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RESEARCH ARTICLE

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Surface energy of preservative-treated southern yellow pine (*Pinus* spp.) by contact angle measurement

Abstract In this study, the contact angles of four different reference liquids (including distilled water, diiodomethane, formadide and glycerol) formed on the surfaces of wood, treated with chromated copper arsenate (CCA) and two other emerging copper-based water-borne systems (commercial names: NW and NS) were measured with sessile drop method. Based on the contact angle data, the surface energy was obtained from the acid-base approach. The total surface energy consisted of Lifshiz-van der Waals parameter and acid-base parameter. Results showed that the NW and CCA treatments made the wood surface more hydrophobic while the NS treatment had the reverse effect on the wood surface mainly owing to the increased penetration of earlywood. By using three liquids, diiodomethane, formamide and distilled water, the total surface energy obtained for untreated earlywood, untreated latewood, CCA-treated earlywood, CCA-treated latewood, NW-treated earlywood, NW-treated latewood, NS-treated earlywood and NS-treated latewood were 43.1, 44.5, 43.4, 45.1, 49.4, 40.6, 46.0 and 40.9 mJ/m^2, respectively. The surface energy of CCA-treated wood was almost the same as untreated wood. After NW and NS treatments, the surface energy of both earlywood and latewood changed a little. However, the change was not so obvious as to draw any further conclusion concerning the influence of NW and NS treatments on the surface energy of wood.

Keywords wood, surface energy, preservative, contact angle, acid-base approach

1 Introduction

It is widely recognized that the wettability and surface free energy of wood are useful parameters which provide information on the interaction between adhesives or coating materials and the wood surface (Gunnells et al., 1994; Nylund et al., 1998; de Meijer et al., 2000; Walinder, 2000). One of the most common approaches to determine the wettability and surface energy of solids is the contact angle technique. To measure the contact angle between liquids and wood surfaces, three methods have been applied, which include the sessile drop method, the rising height method and the Wilhelmy method (Pétrissans et al., 2003). Among these methods, the sessile drop method using advancing contact angles is the most traditional and is extremely suited to investigations on wood.

Chromated copper arsenate (CCA) has been used as a wood preservative for about 70 years. Recently, it was phased out from the residential markets in many countries, owing to the potential threat of arsenic to human health, and the lack of a satisfactory method to recycle waste CCA-treated lumbers even now. As substitutes to CCA, some copper-based waterborne preservatives such as NW and NS were developed. These preservatives are different from CCA in chemical structure, which may result in different surface properties. Several investigations have been done on the surface properties of CCA-treated wood (Zhang et al., 1997; Maldas and Kamdem, 1998a, 1998b), but up to now, there is no research concerning the surface energy of wood treated with these emerging wood preservative systems. This study investigates the effect of CCA, NW and NS treatments on the surface energy of wood.

2 Materials and methods

2.1 Materials

The untreated wood, the CCA, NW and the NS-treated southern yellow pine (*Pinus* spp.) are all provided by Osmose Inc. in Buffalo, U. S. A. These lumbers are from the same forest

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source. According to the data provided by the company, the theoretical retention of CCA, NW and NS treated lumbers are 0.40, 0.25 and 0.20 pcf, respectively. Twelve samples with a dimension of 60(L) mm × 40(R) mm × 6(T) mm were cut from each group of untreated and treated lumbers. The samples were conditioned at 20°C and 65% relative humidity to an average equilibrium moisture content of $10 \pm 2\%$.

The reference liquids used in this study were distilled water, formamide (99.5%, A. C. S. Reagent, Aldrich Chemical Co.), Diiodomethane (>98%, GC, Fluka Chemie AG CH-9471 Buchs) and glycerol (95% Analytical Reagent, Mallinckrodt chemical works). Their surface tensions and surface energy components are shown in Table 1.

