Wood wetting with various liquids

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Abstract: *Wood wetting with various liquids*. Wood wetting with standard liquids is a complex process controlled by chemical composition of the liquids used, properties of the substrate, interactions among unsaturated force fields across the phase boundary between wood and liquid as well as by secondary effects of a range of factors implied by specific properties of the wood and the liquids used. The results suggest that both disperse and polar components of the wood surface free energy are necessary to quantify separately. The $\gamma_{SV}{}^{d}$ values have been found properly determined at the phase boundary between wood with α-bromonaphtalene and between wood and diiodomethane; the $\gamma_{SV}{}^{p}$ values at the phase boundary between wood and apolar-polar liquids with the polar component bigger than the polar component of wood. In our case, such liquid was water. Thus, the wood surface free energy values γ_{SV} representing the sum of the disperse and polar component $\gamma_{SV}{}^{d}$ and $\gamma_{SV}{}^{p}$, respectively, determined as described in this paragraph are higher than the wood surface free energy values determined with one liquid only.

Keywords: wetting, apolar liquids, apolar-polar liquids, contact angle, surface free energy, beech wood

INTRODUCTION

Wetting of wood surface with liquids has the decisive role for adhesion of liquid and solid materials to the wood. This is important for gluing, surface treatment and modification of wood.

The capacity of a liquid to wet the surface of a solid is assessed through the size of the contact angle between the two materials. The values of contact angle measured at the phase boundary with a liquid standard provide the base for determining the thermodynamic characteristics of the wood surface –surface free energy and its components.

As liquid standards perform liquids constrained in wood surface wetting, that means apolar and apolar-polar liquids showing additive properties for surface free energy. The differences in the chemical composition of these liquids affect the origin and character of their phase boundary with wood. These differences are manifested through different values of surface free energy and its components.

The main subject of the papers published in the recent 15 years has been the measurement of surface free energy of wood γ_{SV}, its components – disperse and polar: $\gamma_{SV}{}^{d}$ and $\gamma_{SV}{}^{p}$, Lifshitz van der Waals component $\gamma_{SV}{}^{LW}$ and Lewis acid-base component $\gamma_{SV}{}^{AB}$. These methods also use experimentally measured values of the contact angle at the phase boundary between wood and liquid standards. In general, there are used parallel three liquids differing in their surface free energy. The contact angle is measured at the beginning of wetting process. The time interval for all the simultaneously used liquids is always the same, not considering differences in their chemical and physical properties. The most frequently used liquid standards are α-brom-naphtalene, diiodomethane, formamide, ethylene glycol, glycerine and water (GARDNER 1996, ZHANG *et al.*. 1997, GINDL *et al.* 2001, GINDL and TSCHEGG 2002, BLANCHARD *et al.* 2009, PIAO *et al.* 2010 and other). These liquids are apolar or apolar-polar, with additive ptoperties of surface free energy. The wood wetting with these liquids is constrained.

LIPTÁKOVÁ and KÚDELA (1994) calculated surface free energy based on the contact angle θ_{w} associated with an ideally smooth surface. The values of this contact angle are generally smaller than the values of the contact angle θ_{0} occurring at the beginning of the wetting process.

This results in higher values of surface free energy and its polar share for θ_w. We propose this angle as more fitting for calculation of thermodynamic characteristics expressing interactions at the phase boundary between wood and liquid or solid substances. However, neither this method has been accepted without doubts (SUNGUO and JOHANSSON 1996, PIAO *et al*. 2010).

Summarising the results, there were found differences in contact angle values and free energy values for the same material between the authors. There should be, however, no differences in surface free energy values.

The aim of our work was to analyse the wetting process in selected wood species, with using liquids of diverse polarity – currently used for determining surface free energy of wood and the components of this energy.

