

SURFACE TENSION AND WETTABILITY OF CCA-TREATED RED MAPLE

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ABSTRACT

The wetting properties of untreated, water-extracted and chromated copper arsenate (CCA)-treated red maple were characterized by contact angle measurements. Conventional experimental and mathematical modeling were employed to evaluate the wetting parameters. Zisman's critical surface tensions, and both acid-base (γ^{AB_s}) and acid (γ^a_s) components of surface tension for CCA-treated wood do not differ much from those of untreated wood. After CCA-treatment, the dispersion (γ^d_s) and Lifshitz-van der Waal (γ^{LW_s}) components of the surface tension increase while the polar (γ^p_s) and base (γ^b_s) components decrease. The high contact angles resulting from the water and CCA treatment of wood compared to untreated wood suggest poor wettability. CCA-treated wood wetted with phenol-formaldehyde (PF) adhesive gave contact angles greater than 90° , i.e., very poor wettability and the time to reach an equilibrium contact angle was three times longer than that for untreated wood.

Keywords: Hardwood, *Acer rubrum L.*, red maple, chromated copper arsenate (CCA), adhesion, wettability, phenol-formaldehyde adhesive, contact angle, critical surface tension, surface free energy, dispersion component, polar component, acid-base component, Lifshitz-van der Waal component.

INTRODUCTION

The manufacture of exterior-grade wood products from preservative-treated wood has been investigated by many researchers (Barnes et al. 1996; Boggio and Gertjeansen 1982; Vick et al. 1996). Preservative-treated wood either does not adhere properly to conventional thermosetting wood adhesives, or the glue line fails. To develop good adhesion between adhesive and CCA-treated wood, a basic understanding of the interface between CCA-treated wood surface and adhesive is essential. However, an important condition for good adhesion between two materials appears to be compatibility between their surface energies (Marian and Stumbo 1962; Hse 1972; Gray 1962; Gardner et al. 1996).

Pizzi (1994) reported that the performance

of adhesion between wood and adhesive may be due to: 1) adsorption, 2) mechanical entanglement/interlocking, 3) electrostatic interactions, and 4) covalent bonding. Vick and Kuster (1992) showed by scanning electron microscopy (SEM) that the surfaces of CCA-treated wood cell walls were covered with mixtures of chromium, copper and arsenic, which block adhesion to CCA-treated wood.

Regardless of the interacting mechanism, interfacial wetting is essential for maximum adhesion. The quality of the interface can be described by using a thermodynamic approach that evaluates the surface energy by measuring the contact angle between solid substrate and liquid adhesive. The laminating industry has long recognized the poor wettability of CCA-treated lumber surface, and researchers have

responded by suggesting planing of CCA-treated surfaces before bonding and using adhesives formulated for CCA-treated wood. Due to health and safety concerns, the surfacing and sanding of preservative-treated wood are not well accepted techniques. Moreover, it is quite difficult to surface (23–27)/1,000-inch thick CCA-treated wafers or 1/60–1/6 inch-thick CCA-treated veneers. This study demonstrates and measures the poor wettability of CCA-treated wood that has not been cleaned by knife-cutting or planing.

The objective of this study is to monitor the modification of the wood surface treated with water and chromated copper arsenate (CCA) by means of contact angle measurement. To achieve this objective, the dispersion and polar components of surface tension were calculated from contact angles using mathematical modeling. This useful information may be used to tailor an adhesive formulation that is compatible with CCA-treated wood surface.

THEORY

Spreading of a liquid on a solid depends on the relative magnitudes of the inter- and intramolecular forces of attraction of the liquid and the solid substrate at the interface (Zisman 1962). Young's equation establishes the relation between the surface tension of solid, air and liquid as follows (Harvey 1962):

$$\cos\theta = (\gamma_s - \gamma_{SL})/\gamma_L \quad (1)$$

where γ_s is the surface tension of solid, γ_L the surface tension of liquid, γ_{SL} the surface tension of solid-liquid interface, and the contact angle (θ) between a solid (S) and a liquid (L). Sumner (1937) derived a relationship similar to Eq. (1) using thermodynamic concept of free energy. To evaluate the wetting properties of a solid, Zisman (1962) proposed an empirical parameter, the critical surface tension of wetting, γ_c , which is defined by the intercept of the straight line plot of $\cos\theta$ vs. γ_L for different liquids with $\cos\theta = 1$. The validity of Young's Eq. (1) is limited to an ideal homogeneous plane and undeformed surface (Adamson 1967). Later, Liptáková and

Kúdela (1994) proposed that the contact angle corresponding to an ideally smooth surface (θ_w) is a function of the contact angle (θ_o) at the beginning of the wetting process and equilibrium contact angle (θ_u) at a time (t_u) of an inhomogeneous surface.

