, wood specimens were dipped in a coupling agent solution at 100°C for 5 min under continuous stirring with a magnetic stirrer. The concentration levels of MAPP were designed to be 12.5, 25, 50, and 75 g/L. The weight ratio between BPO and MAPP was 0.5. The treated specimens were removed from the solution and cooled to room temperature. All maleated or chemically modified specimens (**S1**) were oven-dried at 70°C for 24 h to reach a constant weight to calculate coupling agent retention. Coupling agent retention was determined based on the weight percentage of fixed coupling agent on a maleated wood specimen (Lu et al. 2002).

Heat treatment for chemically modified specimens was conducted to simulate the interface in melt-blended composites from compression and injection molding. A maleated specimen was hot-pressed with a miniature press during the treatment. The pressing cycle for each specimen was 3 min for heating and 1 min for cooling under a pressure of 0.138 MPa, similar to the

TABLE 1. *Properties of coupling agents.*

| Coupling agent [a] | Shape and appearance | Density (g/ml) | Molecular weight [b] | | Acid number (mgKOH/g) | Amount of maleic anhydride (%) | Viscosity (cp)[c] |
			$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)			
E-43	Yellow pallet	0.930	9,100	3,900	47	4.4	400
G-3015	Light yellow pallet	0.913	47,000	24,800	15	1.3	25,000
PEMA	White flour	–	100,000	–	870	–	5

[a] The pH value of 5% PEMA solution at 20°C is 5.2.
[b] $\bar{M}_w$ and $\bar{M}_g$ are weight and number average molar mass, respectively.
[c] The values of viscosity for E-43 and G-3015 were measured at 190°C. The viscosity of PEMA was measured in a 2% solution.

procedure used for manufacturing wood-PVC laminates (Lu et al. 2002). The heating temperature was 210ºC. At the end of the heating period, the press platens were cooled with tap water to 70ºC. The treated specimen (**S2**) was then removed and allowed to cool to room temperature.

Specimens for interface analysis were prepared as follows. A PVC film was first placed between two pieces of chemically modified veneer to create a lap joint specimen (Lu et al. 2002). The assembly was hot-pressed in a miniature press under a pressure of 0.276 MPa and heated at 178ºC for 3 min. At the end of the heating period, the press platens were cooled with tap water to room temperature. All tensile specimens were stored at room temperature for 72 h before testing. The lap joint of wood-PVC laminates was then separated with a Model 1125 INSTRON machine under a tensile load. Finally, fractured surfaces at the wood-PVC interface were randomly selected and used for contact angle analysis. For fractured specimens, the part with PVC indicated a PVC-coupling agent interphase (**S3**), while the wood surface represented a wood-coupling agent inter-

phase (**S4**). All test specimens were conditioned to reach about 5% MC before contact angle measurement and morphology analysis.

Contact angle measurement and water droplet profile

An imaging system was used to measure contact angle and shape and size of water droplets for the prepared specimens. This system consisted of a Meiji microscope, a Cole-Parmer CCD color video camera, a Cole-Parmer fiber optic illuminator, an Invedio signal capture card, an individual Panasonic monitor for zooming images, and a computer (Lu 2003). The magnification number of the microscope was 50 times.

During measurement, a specimen was placed on the top of a miniature workbench in front of, or under the microscope (Fig. 1). A 0.01-ml water droplet fell down on the specimen surface. Static contact angle (θ) was measured in the horizontal direction, while the shape and size of a droplet [e.g., diameter (d), perimeter (ρ), contact area (S)] were observed vertically under the mi-
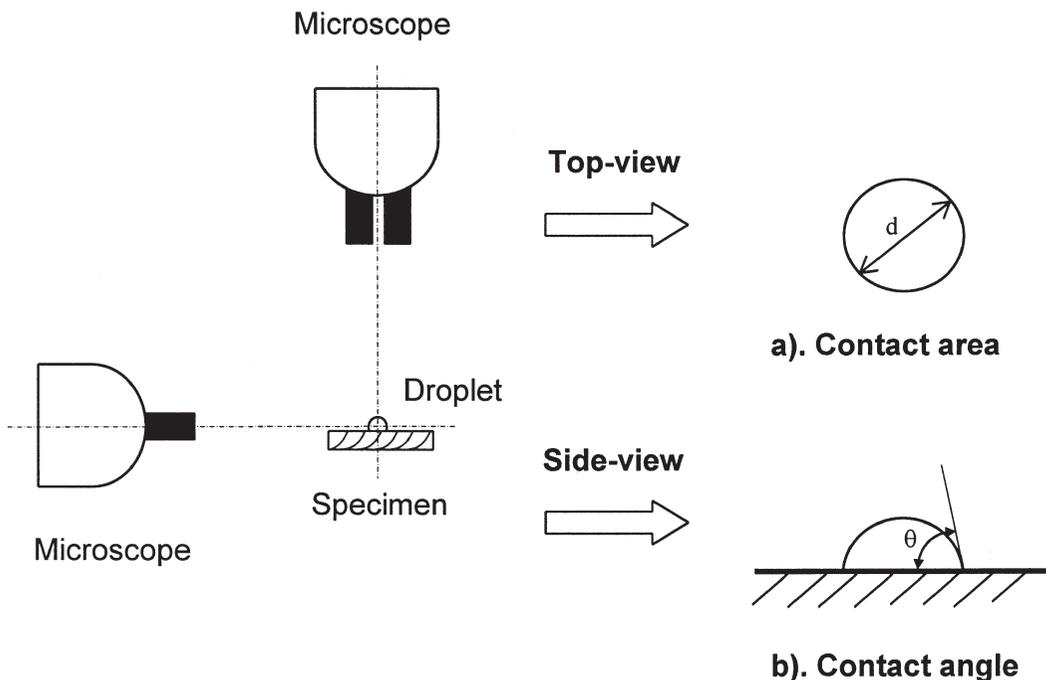
FIG. 1. Two different setups of CCD video camera for measuring the profile of a sessile droplet on modified wood specimens and interphases. a) contact area and b) contact angle.

croscope (Fig. 1). For contact angle, six water droplets on each specimen were observed along and across the grain direction, respectively. Each specimen was also measured with two droplets for profile analysis. The images were captured using the video camera. All captured images were then stored as image files and measured using SigmaScan® software.