MATERIAL AND METHODS

The experimental works were performed with beech wood specimens, $15 \times 15 \times 15$ mm in size. The wetting of specimens was studied on their radial and tangential surfaces treated with microtome. The wood surfaces obtained in this way only depend on the wood anatomical structure (KÚDELA and LIPTÁKOVÁ 2006).
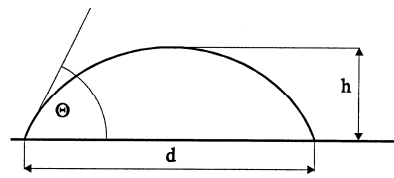

Fig. 1 Parameters of a sessile drop

The specimens pre-treated in this way were placed into a conditioning box, and then acclimated to a 12% moisture content. The moisture content in the specimens was measured gravimetrically before the wetting process itself. For the calculation of contact angle were used the results adapted from ŠTRBOVÁ *et al*. (2013): parameters (diameter and height) of a sessile drop applied onto wood surface – Fig. 1. The wood wetting process was studied with using an analyser DSA30 Standard with the attached programme package. The wood wetting liquids were five (Table 1).

Tab.. 1 Parameters of liquid standards used in study.

Testing liquid	γ [mJ·m^{-2}]	γ^d [mJ·m^{-2}]	γ^p [mJ·m^{-2}]	γ^+ [mJ·m^{-2}]	γ^- [mJ·m^{-2}]	η [Pa·s]
Water	72.80	21.80	51.00	25.50	25.50	0.010
Ethylene glycol	48.00	29.00	19.00	1.92	47.00	0.210
Formamide	58.00	39.00	19.00	2.28	39.60	0.038
α-Bromonaphtalene	44.00	44.00	0.00	0.00	0.00	0.050
Diiodomethane	50.80	50.80	0.00	0.00	0.00	0.028

The equilibrium state in the wetting process was identified according to LIPTÁKOVÁ and KÚDELA (1994) who assign it to the moment when the liquid stops spreading onto the surface and starts receding. This moment can be determined through the drop diameter – d. We considered the contact angle determined in this way as the equilibrium one and the basic one for further calculations.

For applying the liquid onto the specimen surface we used a dosing applicator (injection syringe). The amounts applied were 0.0018 ml each. The varying drop shape was observed in the fibre direction, onto the tangential and radial surface, from the moment of application to the complete soaking into the substrate. The drop image was scanned with a camera and transmitted onto a monitor. The measuring results were automatically assembled in a computer.

The values of contact angle θ_w determined form the wood wetting with one liquid were used for calculation of surface free energy according to the modified equation proposed by NEUMANN *et al*. (1974)

$$\cos\theta = \frac{(0{,}0137 \cdot \gamma_S - 2{,}00) \cdot \sqrt{\gamma_S \cdot \gamma_L} + \gamma_L}{\gamma_L \cdot (0{,}015 \cdot \sqrt{\gamma_S \cdot \gamma_L} - 1)} \quad . \tag{1}$$

The disperse and polar component $\gamma_S{}^d$ and $\gamma_S{}^p$ were calculated according to KLOUBEK (1974), by solving the equations

$$\sqrt{\gamma_S{}^d} = \sqrt{\gamma_L{}^d} \cdot (\frac{1+\cos\theta}{2}) \pm \sqrt{\gamma_L{}^p} \cdot \sqrt{\frac{\gamma_S}{\gamma_L} - (\frac{1+\cos\theta}{2})^2} \qquad (2)$$

$$\sqrt{\gamma_S{}^P} = \sqrt{\gamma_L{}^P}(\frac{1+\cos\theta}{2}) \mp \sqrt{\gamma_L{}^d} \cdot \sqrt{\frac{\gamma_S}{\gamma_L} - (\frac{1+\cos\theta}{2})^2} . \qquad . \qquad (3)$$

RESULTS AND DISCUSSION

During the wetting of beech wood surface with apolar and apolar-polar liquids, the contact angle was always subjected to permanent changes with time. For all the testing liquids used, the study of drop diameter confirmed to earlier observations that the drop diameter augments until a certain moment and then diminishes gradually. This means that the advancing contact angle switched to the receding in all cases. In the preceding text (see p.3) we defined this moment as the equilibrium state. There occurred differences in the time t_u, necessary to reach the equilibrium state as well as differences in the values of contact angles θ_0, θ_u, θ_w. The values of „equilibrium" time (t_u) were different for different liquids (Table 2). It is evident that the time t_u depends on the liquid's polarity. In apolar liquids, the time t_u was shorter in α-bromonaphtalene.