By measuring the contact angles between a solid and a few reference liquids of known values of surface tension (γ_L) and their respective dispersion (γ^d_L), polar (γ^p_L), Lifshitz-van der Waal (γ^{LW}_L), acid (γ^+_L), and base (γ^-_L) components, the surface tension components of the solid can be computed using:

1) Young-Good-Girifalco-Fowkes geometric-mean equation (Girifalco and Good 1957; Fowkes 1972; Nguyen and Johns 1978):

$$\cos\theta = [\{2(\gamma^d_s\gamma^d_L)^{1/2} + 2(\gamma^p_s\gamma^p_L)^{1/2}\}/\gamma_L] - 1 \quad (2)$$

2) Harmonic-mean model (Wu 1971):

$$\cos\theta = 4[\{(\gamma^d_s\gamma^d_L)/(\gamma^d_s + \gamma^d_L) + (\gamma^p_s\gamma^p_L)/(\gamma^p_s + \gamma^p_L)\}/\gamma_L] - 1 \quad (3)$$

3) Acid-base model (Van Oss et al. 1988):

$$\cos\theta = [\{2(\gamma^{LW}_s\gamma^{LW}_L)^{1/2} + (\gamma^+_s\gamma^-_L)^{1/2} + (\gamma^-_s\gamma^+_L)^{1/2}\}/\gamma_L] - 1 \quad (4)$$

MATERIALS AND METHODS

Wood samples

Red maple (*Acer rubrum* L.) blocks 137 × 18 × 5 mm (5.4 in × 0.7 in × .2 in) were conditioned at 20°C (68°F) and 70% relative humidity to an average equilibrium moisture content (EMC) of 10±2%. The wood blocks were pressure-treated with 2% total oxides of chromated copper arsenate (CCA) type C solution, to a retention of 0.8 lb/ft³ (12.8 kg/m³). The wood blocks were also pressure-treated with only water. The treatment schedule consisted of an initial vacuum of 20 kPa (24-in. Hg) absolute pressure for 10 min followed by a pressure of 1.03 kPa (150 psi) for 15 min, and a final vacuum of 15 min. The pressure-treated blocks were stored for a week before oven-drying at 50°C for 24 h, then reconditioned to average EMCs of 10±2%.

TABLE 1. *Ingredients in phenol-formaldehyde adhesive mixture.*

Component	Weight %
Water	9.06
GLU-X (wheat flour)	4.70
Lignoflex (pecan shell flour)	5.50
NaOH (50 wt.%)	3.00
Soda ash	1.00
Liquid PF (GPR 6777)	76.74
Total	100.00

Chemicals

Phenol formaldehyde (PF) (GPR 6777) was obtained from Georgia-Pacific Resin, Inc. The ingredients in the PF adhesive mixture are listed in Table 1. A 50%-concentrate stock solution of chromated copper arsenate (CCA-C) was obtained from Hickson Corporation, Conley, Georgia. All other chemicals, except distilled water, were of analytical grade and were purchased from Aldrich Chemical company.

Contact angle measurement

Contact angles on tangential surfaces of both untreated and treated samples were measured with Rame-Hart, Inc.'s Goniometer, model 100-00-115. The goniometer-microscope tube was set horizontally. The wood specimen rested on a bracket attached to the stage, and a small droplet (0.05 ml) of liquid was placed on the specimen with a micro-pipette. Table 2 lists the liquids and their surface tension components used for contact angle measurement. The contact angle was measured by rotating the microscope eyepiece so that the hairline passed through the point of contact between droplet and wood surface,

and tangent to the droplet at that point. Decreasing time-dependent contact angles for 10 droplets on each wood sample per liquid were measured at relative humidity of 50% and a temperature of 23°C (74°F). The contact angles were recorded at 15, 30, 60, 120, and 300 s, then at 5-min intervals up to 30 min total contact time.

RESULTS AND DISCUSSION

Critical surface tension, γ_c

The critical surface tension values γ_c were determined by plotting the cosine of contact angle vs. the surface tension of a series of liquids (Table 2). The intercept of the rectilinear line and the horizontal line, $\cos \theta = 1$ for zero contact angle is the critical surface tension, γ_c . γ_c calculated for untreated red maple is 46.8 mJ/m², 47.8 mJ/m² for water-treated, and 47.4 mJ/m² for CCA-treated red maple. γ_c values indicate that the critical surface tension differed only slightly after water or CCA treatment. The critical surface tension for untreated red maple calculated in this paper is comparable to γ_c values (47 ± 1 mJ/m²) of untreated hard maple, cherry, red oak (Gardner 1996), and Douglas-fir (Herczeg 1965) available in the literature.