Contact angle measurement was done in 15-s intervals from 0 to 45 s for wetting behavior. For convenient observation, image profiles on each test specimen exposed at 15 s were measured to reveal its isotropic behavior. A ratio (λ) of the minimum diameter to the maximum diameter of

the contact area was calculated to evaluate the profile shape of water droplets. In general, a test specimen with $\lambda = 1$ implies that it is an isotropic material (e.g., thermoplastics), while a specimen with a λ ratio less than 1 indicates the material is anisotropic (e.g., wood). Wettability of specimens with different treatments was determined based on λ ratios and contact angle in this study.

RESULTS AND DISCUSSION

Water droplet morphology

A water droplet on PVC film had a circular shape 15 s after it was placed on the surface ($\lambda =$
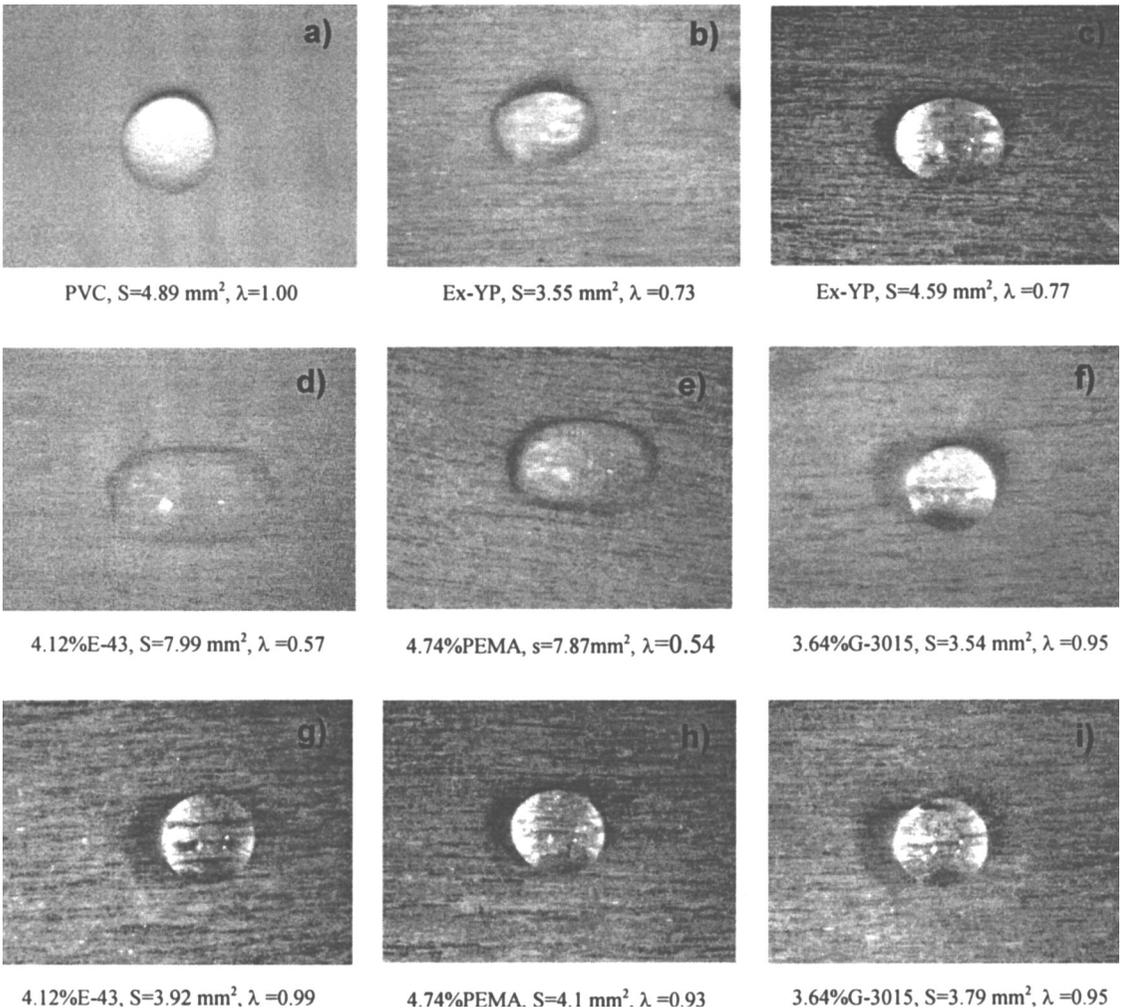
FIG. 2. Morphology of water droplets on extracted yellow-poplar veneer (Ex-YP) after 15 second exposure. a) PVC, b) unmaleated wood, c) wood with heat treatment, d)–f) maleated, and g)–i) heated after coupling treatment.

1.0, Fig. 2a). The droplet diameter and λ value had not changed even after 60-s exposure (Table 2). This was due to the isotropic properties of PVC on wettability. Without coupling treatment, unextracted and extracted yellow-poplar veneers showed their anisotropy with an elliptical water droplet with a λ value of 0.65 and 0.73 on average, respectively (Table 2 and Fig. 2b). Water droplets on unextracted yellow-poplar had a circular shape after heat treatment, (λ = 0.93, Table 3). However, they were elliptical on extracted yellow-poplar veneer with heat treatment (λ = 0.77, Fig. 2c).

Water droplets on maleated wood veneer (S1) presented different profiles. For E-43 and PEMA-treated yellow-poplar veneers, λ ratios were around 0.6 and less than those on unmaleated yellow-poplar (Fig. 2d,e and Table 2). Similarly, E-43- and PEMA-treated red oak veneers (S1) had smaller λ ratios (< 0.65) but larger contact area than unmaleated red oak veneer (Table 2). For both wood species, however, λ ratios of all G-3015-treated veneers were equal to or close to 1 (Fig. 2f and Table 2).

With heat treatment, E-43- and PEMA-treated yellow-poplar specimens (S2) had larger λ ratios and smaller contact area than those without heat treatment (Table 3 and Fig. 2g,h). However, heat treatment did not have significant influence on wettability of G-3015-treated yellow-poplar veneer (Table 3 and Fig. 2i).

