

WETTING OF WOOD SURFACE BY A LIQUIDS OF A DIFFERENT POLARITY¹⁾

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ABSTRACT

Wood wetting by 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.

This paper reports a study of the process of beech wood wetting by liquids differing in polarity. It has been proved that the liquid standards used in evaluation of wood surface properties change their behaviour at the phase boundary with wood, in accordance with the values of surface free energy and the values of its dispersion and polar components. There are differences in time required to reach the equilibrium state at the phase boundary with wood. The wood wetting process is also influenced by the wetting liquid viscosity.

It has been found that the dispersion component of wood surface free energy can be determined with the aid of α -bromonaphthalene, and the polar component γ_s^p with the aid of water. For the comprehensive evaluation of the surface free energy, one single liquid with the values γ_L , γ_L^d and γ_L^p higher than the expected values γ_S , γ_S^d and γ_S^p should satisfy. The total value of surface free energy γ_S of the tested beech wood specimens is the sum of γ_S^d and γ_S^p . In our case this sum was higher than the value accepted till now.

KEYWORDS: Wetting process, contact angle, surface free energy, beech wood, α -bromonaphthalene, formamide, water, ethylene glycol.

INTRODUCTION

The values of contact angle measured at the phase boundary between wood and liquid

1) This paper is devoted to the late Prof. Eva Liptáková who died on December 19, 2008 and would be 80 this year.

standard provide an issue point for the study of thermodynamic properties of wood surface. The values of this angle are used to calculate surface free energy and its components. The hitherto applied methods for calculation of surface free energy differ both in the mathematical apparatus used and in the number of liquids necessary for experimental analysis. The liquid standards commonly used are liquids wetting wood surface to a limited extent only. They can be either non-polar or non-polar-polar by nature, and their surface energy is additive. The differences in chemical structure of liquids influence the formation and character of the phase boundary with wood, and these differences are also reflected in different values of surface free energy and its components (Gindl 2002, Kúdela and Wesslerle 2013) .

The aim of this work was to study the wood wetting process by liquids with different polarities, currently used for determining surface free energy and its components. The primary focus has been set on analysis of the contact angle and on the way of assessment of wood surface free energy and its components.

Theoretical consideration

The cardinal point in study of wood wetting process by liquids is experimental determination of the contact angle corresponding to the equilibrium state, according to the Young's equation

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

where: γ_S - surface free energy of the solid material,
 γ_L - surface free energy of the liquid,
 γ_{SL} - surface free energy at the phase boundary solid – liquid, and
 θ - the equilibrium contact angle.

Eq. (1) only holds for an ideal smooth, homogeneous, non-deformable surface that is in equilibrium with the other phases (Young 1805, Adamson 1967). The practical measurement of contact angle, however, takes place in conditions more or less different from the ideal equilibrium state, as a result of secondary influence of a variety of other factors associated with the wetting process. These factors are system-specific. In case of wood, it is necessary to remember that the material is natural, heterogeneous, porous, hydrophilic and anisotropic. When dealing with a wood-liquid system, the substrate morphology is very important.

The aberration from the equilibrium state can primarily be identified through differences between the advancing contact angle θ_a observed at the moment when the liquid starts to advance on the substrate surface and the receding contact angle θ_r , for the liquid receding from the formerly wetted surface. This phenomenon, known from the literature as the contact angle hysteresis, is explained due to uneven surface of the solid substrate or due to adsorption and penetration of the liquid into the substrate (Zisman 1963, Adamson 1967). As the result, the receding contact angle is always lower than the corresponding advancing one.