Table 1 Surface tension components (mJ/m^2) of liquids used for contact angle measurements (Kaeble, 1971; Wu et al., 1995)

Liquids	γ_L	γ_L^d	γ_L^P	γ_L^{LW}	γ_L^{AB}	γ_L^+	γ_L^-
Diiodomethane	50.8	50.8	0	50.8	0	0	0
Distilled water	72.8	21.8	51.0	21.8	51.0	25.5	25.5
Formamide	58.0	39.0	19.0	39.0	19.0	2.28	39.6
Glycerol	64.0	34.0	30.0	34.0	30.0	3.92	57.4

2.2 Contact angle measurement

The contact angles of different liquids on the radial surfaces of the untreated, CCA, NW and NS treated southern yellow pine were measured by the sessile drop method. The equipment used in this study is VCA 2000 system from AST Inc. (Fig. 1). The sample was rested on a stand with adjustable height and inclination. A droplet of 5 μL of water was placed on the surface of the specimen with a syringe. The grain of the sample is perpendicular to the axe of goniometer-microscope tube. There is a distinct boundary between the earlywood and latewood of the southern yellow pine, and the region of both the earlywood and latewood is relatively broad. As a result, it is possible to measure the contact angles on earlywood and latewood separately. For each liquid, at least three measurements were taken for both earlywood and latewood. If the deviation was very significant, up to eight measurements were taken and the average of these values was used as the final result. The wetting of liquids on wood surfaces is a time-dependent process. The contact angles were traced to form a contact angle-time curve. The time interval between each measurement was estimated as 1 s. The initial contact angle θ_0, which is the contact angle at the beginning of the wetting process, was determined by extrapolating the contact angle-time curve to $t = 0$. This value was used in the calculation of surface energy.

2.3 Calculation of surface energy

Surface energy was calculated according to both geometric mean approach, which is a two liquid method, and a three liquid method—acid-base approach.

In geometric mean method, the surface free energy γ is considered as a sum of a dispersion component γ^d and a polar component γ^p as:

$$\gamma = \gamma^d + \gamma^p \tag{1}$$

The interfacial energy γ_{SL} between a liquid and a solid polymer can be evaluated by the following equation (Girifalco and Good, 1957):

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\left(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}\right) \tag{2}$$

where γ_S is the surface tension of solid (mJ/m^2), and γ_L the surface tension of liquid (mJ/m^2).

The relationship between the surface tension of solid, air and liquid was expressed in Young's equation (Harvey, 1962):

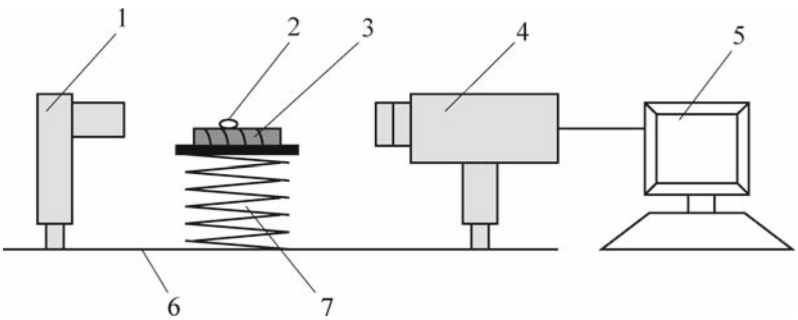
$$\cos\theta = (\gamma_S - \gamma_{SL}) / \gamma_L \tag{3}$$

Combining Eq. (1) and Eq. (2),

$$(1 + \cos\theta)\gamma_L = 2\left(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}\right) \tag{4}$$

In acid-base theory, γ is subdivided into two additive components, one apolar and the other involving acid-base interactions as:

$$\gamma = \gamma^{LW} + \gamma^{AB} \tag{5}$$



1: light source; 2: liquid drop; 3: sample; 4: camera; 5: computer; 6: slideway; 7: movable table.

Fig. 1 Equipment for contact angle measurement

The Young's equation was rewritten into Eq. (6) (van Oss et al., 1988):

$$(1+\cos\theta)\gamma_{\mathrm{L}} = 2\left(\sqrt{\gamma_{\mathrm{S}}^{\mathrm{LW}}\gamma_{\mathrm{L}}^{\mathrm{LW}}}+\sqrt{\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{L}}^{-}}+\sqrt{\gamma_{\mathrm{S}}^{-}\gamma_{\mathrm{L}}^{+}}\right) \qquad (6)$$

where LW represents the apolar electrodynamic Lifshitz-van der Waals interactions, comprising the dispersion (London), orientation (Keesom) and the induction (Debye) interactions in the condensed state. The polar interactions under consideration are of the hydrogen-bonding type and can, in the largest sense, be designated as (Lewis) acid-base (AB) or electron-acceptor/electron-donor interactions. γ^+ is the electron-acceptor constituent, and γ^- is the electron-donor constituent in the polar component (γ^{AB}). There is a relationship between them:

$$\gamma^{\mathrm{AB}} = 2\sqrt{\gamma^{+}\gamma^{-}} \qquad (7)$$

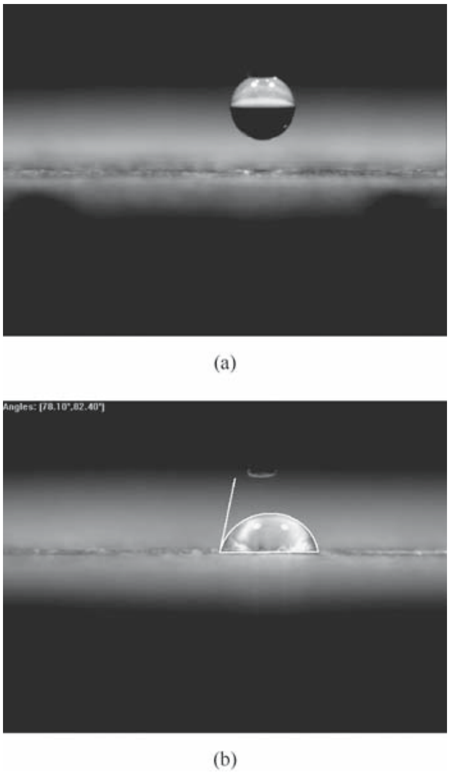
The surface energy of the different surfaces was calculated from the contact angles of two liquids by using Eq. (4) or from the contact angles of three liquids by using Eq. (6) and Eq. (7).

3 Results and discussion

3.1 Contact angles and absorption rate

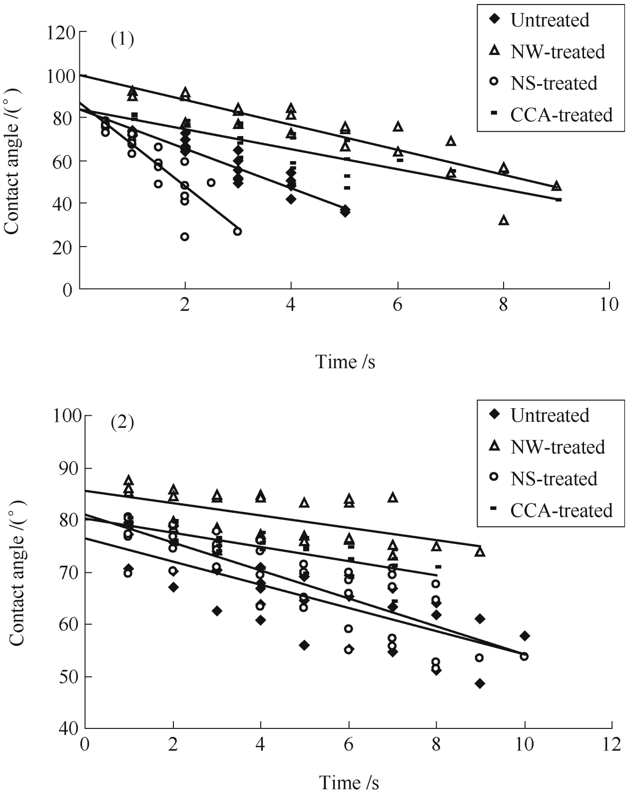
The images in Fig. 2 show the measured contact angles before and after the liquid drop contacts the surface of the sample. The data of contact angles for both sides can be obtained by the system, as we can see in the left side of Fig. 2(b). The time-dependent contact angles of distilled water on the radial surface of untreated, CCA, NW and NS-treated southern yellow pine were shown in Fig. 3. As shown in this Figure, there was a big difference between the $\theta-t$ curves of earlywood and latewood, as well as between the untreated wood and the wood treated by a different preservative. The initial contact angles as well as the slope of the curve, which denoted the absorption rate of distilled water into wood, changed with the treatment method and the wood type, i.e. earlywood/latewood.

The slope of the curve and the initial contact angles of distilled water are clearly shown in Fig. 4. A higher slope value means a faster liquid penetration into wood. As shown in Fig. 4(1), the absorption rate of earlywood is much higher than that of latewood, for all untreated and treated samples. The absorption rate of NS-treated earlywood is extremely high. The effect of different treatments varies a lot. For CCA and NW treatments, the absorption rates of distilled water are slightly lower than untreated control for both earlywood and latewood. For NS treatment, there is little difference on the absorption rate of latewood, but the absorption rate of treated earlywood is much higher than untreated earlywood.