At the wood-PVC interface, wood-coupling agent and polymer-coupling agent interphases (S3 and S4) both presented high hydrophobicity with respect to unmaleated wood specimens (Fig. 3). For extracted yellow-poplar, all maleated interphases had a larger λ ratio than unmaleated wood surface (Table 3). Although there was no significant difference among these surface treatments for G-3015-treated veneer, interphases with E-43 and PEMA had larger λ ratios than E-43- and PEMA-treated veneers (Tables 2 and 3). For most maleated interphases, λ ratios were over 0.90 and close to 1 at the retention level close to 4% (Fig. 3). It also clearly showed that λ ratios of maleated interphases were close to those of maleated veneer with heat treatment (Table 3). However, most interphases

with PEMA had smaller λ ratios than those with E-43 and G-3015.

Static contact angle

For both maleated and unmaleated wood specimens (S1), static contact angle was a decreasing function of wetting time (Figs. 4 and 5). For unmaleated yellow-poplar veneer, the contact angle change was larger than 20° in a wetting period of 45 s (Fig. 4a). At a close retention level, initial contact angle (θ_{int}, i.e., contact angle at zero second) on E-43- and PEMA-treated yellow poplar veneers decreased by over 70° within 45 s (Figs 4b and c). For G-3015-treated veneer, however, θ_{int} decreased only by 2° in the same time intervals (Fig. 4d). Similar trends were also presented on maleated red oak veneer. Like red oak veneer (Fig. 5a), E-43- and PEMA-treated red oak veneer had a larger contact angle change (> 40°) within 45 s (Fig. 5b,c). G-3015-treated red oak veneer, however, had a smaller contact angle change (< 6°) in the same wetting period (Fig. 5d).

Compared with untreated wood veneer with heat treatment, maleated wood with heat treatment (S2) had smaller contact angle changes (Table 4). Initial contact angles on untreated veneer with heat treatment decreased by 30° on average at 45 s. For E-43- and G-3015-treated specimens, contact angle angles were less than 3° within 45 s. Also, initial contact angle on PEMA-treated specimens only decreased by around 6° in the same wetting period. Therefore, surface polarity of maleated specimens significantly decreased after heat treatment.

Fracture surface on PVC film (S3) had large contact angles (around 115°) and small contact angle changes (< 3°) within 45 s (Table 4). For fracture surface on wood (S4), E-43- and G-3015-treated interphases had larger contact angles (around 122°) than PEMA-treated interphases, but all wood-coupling agent interphases (S4) had small contact angle changes (< 3°). Accordingly, maleated wood surfaces were compatible to thermoplastics after fabrication. Also, fracture surfaces on wood veneer (S4) presented wetting behavior similar to

TABLE 2. *Morphology of water droplets on maleated wood veneer after 15-s exposure.*[a]

Material	Wood species	Extraction before coupling	Coupling agent	Retention of coupling agent (%)	Diameter (mm) d_{min}	Diameter (mm) d_{max}	λ ratio (d_{min}/d_{max})	Perimeter, ρ (mm)	Contact area, S (mm²)
PVC	–	–	–	0.00	2.44	2.44	1.00	8.21	4.84
PVC[b]	–	–	–	0.00	2.44	2.44	1.00	8.17	4.76
Maleated wood veneer (**S1**)	Yellow-poplar	Unextracted	–	0.00	2.14	2.44	0.66	7.87	4.13
			E-43	3.64	1.87	3.11	0.60	8.57	4.73
			PEMA	5.21	1.55	2.78	0.56	7.92	4.03
			G-3015	3.49	1.85	1.85	1.00	6.24	2.81
		Extracted	–	0.00	1.95	2.54	0.76	7.64	4.03
			E-43	4.12	2.29	3.88	0.59	10.96	7.78
			PEMA	4.74	2.48	4.63	0.54	10.97	7.83
			G-3015	3.64	2.03	2.15	0.94	6.99	3.51
	Red oak	Extracted	–	0.00	1.53	2.03	0.75	7.32	3.59
			E-43	4.12	1.83	2.91	0.63	8.21	4.57
			PEMA	4.90	2.61	5.32	0.49	11.32	8.41
			G-3015	5.20	1.74	1.76	0.99	5.97	2.56

[a] The values in the last five columns are the average of two observations.
[b] Measured at 60-s exposure.
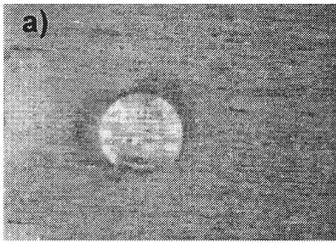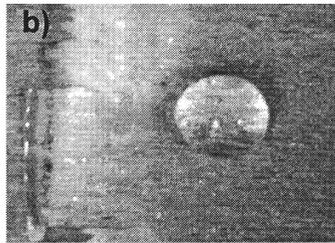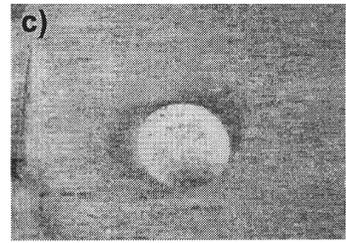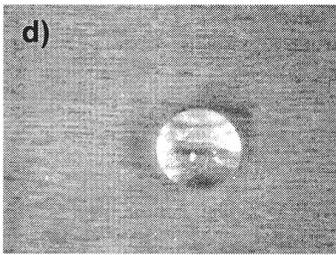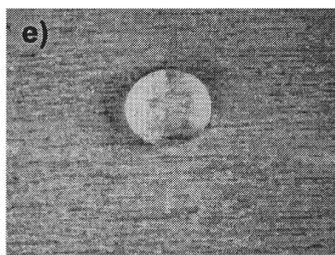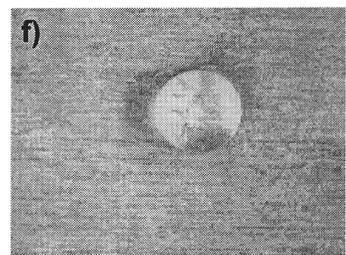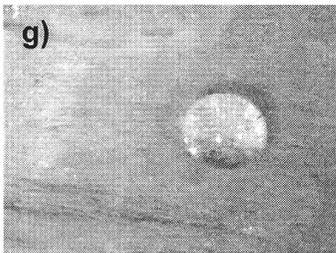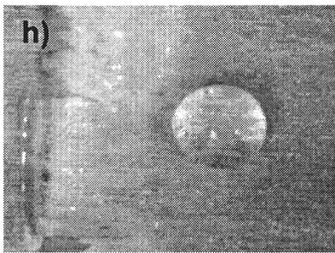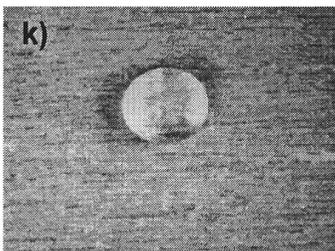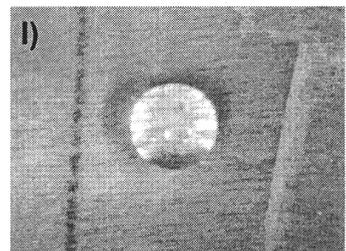
FIG. 3.   Morphology of water droplets on yellow-poplar-PVC interface after 15-s exposure. a)–c) unextracted PVC-coupling agent interphases, d)–f) unextracted wood-coupling agent interphases, g)–i) extracted PVC-coupling agent interphases, and j)–l) extracted wood-coupling agent interphases.