The porous-capillary structure of wood causes the liquid to penetrate into the substrate, which entails changes in the phase boundary properties. The result is a permanent change to the contact angle depending on time, and, in most cases, a total soaking of the liquid into the substrate. This fact is an obstacle for determining the equilibrium contact angle in practice. In the referred literature, the problem has commonly been addressed through estimation of the contact angle within an in-advance-specified time interval. Gray (1961) uses, in context with estimation of the critical wetting tension γ_c , the values of contact angle at the phase boundary with water, ethylene glycol, glycerol and water solution of acetic acid measured in the first seconds of the wetting process. These liquids have been suggested as the ones closest expressing the equilibrium conditions. Further on, the same author, (Gray 1962) supplements this vision with water solutions

of calcium chloride, with the purpose to increase the surface tension of the liquid standard and to reach higher values of the contact angle at the phase boundary with wood. Herceg (1965) worked with glycerol, the mixtures of this compound with water and water solutions of calcium chloride. This author determined the contact angle at the beginning of the wetting process. Nguyen and Johns (1978) progressed the study carried out by Ferris (1974) on compact cellulose films, and they determined the contact angle at the phase boundary between wood of Douglas fir and liquids over the first second. Nguyen and Johns (1978) used glycerol, water, water solutions of calcium chloride and ethylene glycol. Liptáková, in her former papers (Liptáková 1975, 1979), considered as an equilibrium contact angle the angle corresponding to the time $t = 0$, determined through extrapolation of the relation $\cos\theta(t)$. Wehle (1979) pointed out the differences in values of critical surface tension γ_c of wetting of wood and other materials and recommended to estimate the values of equilibrium contact angle at the moment as close as possible to complete surface wetting.

The papers published over the recent 15–20 years have mainly been focussed on calculation of surface free energy of wood γ_s , the components of this energy – dispersion γ_s^d and polar γ_s^p , or the Lifshitz van der Waals component γ_s^{LW} and the Lewis acid-base component γ_s^{AB} . The used methods also profit from experimentally determined values of contact angle at the phase boundary with liquid standards. In most cases, they require a parallel use of two or more liquids with different surface free energy values. The contact angle is determined at the very beginning of the wetting process. The time interval is always the same for all simultaneously used liquids. The differences in chemical and physical properties of the liquids are not taken in consideration. The commonly used liquid standards are the following substances: α -bromonaphthalene, diodomethane, formamide, ethylene glycol, glycerol and water (Gardner 1996, Zhang et al. 1997, Gindl et al. 2000, 2001, Gindl and Tschegg 2002, Wälinder 2002, Blanchard et al. 2009, Piao et al. 2010, and others). In the most recent context using the terms wetting, contact angle and surface free energy, contact is the area of nanocomposite and purpose-modified surfaces free in which a steep increase has been recorded during the last 5 years (Gardner et al. 2013).

Liptáková and Kúdela (1994) analysed the process of wood wetting by water and proposed a basic method for estimation of the contact angle corresponding to an ideally smooth wood surface. The method works with the following Eqs. (2), (3) and (4),

$$\cos \theta_0 = f_1 \cos \theta_w - f_2 \quad (2)$$

$$\cos \theta_U = f_1 \cos \theta_w + f_2 \quad (3)$$

$$f_1 + f_2 = 1 \quad (4)$$

where: θ_0 - the contact angle at the beginning of the wetting process,
 θ_U - the equilibrium contact angle,
 θ_w - the equilibrium contact angle corresponding to the wood substance with surface characterised by roughness of molecular dimensions,
 f_1 - the proportion of this substance at the spot occupied by the liquid and
 f_2 - proportion of void pores and cell capillaries and of cell walls under the drop.

Liptáková and Kúdela (1994) determined the contact angle θ_U at the moment of when a qualitative change arises at the phase boundary. This change means transition from the advancing contact angle to the receding one. The time at which the angle θ_U is determined we label as the time t_U .

The contact angle corresponding to an ideal smooth wood surface θ_w calculated from Eqs. (2-4) with experimentally determined values θ_0 and θ_U is in general smaller than the contact angle at the beginning of the wetting process θ_0 , and it results in higher values of the surface

free energy and its polar component. We proposed this angle as more suitable for calculation of thermodynamic characteristics expressing interactions at the phase boundary between wood and liquid or solid substances (Liptáková et al. 1991, 1995, 2000, Liptáková and Kúdela 1994, 2002, Pecina and Paprzycki 1995, Proszyk et al. 1997, Kúdela and Liptáková 2006). However, even this method has not been accepted without doubts (Sunguo and Johansson 1996, Piao et al. 2010).