(a) Before the liquid drop contacts the surface of the sample; (b) After contact with the surface of the sample.

Fig. 2 Images showing contact angle measurement



(1) earlywood; (2) latewood.

Fig. 3 Time-dependent contact angle of untreated and preservative-treated southern yellow pine (*Pinus* spp.) with distilled water

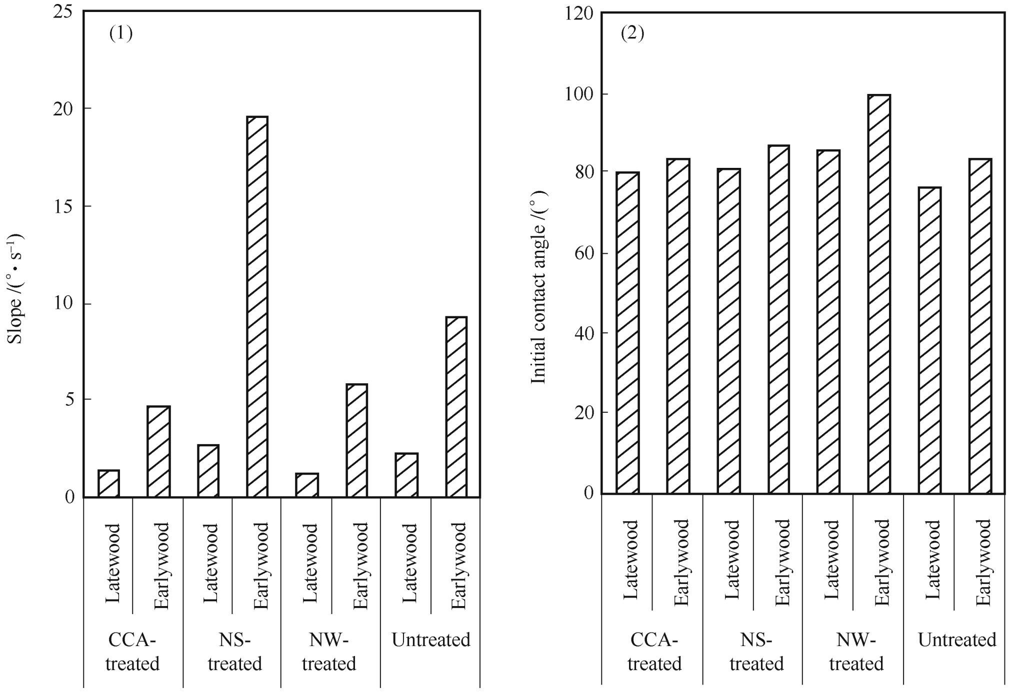


Fig. 4 Slope of time-dependent contact angle curve and the initial contact angle of distilled water on untreated and preservative treated southern yellow pine (*Pinus* spp.) surfaces

The initial contact angles of earlywood are all higher than those of latewood, as illustrated in Fig. 4(2). It suggests that at the beginning of the wetting process earlywood is more hydrophobic than latewood. However, due to the porous character of wood surfaces, wetting is often accompanied by liquid penetration. As a result, both the absorption rate of liquid and the initial contact angle should be the criteria to compare which surface is more hydrophobic or hydrophilic. In earlywood, the size of the pores (mostly tracheids, in this case) is much bigger than in latewood. Although the initial contact angles are higher for earlywood, the liquid penetration on earlywood surface is much faster, which makes the contact angles decrease faster with time.

After preservative treatments, the initial contact angles for both earlywood and latewood increased to a certain degree compared to the untreated control. The change on initial contact angles is most notable after NW treatment, and then after NS treatment and CCA treatment. Because the absorption rates of distilled water on CCA and NW treated wood surfaces are also slower than untreated control, the conclusion can be drawn that CCA and NW treated wood surfaces are more hydrophobic than untreated wood surfaces. However, NS treatment accelerated the water penetration significantly, but only slightly increased the initial contact angle. Consequently, it can be considered that the NS-treated wood surface became more hydrophilic than the untreated wood surface.