Time-dependent contact angle

The equilibrium angle, θ_u at time t_u to reach the plateau was measured, and by extrapolation θ_o at the beginning of the wetting process was determined. The θ_w , corresponding to an ideally smooth surface, was calculated based on the empirical relations proposed by Liptáková and Kúdela (1994). The θ_o , θ_u and θ_w

TABLE 2. *Surface tension components (mJ/m²) of liquids used for contact angle measurements.*

Liquids	γ_L	γ^d_L	γ^p_L	γ^{LW}_L	γ^{AB}_L	γ^*_L	γ^-_L	References
Ethylene glycol	48.0	29.0	19.0	29.0	19.0	1.92	47.0	Kaelble 1971; Wu et al. 1995
n-butanol: water (2:98)	49.0	—	—	—	—	—	—	Swanson and Becher 1966
Diiodo-methane	50.8	—	—	50.8	0	0	0	Wu et al. 1995
n-butanol: water (1:99)	55.0	—	—	—	—	—	—	Swanson and Becher 1966
Glycerol	64.0	34.0	30.0	34.0	30.0	3.92	57.4	Kaelble 1971; Wu et al. 1995
Water	72.8	21.8	51.0	21.8	51.0	25.5	25.5	Kaelble 1971; Wu et al. 1995

TABLE 3. Contact angles Θ_0 , Θ_U , Θ_W , (degree) and time t_U (second) for different red maple samples and liquids.

Wood samples	Liquid	Θ_0	Θ_U	Θ_W	t_U
Untreated	Water	38.5	12.5	13.2	41.5
2% CCA-treated	Water	73.0	64.0	66.8	71.0
Untreated	Glycerol	67.0	45.1	49.4	80.0
Water-extracted	Glycerol	98.0	70.0	82.4	114.0
2% CCA-treated	Glycerol	93.3	79.3	85.8	110.0
Untreated	PF	82.5	79.0	80.5	90.0
Water-extracted	PF	123.0	111.0	119.9	143.0
2% CCA-treated	PF	133.0	118.0	130.1	270.0

values for wood surfaces, using water, glycerol, and PF adhesive, are presented in Table 3. Contact angles vary with the liquid and treatment of the wood. For the PF adhesive, θ_U for CCA-treated wood was 270 seconds compared to 90 seconds for untreated wood, and 143 seconds for water-treated wood. The wetting of CCA-treated wood with PF adhesive was 3 times slower than with untreated wood. The similar trend was noticed with water and glycerol as well.

When the contact angle, θ , is less than 90° , the interfacial energy γ_{SL} should be lower than the surface tension of solid γ_S , indicating good wettability (Harvey 1962). This is true for wetting of untreated wood surface by PF adhesive. But, for both water-treated and CCA-treated wood, θ was more than 90° , i.e., γ_{SL} was higher than γ_S , indicating poor wetting of both water-treated and CCA-treated wood surface by PF adhesive. This may be explained by the rough surface created by the raised grain of wood or/and extractive migration on

surface after water or CCA treatment (Maldas and Kamdem 1998).

Dispersion (γ^D_s) and polar (γ^P_s) surface tension components

With known values of γ_L , γ^d_L and γ^p_L for water, ethylene glycol and glycerol (Table 2) and the corresponding contact angles γ_S , γ^d_S and γ^p_S for wood surfaces were calculated. Surface tension components for wood samples based on two pairs of liquids (i.e., water-ethylene glycol, water-glycerol) using geometric-mean Eq. (2) and harmonic-mean Eq. (3) are presented in Table 4 along with the reported values for different woods species from the literature. It is evident from Table 4 that the water-ethylene glycol combination gave very good agreement between γ_S values calculated by using geometric- and harmonic-mean models. On the other hand, the water-glycerol results are difficult to interpret, in most cases. Even though dispersion and polar components

TABLE 4. Dispersion and polar surface tension components (mJ/m^2) of maple wood calculated from geometric-mean and harmonic-mean models.

Wood samples	Liquid pair	Geometric-mean			Harmonic-mean		
		γ_S	γ^d_S	γ^p_S	γ_S	γ^d_S	γ^p_S
Untreated ^a	Water-Ethylene glycol	76.6	3.9	72.7	68.7	14.9	53.8
Water-extracted ^a	Water-Ethylene glycol	69.5	5.8	63.7	64.7	15.7	49.0
2% CCA-treated ^a	Water-Ethylene glycol	46.9	19.0	27.9	49.1	19.5	29.6
Untreated ^a	Water-glycerol	93.3	0.1	93.2	77.1	7.6	69.5
2% CCA-treated ^a	Water-glycerol	69.5	0.1	69.4	58.9	2.5	56.4
Untreated ^b	Water-Ethylene glycol	64.9	8.8	56.1	61.0	20.1	40.9
Untreated ^b	Water-glycerol	66.2	4.7	61.5	59.5	15.9	43.6

^a Mean contact angles measured at 15, 30 and 60 seconds for red maple.