Tab. 2 Basic statistical characteristics of time t_u values for various liquids

Liquid	Radial surface			Tangential surface		
	Basic stat. characteristic t_u					
	x[s]	s[s]	v[%]	x[s]	s[s]	v[%]
Water	65.7	25.3	38.5	72.0	27.8	38.7
Ethylene glycol	9.9	14.6	148.1	11.4	16.1	140.3
Formamide	3.5	4.9	139.6	3.5	5.0	144.6
α-Bromonaphtalene	0.8	1.0	129.6	0.8	1.2	146.2
Diiodomethane	8.8	12.3	139.7	8.9	10.1	113.4

In liquids displaying apolar-polar properties (water, ethylene glycol, formamide), the time t_u increased with increasing polar component of surface free energy of the liquids. On the other hand, the results obtained with ethylene glycol show also an impact of viscosity – substantially higher in this liquid than in the other tested ones.

We deduce that the differences in performance among the liquids reflect the differences in their surface free energy and viscosity. Our method for determining the equilibrium contact angle θ_u, however, can ensure elimination of viscosity influence in liquids.

The variability of t_u values in frame of the same liquid was the result of the composition unevenness of wood surface and the random location of the drop onto the surface. This is true equally for radial and tangential surfaces. This high variability caused that there was no significant difference in t_u values between the radial and the tangential surfaces.

The different performance of liquids at their phase boundary with wood was also reflected in the values of contact angles θ_0, θ_u and θ_w (Table 3). The highest contact angle θ_0 values at the moment of the drop application were measured in case of redistilled water, the lowest ones in the case of α-Bromonaphtalene. There were not big differences among the other liquids.

At the moment of the drop application onto the surface, there are two different phases (wood substance and air) with different surface energies beneath the drop. In this case, the values of θ_0 were the results of interactions at the phase boundary between wood and water, the morphological and chemical properties of wood surface; while θ_w values only depend on the chemical properties of the substrate (LIPTÁKOVÁ et al. 1998, 2000).

Further we determined the surface free energy and its components. Table 4 displays average values of these items. The surface free energy values varied in quantity and quality, according to the liquid the value was determined with. The results assembled in Table 4 show that the surface free energy values of wood do not only depend on the wood surface properties but also on the chemical structure of the liquid standard used. The differences are rather big, being in contradiction with the surface free energy conception as a material constant of substances.

Tab. 3 Average values of contact angles Θ_0, Θ_u and Θ_w at the phase boundary wood – liquid

Liquid	Radial surface			Tangential surface		
	Θ_0	Θ_u	Θ_w	Θ_0	Θ_u	Θ_w
	[°]					
Water	70.0	20.1	23.9	68.2	16.5	19.7
Ethylene glycol	34.0	11.9	12.4	35.7	10.7	11.4
Formamide	31.6	15.4	15.8	36.2	12.5	13.2
α-Bromonaphtalene	15.6	13.4	13.5	13.7	12.1	12.1
Diiodomethane	38.5	37.9	38.0	40.9	40.5	40.6

Tab. 4 Average values of surface free energy values and its components in beech wood

Liquid	Radial surface			Tangential surface		
	γ_s	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p
	[mJm-2]					
Water	68.0	30.8	37.2	69.6	29.8	39.8
Ethylene glycol	46.4	29.0	17.4	46.8	29.0	17.8
Formamide	55.6	39.3	16.3	56.2	39.3	17.0
α-Bromonaphtalene	42.6	42.6	0.0	42.9	42.9	0.0
Diiodomethane	41.3	40.5	0.8	40.1	39.2	0.9

The surface free energy determined with using apolar liquids (α-Bromonaphtalene and Diiodomethane), was the lowest, practically the same as their disperse component, with the polar component nearly zero. Apolar liquids with disperse component bigger than the disperse component of wood are suitable for determining only the disperse share of the surface free energy of wood.