TABLE 3. *Morphology of water droplets on maleated wood veneer and interphases of wood-PVC composites after 15 second exposure.*[a]

Material	Wood species	Extraction before coupling	Coupling agent	Retention of coupling agent (%)	Diameter (mm) d_{min}	d_{max}	λ ratio (d_{min}/d_{max})	Perimeter, ρ (mm)	Contact area, S (mm²)
Maleated wood with heat treatment (**S2**)	Yellow-poplar	Unextracted	–	0.00	1.98	2.12	0.93	6.93	3.45
			E-43	3.64	2.04	2.16	0.94	7.15	3.68
			PEMA	5.21	1.97	2.23	0.88	7.26	3.76
			G-3015	3.49	2.12	2.16	0.98	7.32	3.86
		Extracted	–	0.00	2.04	2.62	0.77	8.07	4.51
			E-43	4.12	2.16	2.19	0.99	7.40	3.92
			PEMA	4.74	2.14	2.30	0.93	7.57	4.11
			G-3015	3.64	2.10	2.22	0.95	7.30	3.80
PVC-coupling agent interphases (**S3**)	Yellow-poplar	Unextracted	E-43	3.64	2.02	2.11	0.96	7.01	3.51
			PEMA	5.21	1.99	2.22	0.91	7.18	3.74
			G-3015	3.49	2.04	2.16	0.94	7.12	3.63
		Extracted	E-43	4.12	1.89	2.04	0.93	6.75	3.25
			PEMA	4.74	1.92	2.16	0.89	6.99	3.45
			G-3015	3.64	2.16	2.20	0.94	7.44	3.63
Wood-coupling agent interphases (**S4**)	Yellow-poplar	Unextracted	E-43	3.64	2.03	2.23	0.91	7.32	3.30
			PEMA	5.21	2.17	2.25	0.97	7.50	4.00
			G-3015	3.49	2.17	2.31	0.94	7.55	4.09
		Extracted	E-43	4.12	1.99	2.01	0.91	6.80	3.30
			PEMA	4.74	1.92	2.14	0.90	7.01	3.46
			G-3015	3.64	2.02	2.20	0.92	7.18	3.68

[a] The values in the last five columns are the average of two observations.
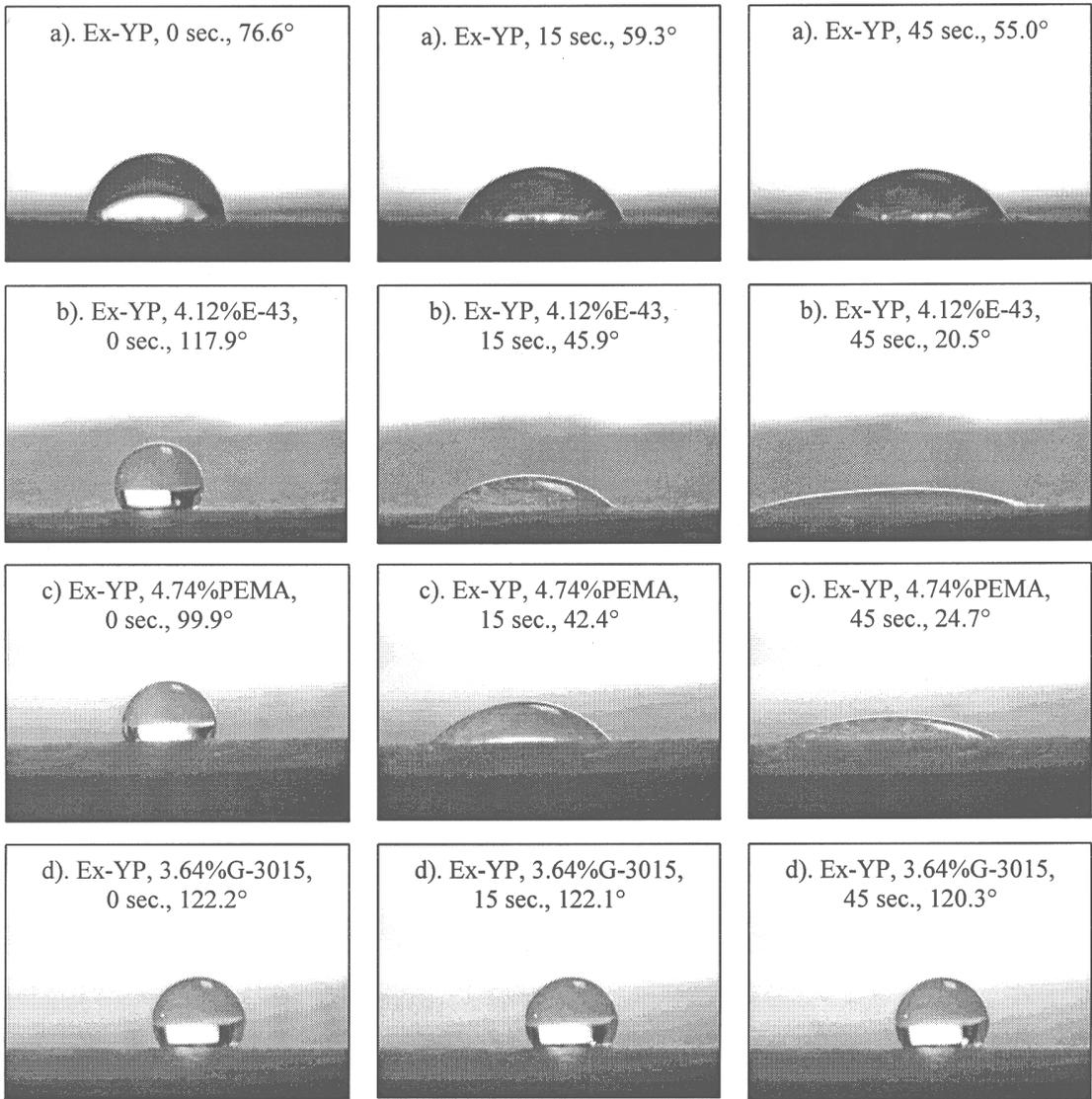
FIG. 4.   Contact angle changes on extracted yellow-poplar specimens (Ex-YP) at different wetting periods. a) unmaleated veneer, b) 4.12% E-43-treated veneer, c) 4.74% PEMA-treated veneer, and d) 3.64% G-3015-treated veneer.