^b Hard maple (Gardner 1996).

TABLE 5. Comparison of acid-base^a, dispersion^b and polar^b surface tension components (mJ/m²) of red maple.

Wood sample	Acid-base					Geometric-mean			Harmonic-mean		
	γ^T_s	γ^{LW}_s	γ^{AB}_s	γ^+_s	γ^-_s	γ^T_s	γ^d_s	γ^p_s	γ^T_s	γ^d_s	γ^p_s
Untreated	47.65	45.51	2.14	0.02	57.01	76.6	3.9	72.7	68.7	14.9	53.8
CCA-treated	52.96	50.8	2.16	0.05	23.38	46.9	19.0	27.9	49.1	19.5	29.6

^a For water-ethylene glycol-diiodomethane.

^b For water-ethylene glycol.

vary for water-ethylene glycol, they follow a consistent and similar trend for untreated and treated woods. Both geometric-mean (GM)- and harmonic-mean (HM) models show that both water and CCA treatments reduce the γ_s and γ^p_s of the wood, while the reverse is true for γ^d_s . The value of γ_s reported in the literature for untreated maple using GM model is 64.9 mJ/m² for water-ethylene glycol (WEG) and 66.2 mJ/m² from water-glycerol (WG) (Gardner 1996). With the HM model, 61.0 mJ/m² was obtained for WEG and 59.5 mJ/m² with WG. For untreated red maple using GM model, γ_s is 76.6 for WEG and 93.3 mJ/m² for WG. With the HM model, γ_s decreases to 68.7 mJ/m² for WEG and to 77.1 mJ/m² for WG (Table 4). The variability of γ_s with the liquid used and the models GM vs. HM is difficult to explain. However, Wu (1982) suggested that the harmonic-mean equation is preferred between low-energy materials (e.g., wood, polymers, organic liquids and water), whereas the geometric-mean equation is preferred between low- and high-energy materials (e.g., mercury, silica and metal oxides). Still to date, there are no independent methods for evaluating absolute value of surface tension components. Thus, no independent check is possible (Nguyen and Johns 1978).

Lifshitz-van der Waal (γ^{LW}_s), acid (γ^+_s), and base (γ^-_s) surface tension components

Table 5 contains the total surface energy γ^T_s , the Lifshitz-van der Waal γ^{LW}_s , the acid-base γ^{AB}_s , and the acid or electron accepting γ^+_s , and the base or electron donating γ^-_s components computed using Eq. (4). For comparison, the total solid surface energy γ^T_s , the dispersion γ^d_s , and the polar γ^p_s components

calculated using Eqs. (2&3) for GM or HM models are also listed in Table 5.

γ^T_s and the Lifshitz-van der Waal (γ^{LW}_s) components of surface tension of red maple wood increase due to CCA-treatment. The acid-base (γ^{AB}_s) and acid (γ^+_s) components of surface tension after CCA treatment was not different from those of untreated wood. The base component γ^-_s after CCA treatment decreases from 57.01 mJ/m² to 23.38 mJ/m². From the acid-base standpoint, CCA treatment on red maple results in an increase of the Lifshitz van der Waals or apolar contribution from 45.51 to 50.8 and a decrease in base or electron donating surface property. Zhang et al. (1997) also reported a decrease in γ^-_s and increase in γ^{LW}_s after CCA treatment of southern pine.

The polar (γ^p_s) components of surface tension also decreases from 72.7 to 27.9 for GM model and from 53.8 to 29.6 for HM as well as the dispersion component. The total surface tension γ^T_s obtained by GM and HM were reduced after CCA treatment while the acid-base method yield higher γ^T_s for CCA-treated red maple wood. It is difficult to judge which of the three methods gives good prediction of surface tension. As the acid-base property of wood surface is often considered as an important characteristic in predicting adhesion performance, Lifshitz-van der Waal/acid-base approach may be a preferred choice for comparing the surface tensions between treated and untreated red maple.

CONCLUSIONS

Higher contact angle and longer time to reach equilibrium angle for PF adhesive on the CCA-treated wood compared to those of un-

treated wood indicated poor wettability of the wood surface. The wood surfaces became hydrophobic after CCA and water treatment. The surface tension components of untreated- and CCA-treated wood were in excellent agreement with the published results of other wood species. The critical surface tensions of untreated and treated wood samples did not differ much. Total surface tension (γ_s^T) obtained by both geometric- and harmonic mean methods for CCA-treated wood is lower compared to untreated wood. But, total surface tension (γ_s^T) obtained by acid-base method for CCA-treated wood is higher compared to untreated wood.

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