Maldas and Kamden (1998) evaluated surface properties of red maple wood treated in various ways. Among others, they investigated the contact angles of this wood with water, glycerol, ethylene glycol and solution of a phenol-formaldehyde resin. The contact angle θ_0 was determined by extrapolation for the time $t = 0$ and the contact angle θ_U at the moment when the liquid has formed a plateau on the substrate surface. The angle θ_U obtained by these authors was lower than the angle θ_U determined by Liptáková and Kúdela (1994), and there were also differences between the two in their character and quality. In our works Liptáková and Kúdela (1994) and Liptáková et al. (1998) we demonstrated that the time t_U necessary to reach the equilibrium state at the phase boundary wood-water was not always the same. The values t_U obtained by several parallel measurements ranged within a wide time interval, as a result of heterogeneous properties of the wood surface. We supposed that the differences in t_U values should also occur at applications of liquids differing by their chemical composition and that these differences would primarily be dependent on the values of surface free energy of the liquid γ_L and the components of this energy.

The equilibrium state at the phase boundary wood-liquid is also dependent on a number of other factors. In literature the description of influence of viscosity and rheological properties associated with the liquid phase can be found (Gray 1961, Liptáková et al. 2000 and others). In the case of a liquid solution, we can also expect influence of several simultaneously occurring physical and chemical processes, e.g. adsorption.

MATERIAL AND METHODS

The experiments were carried out on beech (*Fagus sylvatica* L.) test specimens, with a tangential surface of 15 x 15 mm and a thickness of 5 mm. The tangential surface was microtomed. The mean oven-dry density of the specimens ρ_0 was 685 kg.m⁻³, their equilibrium moisture content was 9 %.

As the liquid phase, we used liquids with different polarity: α -bromonaphthalene, formamide, ethylene glycol and water. The values of surface free energy γ_L , together with the dispersion and polar components γ_L^d and γ_L^p are in Tab. 1. This table also presents the values of viscosity η determined experimentally by a rotation viscosimeter.

Tab. 1: Surface free energy of the used liquids γ_L , dispersion and polar components γ_L^d and γ_L^p and viscosity η .

Liquid	γ_L		γ_L^d		γ_L^p		References	η mPa.s
	(mJ.m ⁻²)	(%)	(mJ.m ⁻²)	(%)	(mJ.m ⁻²)	(%)		
α -bromo-naphthalene	44.0	100	44.0	100.0	0.0	0.0	Gardner (1996)	5.0
Formamide	58.0	100	39.0	67.2	19.0	32.8	Gardner (1996) Gindl et al. (2001)	3.8
Ehtylene glycol	48.0	100	29.0	60.4	19.0	39.6	Gardner (1996) Gindl et al. (2001)	19.9
Water	72.8	100	21.8	29.9	51.0	70.1	Liptáková (1975) Gardner (1996) Gindl et al. (2001)	1.0

Determination of contact angle

We determined experimentally the values of contact angle at the phase boundary between the liquid and wood: The value θ_0 at the beginning of the wetting process and the value θ_U representing the equilibrium contact angle. These two values provided the issue point for calculation of the contact angle value θ_w corresponding to an ideally smooth wood surface, according to Eqs. 2-4.

The contact angles θ_0 and θ_u were calculated from the shape of the drop according to the following equation

$$\operatorname{tg} \theta / 2 = 2h/d \quad (5)$$

where: h - the drop height and,
 d - the width of the interface between the wood substrate and liquid, measured parallel to grain (Fig. 1).

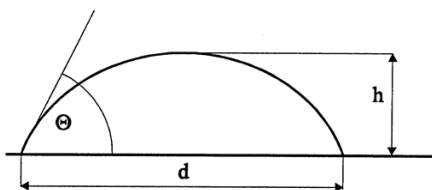


Fig. 1: Sessile drop parameters for calculation of contact angle.

Each liquid was tested on 60 samples (5 liquids, altogether 300 measurements). The experiments were running at a temperature $t = 20^\circ\text{C}$ and relative air humidity $\varphi = 65\%$.