maleated wood veneer with heat treatment (**S2**) (Table 4).

In summary, G-3015-treated wood specimens had higher λ ratios (close to 1) and large and unchanged contact angles (around 120°), i.e., they had an unwettable surface. E-43- and PEMA-treated wood veneers, however, had smaller λ ratios ($<$ 0.7) and changeable contact angles, i.e., they had a wettable surface. Therefore, wetting behavior of E-43- and PEMA-treated ve-

neers was similar to that of wood surface. However, G-3015-treated veneer presented the wetting characteristics similar to PVC film. As a result, E-43 and PEMA-treated surfaces were more like wood in character, while G-3015-treated surfaces acted more as thermoplastics.

Most maleated interphases and maleated specimens with heat treatment had higher λ ratios ($>$ 0.90) and smaller contact angle changes ($<$ 6°) within 45 s than wood veneer with heat

TABLE 4. *Contact angle changes on maleated yellow-poplar veneer with heat treatment and maleated interphases of wood-PVC composites.* [a, b]

Material	Species	Coupling agent	Retention of coupling agent (%)	Static contact angle, θ		
				0 sec.	15 sec.	45 sec.
Maleated wood with heat treatment (**S2**)	Yellow-poplar	–	0.00	108.2 (3.9)	88.5 (4.0)	76.6 (3.1)
		E-43	4.12	122.2 (2.3)	121.0 (3.8)	121.9 (4.7)
		PEMA	4.74	110.9 (3.4)	105.7 (2.6)	105.1 (2.7)
		G-3015	3.64	121.7 (2.6)	121.0 (1.6)	119.5 (4.3)
PVC-coupling interphases (**S3**)	Yellow-poplar	E-43	4.12	114.5 (1.4)	113.4 (2.6)	113.7 (2.4)
		PEMA	4.74	115.6 (1.4)	114.9 (3.9)	112.9 (2.6)
		G-3015	3.64	113.9 (1.6)	112.6 (1.4)	113.4 (2.1)
Wood-coupling interphases (**S4**)	Yellow-poplar	E-43	4.12	122.6 (3.6)	121.3 (5.8)	122.1 (5.5)
		PEMA	4.74	113.8 (3.8)	111.2 (1.6)	111.2 (2.3)
		G-3015	3.64	121.9 (6.1)	122.3 (5.4)	122.5 (6.6)

[a] All specimens were extracted before the coupling and heat treatments.
[b] All contact angle data were measured along the wood grain direction.

treatment. Moreover, the wetting behavior of maleated specimens with heat treatment was similar to that at the interface. This implies that after fabrication maleation significantly increases hydrophobicity of maleated composite specimens and thus improves compatibility between wood and thermoplastics. It also has a practical significance that wettability at the interface, especially at the wood-coupling agent interphases, can be estimated with maleated wood veneer with heat treatment.

Effect of wood microstructure

Wood is a hygroscopic material. The porosity of wood varies with its species and microstructure (Haygreen and Bowyer 1994). Yellow-poplar is a diffuse-porous hardwood, while red oak is a ring-porous hardwood. Red oak veneer has a rougher surface than yellow-poplar veneer due to the significant difference between its early wood and late wood and the scratchlike pattern of red oak after rotary cutting (Vick 1999). Therefore, contact angle on extracted red oak veneer was larger than that on extracted yellow poplar because of the roughness (Figs. 4a and 5a).

Capillary effects made red oak veneer with larger pore diameter vessels on early wood have faster wetting speed than yellow-poplar with smaller pore diameter vessels. Red oak has radially oriented rays that can allow excessive flow and overpenetration (Vick 1999). Also, red oak species usually have many open checks in the loose side during rotary cutting by a knife. This imperfection on red oak veneer also causes liquid overpenetration. As shown in Figs. 4a and 5a, contact angle on red oak veneer decreased by 35° but on yellow-poplar only by 22° within 45 s.

