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# INFLUENCE OF MOISTURE CONTENT OF BEECH WOOD ON WETTING AND SURFACE FREE ENERGY[1]

**Jozef Kúdela – František Wesserle – Ján Bakša**

## ABSTRACT

Beech wood (*Fagus sylvatica,* L.) wetting with standard liquids significantly depends on their chemical composition. Our results suggest that suitable liquids for determining the values of disperse component $\gamma_{SV}^{d}$ of wood surface free energy are apolar liquids (in our case α-bromonaphtalene or diiodomethane); and for polar component $\gamma_{SV}^{p}$ apolar-polar liquids with the polar component bigger than the polar component of wood (in our case water). The wood surface free energy $\gamma_{SV}$ representing the sum of the disperse and polar component $\gamma_{SV}^{d}$ and $\gamma_{SV}^{p}$ obtained in this way is higher than the wood surface free energy determined with one liquid only.

Wood moisture content has been confirmed as an important factor influencing the parameters of wetting process as well as the values of surface free energy and its components. With increasing wood moisture content, the period for reaching the equilibrium $t_u$ was prolonged, contact angles increased in all experimental variants and surface free energy decreased over the whole moisture range.

**Key words:** beech wood, moisture content, wetting, apolar liquids, apolar-polar liquids, contact angle, surface free energy

## INTRODUCTION

Wood surface properties much affect wood wetting with liquids and the adhesion of liquid and solid substances to the wood. Understanding these effects is necessary for wood gluing, surface treatment and modification. These attributes are essential for improving the adhesion of coating and gluing materials to wood and, consequently, for improving the stability of solid films and glued joints.

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 on 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. The methods used for calculating thermodynamic characteristics are differing in the mathematical tools used as well as in the number of test liquids necessary for performing the experimental works (GARDNER 1996, GINDL and TSCHEGG 2002, WÅLINDER 2002, BLANCHARD *et al.* 2009, PIAO *et al.* 2011).

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For liquid standards are used liquids constrained in wood surface wetting. There are used polar liquids and unpolar-polar liquids, showing additive properties for surface free energy. The differences in chemical composition of the liquids affect the formation and character of the phase boundary with wood, and they are manifested on diverse values of surface free energy and its components.

The main problem in studying processes of wood wetting with liquids is the experimental determination of the contact angle corresponding to the equilibrium state according to the Young equation. The equation only holds for the ideally smooth, homogeneous and not-pliable surface, being in equilibrium with the other phases (YOUNG 1805, ADAMSON 1967). The wood's porous-capillary structure enables liquids to penetrate into the substrates and to modify the character of the phase boundary. The penetration causes time-dependent permanent changes in the contact angle, and, in most cases, a complete soaking of the liquid into the substrate. This fact is a serious obstacle for measuring the equilibrium contact angle. In the literature, this problem is usually overcome by calculating the contact angle either at the very beginning of the wetting process or at a certain time determined in advance (GRAY 1961, 1962, HERCEG 1965, NGUYEN and JOHNS 1978, WEHLE 1979). The whole problem turns much more intricate due to wood anisotropy; and then arises a question of which of the anatomic directions should be considered as the primary one in wood wetting.

The papers published in the recent 15 years have mostly discussed measuring of surface free energy of wood $\gamma_{SV}$, 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 $\gamma_{SV}^{AB}$. The methods used also work with 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 simultaneously used liquids is always the same, despite differences in their chemical and physical properties. The most frequently used liquid standards are α-bromo-naphtalene, diiodomethane, formamide, ethylene glycol, glycerine and water (GARDNER 1996, ZHANG *et al.* 1997, GINDL *et al.* 2000, 2001, GINDL and TSCHEGG 2002, WÅLINDER 2002, BLANCHARD *et al.* 2009, PIAO *et al.* 2011 and other). These liquids are apolar or apolar-polar, with additive nature of surface free energy. The wood wetting with these liquids is constrained.

LIPTÁKOVÁ and KÚDELA (1994) elaborated a method for finding the contact angle corresponding to an ideal smooth wood surface. These authors recorded the contact angle $\theta_u$ at the moment when the liquid starts receding from the wood surface. Just at this moment, the contact angle at the phase boundary between wood and liquid turns its character form advancing to receding. For calculation of the contact angle $\theta_w$ corresponding to an ideally smooth surface, there are used experimentally obtained values $\theta_0$ and $\theta_U$. The latter contact angle is in general smaller than the angle $\theta_0$ at the beginning of the wetting process, and it gives higher values of surface free energy and of its polar component. This angle is considered as more appropriate for calculation of wood surface free energy and thermodynamic variables characterising the interactions at the phase boundary between liquid and solid materials (LIPTÁKOVÁ and KÚDELA 2002, PECINA and PAPRZYCKI 1995, PROSZYK *et al.* 1997).