The liquid was applied on the wood surface with a micro-syringe in amounts of 0.002 ml. The application was localised on tangential surface of early wood. The drop shape was projected on the screen of photometric equipment, magnified 25 times, and the drop change with time was scanned with a digital camera. The parameters h and d were determined immediately after the drop separation from the needle point and then at regular time intervals, until the total soaking of the drop into the substrate.

The contact angle θ_0 was determined immediately after the drop separation from the needle point, i.e. at a time $t = 0$, the equilibrium contact angle θ_U was determined at the moment when the drop started to contract (time t_U).

Determination of surface free energy

Surface free energy values were calculated according to Neumann et al. (1974) from the equation

$$\cos \theta = \frac{(0.015\gamma_s - 2.00)\sqrt{\gamma_s\gamma_L} + \gamma_L}{\gamma_L(0.015\sqrt{\gamma_s\gamma_L} - 1)} \quad (6)$$

with the experimentally determined values of contact angle θ measured at the phase boundary with the corresponding liquid. In the case of wood, the angle θ was substituted with the corresponding contact angle θ_w . The surface free energy values γ_L for the used liquids are listed in Tab. (1).

Dispersion and polar component of surface energy γ_s^d and γ_s^p were calculated following Kloubek (1974). This author derived equations for calculation of the dispersion and polar

components of surface free energy of the substrate in the following form:

$$\sqrt{\gamma_s^d} = \sqrt{\gamma_L^d} \frac{1 + \cos \theta}{2} \pm \sqrt{\gamma_L^p} \sqrt{\frac{\gamma_s}{\gamma_L} - \left(\frac{1 + \cos \theta}{2}\right)^2} \quad (7)$$

$$\sqrt{\gamma_s^p} = \sqrt{\gamma_L^p} \frac{1 + \cos \theta}{2} \mp \sqrt{\gamma_L^d} \sqrt{\frac{\gamma_s}{\gamma_L} - \left(\frac{1 + \cos \theta}{2}\right)^2} \quad (8)$$

Eqs. (7) and (8) enable us to calculate the dispersion and polar components of surface free energy of the substrate when we know the values of surface free energy of the substrate γ_s , and surface free energy of the liquid standard γ_L together with its dispersion and polar components γ_L^d and γ_L^p .

RESULTS AND DISCUSSION

The drop, immediately after its contact with the wood surface, was spreading over the surface, and, at the same time, soaking into the wood porous structure. The drop parameters h and d were continually changing, and the contact angle was continually changing, too. The value of this angle was decreasing over the whole measuring period (Fig. 2). As we can see in Fig. 2, the contact angle did not decrease at a constant rate. During the initial phases of spreading and soaking, the rate was higher, and it was getting slower towards the end of the process. Between the liquids, it has also been confirmed a significant difference in time necessary for a complete drop soaking. The most rapid contact angle change was observed for α -bromonaphthalene, followed by formamide, ethylene glycol and water. The different behaviour of the liquids is considered to be the result of their different surface energies and viscosities. An important influence of viscosity on the contact angle change was most evident in case of ethylene glycol, the viscosities of which is considerably higher compared to viscosities of the other tested liquids.

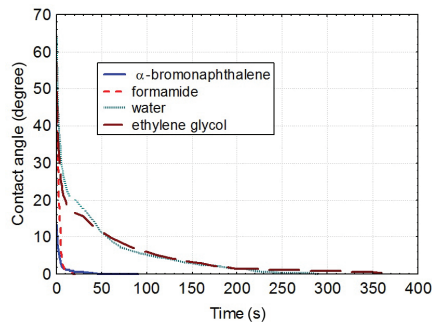


Fig. 2: Time-dependent change of contact angle (average value). a) α -bromonaphthalene, b) formamide, c) ethylene glycol, d) water.

The time-dependence of the contact angle does not enable us to determine the equilibrium contact angle. For the same time at which we measure the equilibrium contact angle, we can sometimes obtain different results for the angle's character (advancing, receding) – due to the variability of the contact angle change with time. This is not only true for different liquids, but it also holds within a single liquid.