On wood veneer, capillary effects on cut fiber tracheid and vessel lumens make wetting liquids spread much easier along the grain direction than the cross direction (Shi and Gardner 2001). Also, the direction along wood grains is smoother than the cross direction. Hence, the direction along grains had larger surface tension than the cross direction. In this study, contact angle in the direction along wood grains was generally smaller than that in the cross direction (Table 5). For E-43-treated yellow-poplar veneer, contact angle across grains was 10–20 degrees larger than that along grains (Fig. 6). The difference on contact angle increased with increase of E-43 retention. For PEMA-treated yellow-poplar veneer, the contact angle difference between these two directions was as large as 20 degrees and it was almost independent of PEMA retention. However, G-3015-treated specimens did not present a significant directional difference on contact angle, although contact angle across wood
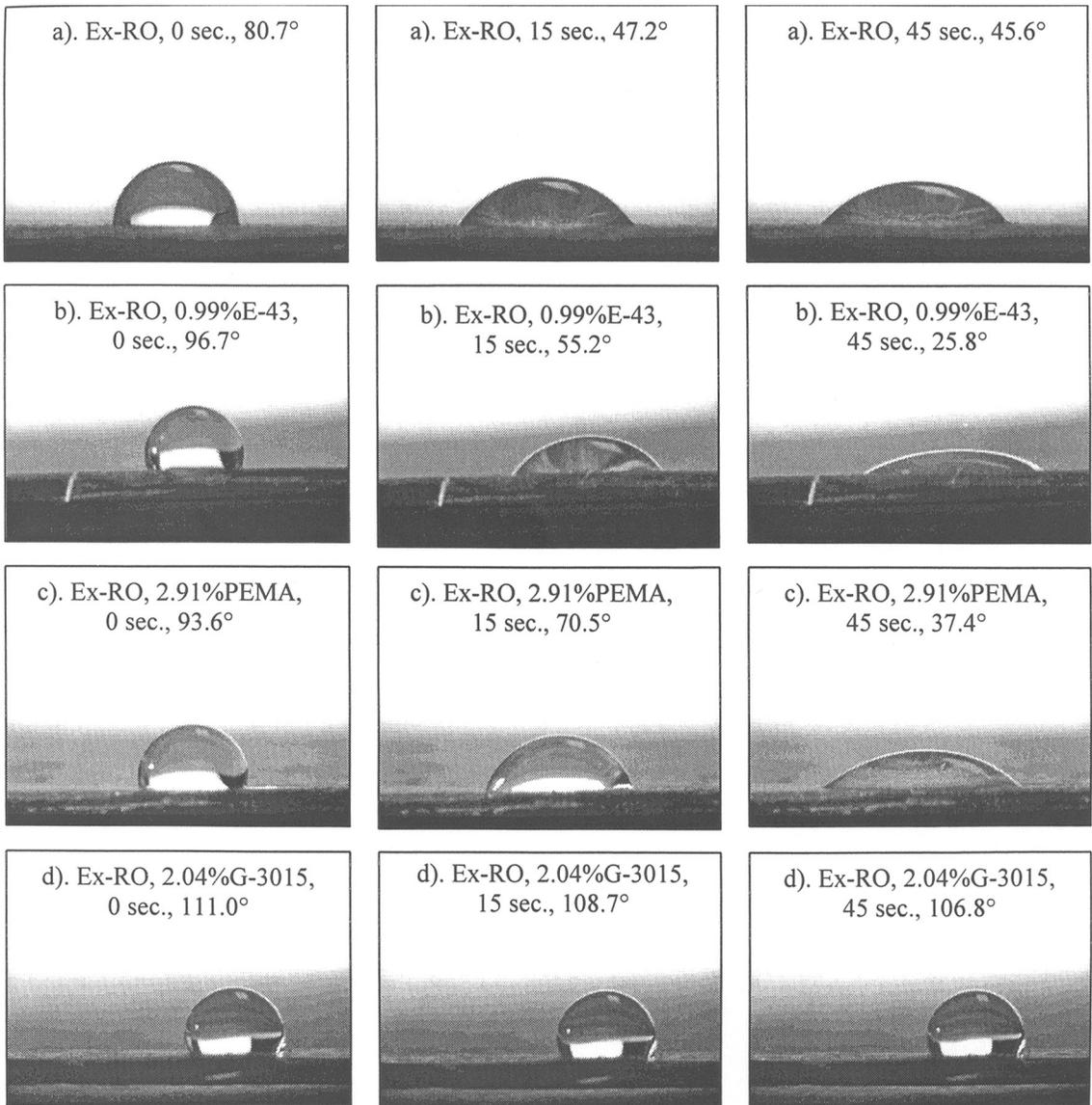
FIG. 5.   Contact angle changes on extracted red oak specimens (Ex-RO) at different wetting periods. a) unmaleated veneer, b) 0.99% E-43-treated veneer, c) 2.91% PEMA-treated veneer, and d) 2.04% G-3015-treated veneer.

grains was slightly larger than that along wood grains (Fig. 6).

Effect of extractives

Jordan and Wellons (1977) reported that extractives significantly influenced wettability of wood. Most hardwood extractives (such as triterpenes, lignians, steroids, fats, and waxes) exist as oils or resins on wood surface, and they are non-polar or less polar (Fengel and Wegener 1984). These organic compounds unfavor the wettability of yellow-poplar and red oak veneers. For yellow-poplar veneer, contact angles along and cross wood grains on unextracted specimens were around 22 and 13 degrees larger than those on extracted specimens, respectively (Table 5). There-