The initial contact angles of other reference liquids on untreated, NW, NS and CCA-treated wood surfaces were all obtained by the same method. The result was listed in Table 2. The contact angles varied with the liquids applied due to their different chemical properties. The structures of water, formamide and diiodomethane are H_2O, $HCONH_2$ and CH_2I_2, respectively. The chemical groups presented in these liquids may also exist on wood surface. According to Shen et al. (1998), the surface of pine wood is mainly rich in C–O, CH_2 and C=O groups. Therefore, by using the contact angle data of different liquids, the surface energy of wood can be determined.

Table 2 Initial contact angles (contact angle at the beginning of wetting) of different reference liquids on the tangential surfaces of untreated and preservative-treated southern yellow pine (*Pinus* spp.) (°)

Sample		Distilled water	Formamide	Diiodomethane	Glycerol
Untreated	Earlywood	83.7	27.3	36.3	90.7
	Latewood	76.4	34.1	39.2	83.0
NW-treated	Earlywood	99.4	50.3	24.7	90.0
	Latewood	85.6	49.3	41.7	89.6
NS-treated	Earlywood	86.8	49.3	27.9	100.2
	Latewood	81.0	59.9	37.5	90.6
CCA-treated	Earlywood	83.5	40.8	35.3	81.3
	Latewood	80.1	45.1	34.7	85.6

3.2 Surface energy of untreated and preservative-treated wood

By using Eq. (6) and Eq. (7), the surface energy and surface tension components were calculated from acid-base approach.

According to reference, the liquid group of diiodomethane, distilled water and formamide could present the most accurate result. The results are listed in Table 3. As shown in this table, the total surface energy of untreated and treated earlywood or latewood ranges within 40–50 mJ/m^2, and it is mainly contributed to the LW component, which agrees well with the results obtained in the previous measurements for wood (Shen et al., 1998). The total surface energy and the surface tension components of CCA-treated wood are almost the same as untreated wood, suggesting that CCA treatment has little effect on the surface energy of wood. After NW and NS treatments, some change was noted, that is, the surface energy increased for earlywood and decreased for latewood, although the average value for the whole wood keeps almost the same as the untreated wood.

Table 3 Surface tension components (mJ/m^2) of untreated and treated southern yellow pine (*Pinus* spp.) from acid-base model (reference liquids: diiodomethane, distilled water, formamide)

Samples		γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S^T
Untreated	Earlywood	41.43	5.77	0.13	1.70	43.13
	Latewood	40.02	3.45	1.44	4.47	44.48
NW-treated	Earlywood	46.25	1.30	1.96	3.19	49.44
	Latewood	38.73	1.59	0.55	1.88	40.61
NS-treated	Earlywood	45.08	0.65	0.35	0.95	46.03
	Latewood	40.87	0.00	5.89	0.02	40.89
CCA-treated	Earlywood	41.89	2.43	0.23	1.51	43.40
	Latewood	42.15	1.20	1.81	2.95	45.10

Note: $\gamma_S^T = \gamma_S^{LW} + \gamma_S^{AB}$

By using geometry-mean method and selecting diiodomethane and distilled water as the reference liquid pair, similar result was obtained, as shown in Table 4. Although the surface energy of NW and NS-treated earlywood and latewood both changed a little, the change was not so obvious as to draw any further conclusion concerning the influence of NW and NS treatments on the surface energy of wood.

Table 4 Dispersion (γ_S^d) and polar (γ_S^P) surface tension components (mJ/m^2) of untreated and treated southern yellow pine (*Pinus* spp.) from geometric-mean model (reference liquid pair: diiodomethane and distilled water)

Samples		γ_S^d	γ_S^P	γ_S^T
Untreated	Earlywood	41.43	2.10	43.53
	Latewood	40.02	4.68	44.70
NW-treated	Earlywood	46.25	0.03	46.28
	Latewood	38.73	2.01	40.74
NS-treated	Earlywood	45.08	0.98	46.06
	Latewood	40.87	2.93	43.80
CCA-treated	Earlywood	41.89	2.08	43.97
	Latewood	42.15	2.98	45.13

4 Conclusions

Judging from both the initial contact angle and the penetration rate of distilled water on untreated and preservative-treated wood, the NW and CCA treatments make the wood surface more hydrophobic while the NS treatment has a reverse effect; The surface energy and its components changed marginally after CCA treatment, but there is some change on both earlywood and latewood of NW and NS-treated wood. However, the change is not so obvious as to draw any further conclusion concerning the influence of NW and NS treatments on the surface energy of wood.

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