Liptáková and Kúdela (1994) suggest that the equilibrium should be reached at the moment when the drop starts receding from the formerly wetted surface, i. e. at the moment when the advancing contact angle is turned to a receding one. This moment can be determined based on the change of the parameter d with time. As far as the parameter d is increasing, the contact angle is advancing. At the moment when the drop starts receding from the formerly wetted surface, the parameter d starts to decrease (Fig. 3). Also in this work we considered this moment as the moment of reaching the equilibrium contact angle. We determined this time separately for each measurement, together with the value of the corresponding contact angle θ_U . As we can see in Fig. 4, the position of the equilibrium contact angle θ_U on different curves expressing the dependence $\theta_U(t)$ is a case-specific one.

There were differences in intervals of equilibrium time (t_U) between the separate testing sets. It is evident that the time t_U was dependent on the liquid's polarity (Tab. 1). In case of non-polar liquids (α -bromonaphthalene), t_U was close to zero. In case of a non-polar-polar liquid (formamide, water), there was a shift to positive values, increasing with increasing polar component of surface free energy of the liquid. On the other hand, the results obtained for ethylene glycol also manifested the influence of viscosity.

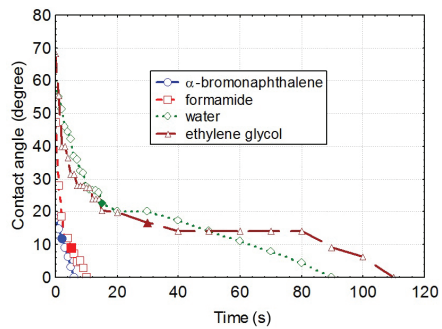
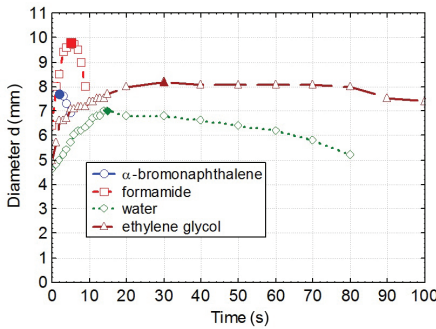


Fig. 3: Time-dependent change in diameter of a drop-substrate interface for selected specimens.

Fig. 4: Time-dependent change in contact angle with plotted equilibrium contact angle values for the specimens from Fig. 3.

The values of equilibrium contact angle θ_U determined in this way, were independent of the liquid viscosity. Similar results for glycerol on red maple wood surface were obtained by Maldas and Kamden (1998).

Also within each single liquid, the t_U range was wide, and the distribution followed the gamma pattern (Fig. 5). The variability of t_U values in frame of a single liquid was the result of wood surface heterogeneity and random location of the drop on the wood surface.

In case of α -bromonaphthalene, the value of t_U rapidly converged to zero, so the values θ_0 and θ_U were in general equal. The nature of phase boundary between α -bromonaphthalene and wood was evidently different from the other liquids. It is necessary to consider this fact in calculation of the values of θ_W .

Re-arranging Eq. (9) we obtain:

$$\cos \theta_W = (\cos \theta_U - f_2) / f_1 \quad (9)$$

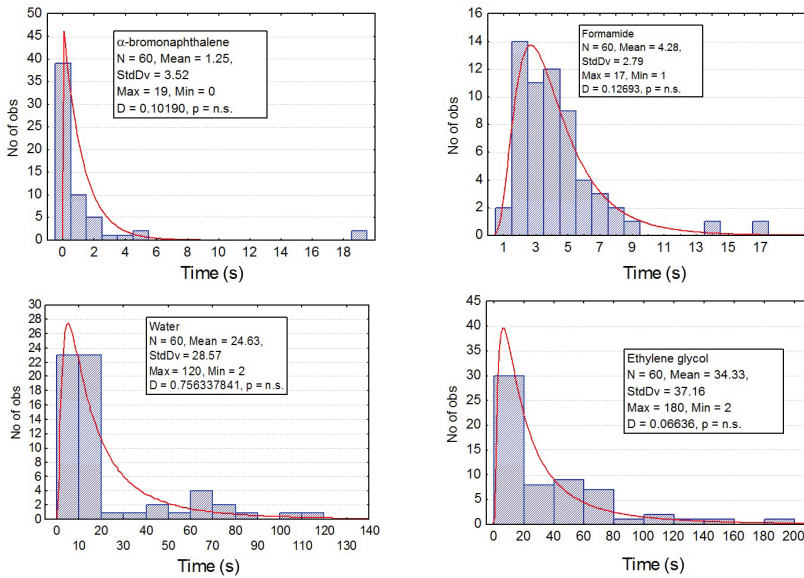


Fig. 5: Distribution curves fitting tU for the tested liquids.

Eq. (9) enables to obtain the value contact angle θ_W corresponding to an ideally smooth wood surface from the values θ_U, f_1 and f_2 . The parameters f_1 and f_2 can be acquired from liquids manifesting at their phase boundary with wood fully developed all phases of the wetting process: in our case formamide, ethylene glycol and water (Tab. 2). The values of parameters f_1 and f_2 are primarily controlled by morphological properties of the wood surface. They are equivalent in quality and can outline a pattern of wood surface porosity. The individual values can also be influenced by several accompanying phenomena with properties depending on specific physical and chemical properties (viscosity) of the used liquid. We did not consider influence of these phenomena, and in the case of the phase boundary between wood and α -bromonaphthalene, we calculated the value of θ_W with f_1 and f_2 substituted with the average values.

Tab. 2: Basic statistical characteristics f_1 and f_2 for phase boundary between wood and formamide, ethylene glycol and water.

Liquid	Parameter	Basic statistical characteristics					
		\bar{x}	x_{min}	x_{max}	s	v (%)	n
Formamide	f_1	0.740	0.514	0.954	0.109	14.75	60
	f_2	0.260	0.046	0.486	0.109	41.91	
Ethylene glycol	f_1	0.784	0.594	0.975	0.079	10.02	60
	f_2	0.216	0.025	0.406	0.079	36.32	
Water	f_1	0.752	0.541	0.914	0.093	12.36	60
	f_2	0.248	0.086	0.459	0.093	37.41	

\bar{x} – average, s – standard deviation, v – variation coefficient, n – number of measurements (the same symbols are used in Tabs. 3 and 4)

The values of the measured and calculated contact angles θ_0 , θ_U and θ_W are listed in Tab. 3. The different behaviour of liquids at the phase boundary with wood was also reflected on the different contact angle values. The differences between the values of θ_0 and θ_U reflect the different nature of the phase boundary of wood and non-polar and non-polar-polar liquids. The negligible difference between these two values in the case of α -bromonaphthalene reveals that wood wetting with this liquid mainly occurred within the range of receding contact angle. However, the wetting process at the phase boundary with formamide, ethylene glycol and water was fully developed, including the time for advancing contact angle. Therefore, we had no problems with determining the values of θ_0 , θ_U and θ_W . The values θ_U and θ_W increased proportionally with increasing the liquid's polar component.

Tab. 3: Basic statistical characteristics of contact angles θ_0 , θ_U and θ_W ($n = 60$).

Liquid	θ_0	s	v	θ_U	s	v	θ_W	s	v
	(degree)		(%)	(degree)		(%)	(degree)		(%)
α -bromo-naphthalene	13.3	5.8	43.6	11.9	4.3	36.1	13.7	5.0	36.5
Formamide	61.6	14.7	23.9	10.8	3.5	32.4	12.7	4.3	33.8
Ethylene glycol	57.0	11.4	20.0	14.3	4.9	34.3	16.3	5.8	35.6
Water	63.9	13.5	21.1	20.8	8.4	40.4	24.4	10.5	43.0

The values of θ_W were also used for calculation of wood surface free energy θ_S together with its dispersion and polar components γ_S^d and γ_S^p , respectively. The results are listed in Tab. 4 and compared, in the same table, with the values determined on the basis of θ_0 . In both cases, it was shown that the determined values of wood surface free energy are not only the results of wood surface properties, but they also depend on chemical composition of the used liquid standard. The differences are relatively high, which is in contradiction with the concept of surface free energy considered as a material constant of a substance.