TABLE 5. *Initial contact angle on maleated wood veneer.*

Material	Species	Coupling agent	Extraction before treatment	Orientation to wood grains[a]	Initial contact angle, θ_{int} [b] (degrees)			
Wood veneer	Yellow-poplar	–	Unextracted	//	107.8 (3.1)			
				⊥	125.7 (5.0)			
		–	Extracted	//	86.0 (3.4)			
				⊥	112.4 (5.6)			
Maleated wood veneer (**S1**)	Yellow-poplar	E-43	Unextracted		**2.16%**	**3.64%**	**7.14%**	**8.05%**
				//	103.1 (8.7)	84.2 (8.2)	69.8 (5.4)	64.8 (6.5)
				⊥	119.2 (11.4)	112.1 (3.1)	99.5 (5.3)	96.5 (6.0)
			Extracted		**2.95%**	**4.12%**	**6.83%**	**7.41%**
				//	114.8 (4.5)	104.7 (4.2)	89.6 (4.6)	93.0 (6.2)
				⊥	126.4 (5.5)	114.5 (5.1)	112.9 (2.8)	110.6 (4.4)
		PEMA	Unextracted		**5.21%**	**9.67%**	**15.88%**	**25.00%**
				//	83.2 (8.7)	92.2 (5.2)	104.6 (5.4)	104.7 (5.3)
				⊥	109.5 (5.5)	112.0 (7.3)	115.3 (7.8)	113.6 (5.9)
			Extracted		**4.74%**	**9.54%**	**16.08%**	**23.90%**
				//	81.0 (4.3)	90.1 (5.7)	91.5 (6.9)	92.8 (4.9)
				⊥	109.2 (2.5)	106.5 (7.4)	115.6 (4.0)	109.4 (7.2)
		G-3015	Unextracted		**1.89%**	**3.49%**	**6.02%**	**9.48%**
				//	123.0 (6.1)	118.5 (4.2)	118.4 (4.6)	116.6 (5.4)
				⊥	127.0 (7.1)	132.2 (5.6)	123.9 (4.3)	121.8 (5.6)
			Extracted		**2.17%**	**3.64%**	**6.35%**	**10.54%**
				//	125.8 (6.3)	113.5 (3.9)	117.3 (5.8)	119.2 (6.1)
				⊥	122.9 (5.0)	121.7 (3.8)	124.3 (4.0)	118.9 (8.4)
	Red oak	E-43	Extracted		**0.25%**	**0.99%**	**4.10%**	**6.17%**
				//	109.6 (6.3)	99.4 (5.4)	91.4 (7.5)	93.1 (7.5)
				⊥	109.2 (2.5)	98.6 (6.1)	90.8 (7.0)	83.2 (5.5)
		PEMA	Extracted		**2.91%**	**4.90%**	**12.01%**	**17.44%**
				//	78.0 (5.1)	80.8 (3.2)	85.8 (4.9)	93.2 (6.8)
				⊥	111.1 (7.8)	114.1 (6.1)	96.4 (7.1)	107.5 (4.2)
		G-3015	Extracted		**0.45%**	**2.04%**	**5.20%**	**11.46%**
				//	112.0 (3.8)	115.9 (7.0)	110.6 (4.9)	118.8 (7.7)
				⊥	115.0 (3.0)	115.4 (5.4)	125.1 (8.4)	121.2 (9.1)

[a] // and ⊥ indicate the direction parallel and perpendicular to the wood grain, respectively.

[b] The values in bold are retention levels of coupling agent, while the values in parentheses are standard deviations.

fore, extracted wood veneer had higher polarity than unextracted veneer. This was likely due to the fact that more hydroxyl groups of lignocellulose freely exposed on the wood surface and resulted in a more hydrophilic surface after extractives were removed (Lu et al. 2002).

As shown in Fig. 7, initial contact angle on E-43- and PEMA-treated yellow-poplar veneers were sensitive to extractives. However, extractives did not influence initial contact angle on G-3015-treated veneer. For E-43, initial contact angle difference between extracted and unex-tracted veneers was around 20°, almost independent of E-43 retention. For PEMA, the difference on initial contact angle between extracted and unextracted veneers was proportional to PEMA retention.

Effect of coupling agents

Wettability of chemically modified wood veneer (**S1**) was influenced by different coupling agents, because the difference in the wetting behavior of maleated wood specimens mainly lies
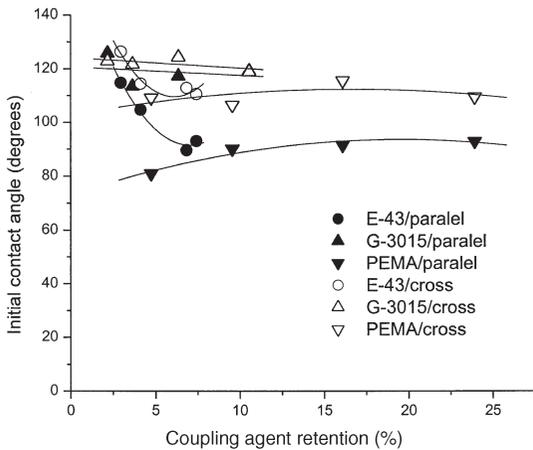
FIG. 6.   Effect of wood grain directions on initial contact angle on maleated yellow-poplar veneer with extraction.

in the structure and coupling action of these coupling agents. E-43 has a higher acid number than G-3015, but a smaller molecular weight than G-3015 and PEMA. Among these three coupling agents, PEMA has the largest molecular weight and acid number (Table 1). Due to the limitation of maleation at the interface (Lu et al. 2002), there were many free or ungrafted maleaic anhydride (MA) groups on surfaces of PEMA- and E-43-treated wood veneers.

Compared with E-43 and PEMA, G-3015 has less MA groups on its molecular chains (Table 1). For G-3015, some MA groups reacted with hydroxyl groups (-OH) of lignocellulose through graft copolymerization and formed an ester linkage with wood (Felix and Gatenholm 1991). However, some free or ungrafted MA groups of G-3015 may be buried in its large molecular chains (Lu et al. 2002). Therefore, wood specimens treated with E-43 and PEMA had higher polarity, but G-3015 produced a less polar or non-polar structure at the interface.

As shown in Table 1, PEMA has more functional groups on its molecular chains than E-43 per unit weight. After coupling treatment, therefore, PEMA-treated specimens had more free carboxyl groups on the veneer surface than that of E-43-treated specimens. These free –COOH groups can easily form hydrogen bonding through intra- or intermolecular chains of PEMA and through their interaction with the hydroxyl groups

of lignocellulose molecules by dehydration (Filex and Gatenholm 1991). The chemical structure of PEMA was preferred to produce hydrogen bonds between –COOH groups on its molecular chains and the hydroxyl groups of lignocellulose and between MA groups of its intramolecular chains. The hydrogen bonding structure interfered with the wetting of water on wood surface and thus decreasing surface polarity of treated veneer. This may be the reason that the wetting behavior of PEMA was opposite to that of E-43 (Fig. 7). Hence, the wetting behavior of these two coupling agents with high acid number reflected their ability to form hydrogen bonding with the hydroxyl groups of lignocellulose.