To determine the polar share of surface free energy of wood, there are needed liquids whose surface free energy shows additive properties. The differences between the values γ_{LV}^p (Table 1) and the determined values γ_{SV}^p (Table 4) allow us to conclude that crucial values for determining the polar share of surface free energy of wood are the values obtained with water.

The results also imply that the surface free energy of wood cannot be determined completely with using one single liquid from the ones discussed in this paper. The disperse and the polar share of the surface free energy of wood are possible to determine separately with using appropriate an apolar and an apolar-polar standards.

The surface free energy of materials represents the sum of its disperse and polar shares, consequently, the surface free energy of the studied surfaces is higher that the energy obtained with using one liquid only.

The surface free energy values γ_{SV} and the values of its disperse and polar components γ_{SV}^d and γ_{SV}^p obtained in this way are higher than the values reported in the literature. This is due to the liquid used as well as due to the methods used for determining the equilibrium contact angle.

Our results show that the values of surface free energy of wood γ_{SV} as well as the values of its disperse and polar components γ_{SV}^d and γ_{SV}^p are in general higher than it has been supposed until now – in the case when the disperse component of wood is determined with using apolar liquids with their disperse component higher than the disperse component of wood and the polar component of wood is determined with using apolar-polar liquids with their polar component higher than the polar share of wood expected. Consequently, there also

will occur stronger cohesion in wood and stronger adhesion at the phase boundary between the wood and liquid or solid materials. This fact, however, will not have a decisive influence on the relations between wood and these materials, including coating materials and glues described in (LIPTÁKOVÁ *et al.* 2000, LIPTÁKOVÁ and KÚDELA 2002, PROSZYK *et al.* 1997, KÚDELA and LIPTÁKOVÁ 2006, PECINA and PAPRZYCKI 1995 and others).

CONCLUSION

Our results have confirmed that the wood wetting with standard liquids depends on the chemical structure of the liquids used, on the properties of the substrate, on the interactions of unsaturated force fields at the phase boundary between wood and liquids and also on secondary effects of a large number of factors implied by the specific properties of wood and of the liquids used.

The currently used liquid standards for assessment of wood surface properties perform in a different way at the phase boundary with wood. The interactions of surface forces during wood wetting with apolar liquids are controlled by dispersion forces, that means by forces with apolar character. The equilibrium occurs at the beginning of the wetting process.

Apart from dispersion forces, at the phase boundary between wood and apolar-polar liquids, polar forces act too. Also in this case, the interaction among apolar forces occurs at the beginning of the wetting process, the polar forces, however, come into effects gradually. The equilibrium occurs at the time t_u, which is the time of the equilibrium contact angle θ_u. The contact angle θ_u and the derived value of the contact angle corresponding to the ideally smooth wood surface θ_w grow proportionally with growing polar share of the surface free energy γ_{LV}^p.

These results suggest that it is necessary to determine the disperse and the polar components of surface free energy of wood separately. For determining the values of γ_{SV}^d were found suitable the results obtained at the phase boundary between wood and α-Bromonaphtalene and Diiodomethane; for determining γ_{SV}^p, the results obtained at the phase boundary between wood and apolar-polar liquids with polar component bigger than the polar component of wood. In our case, such liquid was water. Thus, the surface free energy of wood γ_{SV} is the sum of the determined disperse and polar shares γ_{SV}^d and γ_{SV}^p.

LITERATURE

1. BLANCHARD V., BLANCHET P., RIEDL B. 2009: Surface energy modification by radiofrequency inductive and capacitive plasmas at low pressures on sugar maple: an exploratory study. Wood Fiber Sci. 41(3): 245–254.