Tab. 4: Basic statistical characteristics of surface free energy of wood γ_S and its dispersion and polar components γ_S^d and γ_S^p determined based on θ_W and θ_0 . ($n = 60$).

Liquid	Angle	$\bar{\gamma}_S$	s	$\bar{\gamma}_S^d$	s	$\bar{\gamma}_S^p$	s
		(mJ.m ⁻²)					
α -bromo-naphthalene	θ_W	43.03	0.92	42.99	0.95	0.04	0.03
	θ_0	43.34	2.31	43.02	1.28	0.32	2.10
Formamide	θ_W	56.54	0.99	40.00	0.17	16.56	0.16
	θ_0	35.52	7.80	32.60	5.45	2.92	2.65
Ethylene glycol	θ_W	45.96	1.35	29.49	0.07	16.47	1.29
	θ_0	30.55	5.18	25.15	2.58	5.45	2.73
Water	θ_W	66.34	5.06	25.18	2.20	41.13	7.22
	θ_0	51.33	9.72	40.91	5.55	10.42	5.55

The differences between the values of surface free energy determined on the basis of θ_W and θ_0 are the result of different behaviour of forces of non-polar and polar nature acting at the phase boundary between the liquid and wood. These differences can only be neglected in the case of α -bromonaphthalene. In this case, there has not been confirmed a statistically

significant difference between the values of γ_S and γ_S^d . Non-polar α -bromonaphthalene is a tool for determining the dispersion component of the wood surface free energy alone. The actual values of γ_S and γ_S^d are approximately by $1 \text{ mJ}\cdot\text{m}^{-2}$ lower than the values of γ_L and γ_L^d for α -bromonaphthalene. Therefore, it has been confirmed that at the beginning of the wetting process, interactions among non-polar forces take place at the phase boundary with wood. The conspicuous differences between the values of surface free energy determined on the basis of θ_W and θ_0 in the case of formamide, ethylene glycol and water are obviously caused by a lower rate of interactions between surface forces of polar nature. It is evident that the differences between the surface free energy values determined on the basis of θ_W and θ_0 prove that the equilibrium contact angle at the beginning of the wetting process can only be determined under supposition that we are working with a non-polar liquid standard.

The values of γ_S^d determined by using non-polar-polar liquids are lower than the value obtained with α -bromonaphthalene, and they further decrease with increasing polar share of surface free energy of the testing liquids following the order: formamide – ethylene glycol – water. Based on differences between the values of γ_L^d refereed in Tab. 1 and the determined values of γ_S^d , we can conclude that the dispersion component of surface free energy determined using the testing liquids is not the realistic one. This component can only be determined when using liquids with higher γ_L^d values than the supposed γ_S^d value of the substrate is. This requirement was in our case met with α -bromonaphthalene, only.

Determination of the polar component of wood surface free energy is only possible with liquids the surface free energy of which is additive. The determined values of γ_S^p raised with the polar component of surface free energy γ_L^p in the following order: formamide – ethylene glycol – water. From the differences between the γ_L^p values in Tab. 1 and the determined values γ_S^p (Tab. 6) we can conclude that determination of the polar component of wood surface free energy is possible with the results obtained with water. The polar component of surface free energy has a value of $41.7 \text{ mJ}\cdot\text{m}^{-2}$. The interactions between polar forces at the phase boundary between a liquid and wood take place gradually, from the beginning of the wetting process up to reaching the time t_U , the value of which is dependent on polarity of the liquid standard.