The influence of coupling agent retention on initial contact angle of chemically modified
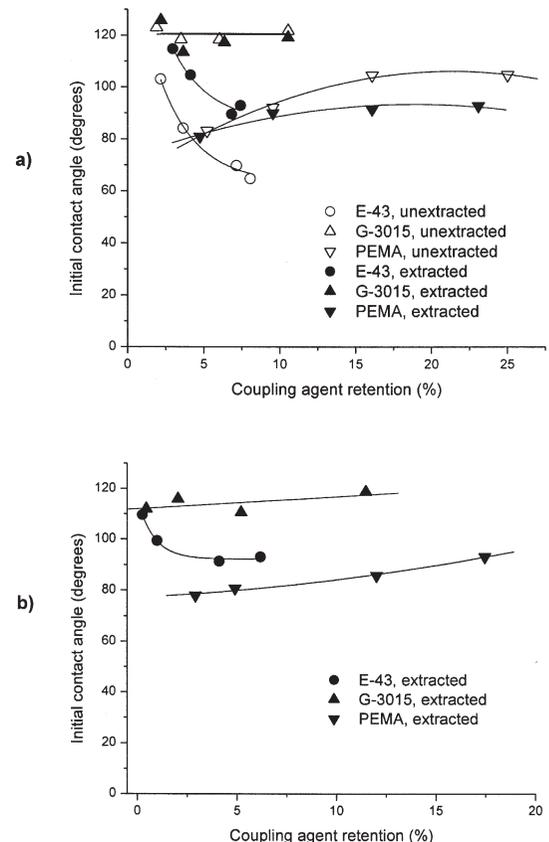
FIG. 7.   Effect of coupling agent retention on initial contact angle along wood grains on a) maleated yellow-poplar veneer and b) maleated red oak veneer.

yellow-poplar veneer (**S1**) was presented in Table 5 and Fig. 7. For E-43, initial contact angle decreased with increase of coupling agent retention, while it increased with increase of retention in the case of PEMA. For E-43 and PEMA, retention influenced initial contact angle of maleated veneer. However, initial contact angle was independent of retention for G-3015-treated wood veneer (Fig. 7a). Similar wetting behavior was also presented for maleated red oak veneer (Fig. 7b).

The effects of most wood macro properties on wettability of treated veneer were removed by maleation because coupling agents formed a film on wood surfaces. Wood species, roughness and porosity, surface polarity, and other macro properties had no significant influence on wetting behavior of maleated specimens due to covering by the polymeric film. As shown in Tables 2, 3, 5 and Figs. 2, 4, and 5, maleated wood veneer had different λ ratios and initial contact angles, which was primarily resulted from coupling treatment. Therefore, the wettability of maleated wood veneer was more related to molecular structure, acid number, and amount of free or ungrafted MA groups of coupling agents (Lu et al. 2002).

Effect of heat treatment

Heat treatment had an influence on the wetting behavior of maleated wood specimens. Heat treatment usually causes wood extractives to migrate to the surface and increases its hydrophobicity (Hemingway 1969). This is the main reason that unextracted wood veneer with heat treatment had higher λ ratios than unextracted veneer without heat treatment (Tables 2 and 3).

Heated at higher temperatures and longer time, wood would generate volatile decomposition products from polysaccharides and a charred residue of lignin (Hancock 1963; Elder 1990). In this study, the heating temperature (210ºC) for wood veneer was close to the decomposition temperatures of hemicellulose (225–325ºC) and lignin (250–500ºC), but much less than the decomposition temperature of cellulose (325–375ºC) (Shafizadeh and McGinnis

1971). Therefore, heating wood veneer for short time (3 min) would lead to slight and slow pyrolytic degradation of xylan and surface dehydration and charring of lignin. These pyrolytic products increased surface hydrophobicity of wood veneer.

As shown in Tables 2 and 3, all maleated specimens with heat treatment (**S2**) had larger λ ratios (> 0.90) than wood veneer and E-43- and PEMA-treated veneers without heat treatment. Moreover, maleated specimens with heat treatment (**S2**) had λ ratios close to the wood-coupling agent interphases (**S4**) (Tables 3 and 5). This indicated that maleated veneer with heat treatment had wetting behavior similar to the wood-polymer interface. On the other hand, di- and mono-carboxyl groups (i.e., hydrolyzed products of free or ungrafted MA groups of coupling agents) formed hydrogen bonding under heating (Felix and Gatenholm 1991), which reduced the surface polarity of maleated veneer and increase its hydrophobicity. Therefore, wettability of maleated specimens was decreased by heat treatment.

CONCLUSIONS

Wood veneer treated with three MA-containing coupling agents presented different wetting behaviors. E-43- and PEMA-treated veneers had a hydrophilic surface, whereas G-3015-treated veneer had a hydrophobic surface. The surface polarity of maleated veneer was mainly related to molecular structure, acid number, and amount of free or ungrafted maleic anhydride groups of coupling agent. Because of covering by coupling agents, wood species, roughness and porosity, surface polarity, and other macro properties of wood did not remarkably influence the wettability of maleated specimens.

The morphology of water droplets revealed their wetting behavior on chemically modified surfaces. For E-43- and PEMA-treated veneers, a water droplet had an elliptical shape on the initial contact with wood veneer. However, a water droplet on a G-3015-treated specimen was more close to a circular shape. This indicated

that E-43- and PEMA-treated wood veneers were more like wood in character, while G-3015-treated wood veneer acted more like thermoplastics.

Contact angle measurement indicated that all maleated interphases and maleated veneer specimens with heat treatment had a hydrophobic surface with respect to wood veneer with heat treatment. Maleated surfaces with heat treatment were different in wettability from those with coupling treatment, but similar to fracture surfaces from shear test. Consequently, maleated surfaces were compatible to thermoplastics after heating. This also indicated that wood-PVC interface can be simulated with maleated wood surface with heat treatment for interfacial characteristics.

Initial contact angle was influenced by coupling agent type, acid number, and retention of coupling agent, and direction of wood grains. Initial contact angle decreased with increase of E-43 retention but increased with increase of PEMA retention. However, it was independent of G-3015 retention. For E-43 and PEMA, initial contact angle cross wood grain was larger than that along wood grains. There was no significant directional effect on initial contact angle on G-3015-treated surface.

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