2. GARDNER D. J. 1996: Application of the Lifshitz – van der Waals acid – base approach to determine wood surface tension components. Wood Fiber Sci., 28(4): 422–428.

3. GINDL M., SINN G., GINDL W., REITERER A., TSCHEGG S. 2001: A comparison of different methods to calculate the surface free energy of wood using contact angle measurements. Colloids and Surfaces. A: Physicochemical and Engineering Aspects, 181: 279–287.

4. GINDL M., TSCHEGG S. 2002: Significance of the acidity of wood to the surface free energy components of different wood species. Langmuir 18: 3209–3212.

5. KLOUBEK J. 1974: Calculation of surface free energy components of ice according to its wettability by water, chlorbenzene and carbon disulfide. J. Colloid Interface Sci., 46: 185–190.

6. KÚDELA J., LIPTÁKOVÁ E: 2006. Adhesion of coating materials to wood. J. Adhesion Sci. Technol., 20(8): 875–895.

7. LIPTÁKOVÁ E., KÚDELA J., BASTL Z., SPIROVOVÁ I. 1995: Influence of mechanical surface treatment of wood the wetting process. Holzforschung, 49(4): 369–375.

8. LIPTÁKOVÁ E., KÚDELA J. 1994: Analysis of the wood – wetting process. Holzforschung, 1994, 48(2): 139–144.

9. LIPTÁKOVÁ E., KÚDELA J. 2002: Study of the system wood – coating material. Part 2. Wood – solid coating material. Holzforschung, 56: 547–557.

10. LIPTÁKOVÁ E., KÚDELA J., SARVAŠ J. 1998: Problems concerning equilibrium state on the phase boundary wood liquid material. In: Wood structure and properties´98 (Eds. S. Kurjatko and J. Kúdela). Zvolen: Arbora Publishers, p. 109–114.

11. LIPTÁKOVÁ E., KÚDELA J., SARVAŠ J. 2000: Study of the system wood - coating material I. Wood – liquid coating material. Holzforschung, 54(2): 189–196.

12. NEUMANN A. W. et al. 1974: An equation of state approach to determine surface tensions of low- energy solids from contact angles. Colloid Interface Sci., 49(2): 291–303.

13. PECINA H., PAPRZYCKI O. 1995: Lack auf Holz. Hannover: Vinzentz Verlag, 175 p.

14. PIAO C., WINANDY J. E., SHUPE T. F. 2010: From hydrophilicity to hydrophobicity: a critical review: Part I. Wettability and surface behavior. Wood Fiber. Sci., 42(4): 490–510.

15. PROSZYK S., KRYSTOFIAK T., WINNIK A. 1997: Studies on adhesion to the wood of two component PVAC adhesives hardened with aluminium chloride. Folia Forestalia Polonica, Seria B. 28: 99–105.

16. SUNGUO W., JOHANSSON I. 1996: Evaluation of a polar and acid base properties of woodsurfaces by contact angle measurements. In: Modern adhesion theory applied on coating and gluing of wood. Stockholm: Forskarskolan Träoch Träfiber, p. 1–27.

17. ŠTRBOVÁ M., WESSERLE F., KÚDELA J. 2013: Contact Angle Measurement on Wood by Drop Shape Analysis. In: Science for Sustainability. Györ – Sopron: University of West Hungary, p. 16–22.

18. ZHANG H. J., GARDNER D. J., WANG J. Z., SHI Q. 1997: Surface tension, adhesive wettability and bondability of artificially weathered CCA treated southern pine. Forest Prod. J., 47(10): 69–72.

Streszczenie: *Zwilżalność drewna róznymi cieczami.* Zwilżanie drewna cieczami jest złożonym procesem związanym ze składem chemicznym cieczy, własnościami substratu, interakcjami pomiędzy układami sił na granicy faz oraz wieloma czynnikami związanymi z własnościami cieczy oraz podłoża. Praca przedstawia rozważania oraz wyniki eksperymentów zwilżalności drewna za pomocą róznych cieczy.

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