The results also show that the complete evaluation of wood surface free energy is not possible with using only one of the liquids tested. The liquid used as a liquid standard should not only have higher values of γ_L , but, at the same time, also higher values of γ_L^d and γ_L^p , compared to the expected values γ_S , γ_S^d and γ_S^p . Because such a liquid has not been recognized in wood surface evaluation so far, we suggest that it should be allowed to determine the dispersion and polar components separately, by means of a non-polar and non-polar-polar liquid standards, respectively. In such a way, we obtained for the tested beech wood specimens a dispersion component γ_S^d of $43.0 \text{ mJ}\cdot\text{m}^{-2}$ and a polar one γ_S^p of $41.7 \text{ mJ}\cdot\text{m}^{-2}$. Because the surface free energy of a material is the sum of its dispersion and polar component, the surface free energy of the evaluated wood surface γ_S was $84.7 \text{ mJ}\cdot\text{m}^{-2}$. The dispersion and polar components of wood surface free energy were. This confirms that the wood surface nature is non-polar-polar.

The values of beech wood surface free energy γ_S and its dispersion and polar components γ_S^d and γ_S^p obtained by the described way were higher than the corresponding values reported in literature (Wehle 1979, Liptáková et al. 1995, Scheikl and Dunky 1998, Gindl 2002 and others). This is connected with choice of a suitable liquid and also the methods for determination of the equilibrium contact angle. In the case when the authors used for the calculation of surface free energy and its components the values of contact angle determined at the beginning of the wetting process (Liptáková 1979, Zhang et al. 1997, Gindl et al. 2001, and others), the results are primarily influenced by interactions among surface forces of non-polar nature. The final

values γ_S are more or less similar to the values of the dispersion component of surface free energy γ_S^d , while, on the other hand, the polar component γ_S^p is recorded only partially. Liptáková and Kúdela (1994), Liptáková et al. (1995), Proszyk et al. (1997), and several others carried out their calculations of γ_S , γ_S^d and γ_S^p on the background of the values of the equilibrium contact angle θ_U at the phase boundary wood-water. The results of these authors are consistent with the values of polar component of wood surface free energy γ_S^p reported in this work, but they do not, however, cover the whole range of values of the dispersion component of surface free energy.

Our results show that the values of wood surface free energy γ_S together with its dispersion and polar components γ_S^d and γ_S^p are in general higher than it has been supposed so far. Consequently, there would also be higher values of wood cohesion and adhesion forces at the phase boundary wood-liquid and wood-solid material. This fact, however, should not mean a considerable change of the relations between wood and these materials, including the coating and gluing materials described in some previous works (Liptáková et al. 2001, Liptáková and Kúdela 2000-2, Proszyk et al. 1997, Kúdela and Liptáková 2006, Pecina and Paprzycki 1995 and others).

CONCLUSIONS

Based on the analysis of the obtained results we can draw the following conclusions:

The different liquid standards currently used in testing of wood surface properties have different behaviour at the phase boundary with wood. Interactions among surface forces associated with wood wetting with non-polar liquids are effects of the dispersion forces, i.e. forces of non-polar nature. The equilibrium takes place at the beginning of the wetting process.

In the case of a phase boundary between wood and a non-polar liquid, there are present, besides the dispersion forces, also the polar ones. Also in this case, interactions of non-polar forces occur at the beginning of the wetting process; the polar forces, however, take effect gradually. The equilibrium is reached at the moment t_U , at which we determine the equilibrium contact angle θ_U . The values of t_U are specific for the individual liquids.

Viscosity of a liquid lowers the rate of the wetting process, however, without any impact of the values of the contact angle θ_U .

Our results allow us to suggest that it is inevitable to determine separately the dispersion and the polar component of wood surface free energy. We have found out that the values of γ_S^d can be determined by means of the values obtained at the phase boundary between wood and α -bromonaphthalene, the values of γ_S^p can be determined based on the values obtained at the phase boundary between wood and water. In the case of evaluated beech wood surface, the dispersion component γ_S^d obtained in this way had a value of 43.0 mJ.m⁻², and the polar component γ_S^p had a value of 41.7 mJ.m⁻². The total value of beech wood surface energy γ_S was calculated as the sum of γ_S^d and γ_S^p and represented 84.7 mJ.m⁻².

The wood surface free energy can also be determined with a single liquid, if the liquid has the values of γ_L , γ_L^d and γ_L^p higher than the expected values of γ_S , γ_S^d and γ_S^p .

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