The values of $\theta_0$ and $\theta_u$ have been found to be controlled by interactions at the phase boundary between wood and liquid, and by morphological and chemical properties of the wood surface. The values of $\theta_w$ are exclusively the matter of the chemical composition of two neighbouring phases. In such a way, also the values of wood surface free energy calculated from $\theta_0$ and $\theta_w$ will significantly differ in quantity and quality. The variability of the contact angle $\theta_w$ should depend only on the variability in chemical composition of randomly cross-cut cell elements in individual wood species. Our experience and study results allow us to propose $\theta_w$ values as the base for study of phenomena at the wood – liquid phase boundary.

Comparing the results among several authors, there are differences in contact angle values and free surface energy values obtained for the same material by different authors. At the same time, there should be no differences in the surface free energy. The variability can be due to different properties of bulk material and the material surface, different testing liquids and different testing conditions. Kúdela (2014) observed that differences in surface free energy of wood followed from different polarities of the testing liquids.

Wood is a hygrophilous material, so wood surface wetting requires to consider in context of diverse wood moisture content, to know how this parameter is reflected in the values of surface free energy of wood.

The impact of wood moisture content on wood surface wetting is needed to understand for wood surface treatment and gluing. Wood moisture content can significantly influence surface forces interactions, and thus affect not only the interface wood – liquid coating but also the stability of the final system wood – solid coating.

The influence of wood moisture content on wood surface wetting with standard liquids and on wood surface free energy values was studied by SINH (1979). This author investigated the contact angle between beech wood and water, formamide and ethylene glycol, changing over the wood moisture range of 0–30 %. For all these three liquids, the contact angle $\theta_0$ values increased with increasing wood moisture content in the bound water range. The surface free energy values displayed a decreasing trend with increasing wood moisture content, the experimental results, however, do not allow us to drive unequivocal conclusions.

In our earlier work (KÚDELA and WESSERLE), we studied the influence of beech wood moisture content in bound water range on wetting of the surface of this wood with water. Experimental results showed that the wetting of wood surface was significantly reduced with increasing wood moisture content over the bound water range and that this fact was also responded by bigger contact angle values.

Over the entire moisture range, surface free energy decreased, due to the considerably decreasing polar component.

The aim of this work was to identify the influence of wood moisture content on wood surface wetting process with liquids of different polarities. This served for determining surface free energy of wood and the components of this energy based on the results obtained with wood wetting with several liquids under several initial wood moisture contents.

## MATERIAL AND METHODS

The experimental work was performed with beech wood (*Fagus sylvatica,* L.) specimens, with the size of 15 × 15 × 15 mm. 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).

The microtomed specimens were placed into a conditioning box, and then acclimated to various moisture content values, over the bound water range (0–30 %) The moisture content in the specimens was measured gravimetrically before the wetting process itself. For the calculation of contact angle, there were used the results adapted from ŠTRBOVÁ *et al.* (2013): parameters (diameter and height) of a sessile drop applied onto wood surface – Fig. 1b.

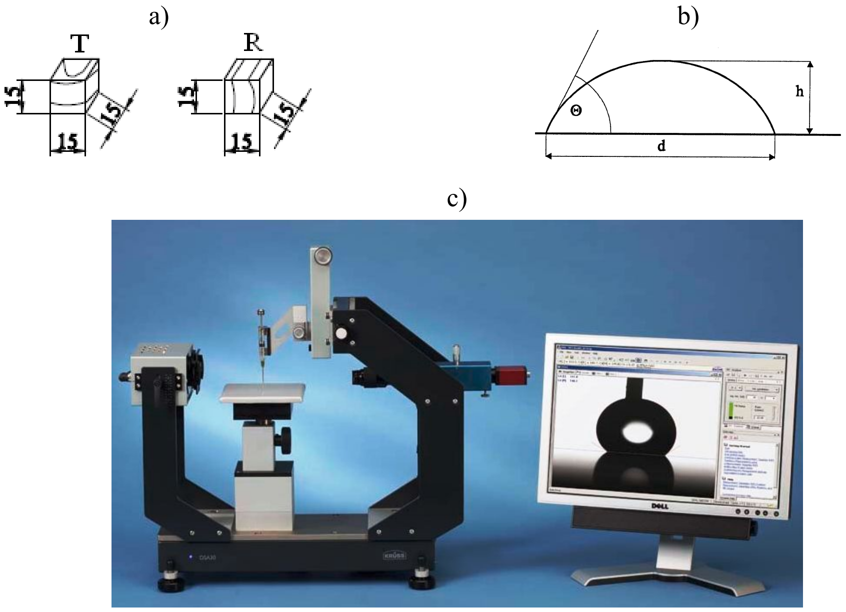

Fig. 3 a) test specimens, b) measured parameters of sessile drop, c) equipment for analysis of wetting of solid surfaces

The wood wetting process was studied with using an analyser DSA3 Standard (Fig. 1c) with attached programme package. The wood wetting liquids were five (Table 1).

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

| Testing liquid | $\gamma_L$ [mJ·m$^{-2}$] | $\gamma_L^d$ [mJ·m$^{-2}$] | $\gamma_L^p$ [mJ·m$^{-2}$] | $\gamma^+$ [mJ·m$^{-2}$] | $\gamma^-$ [mJ·m$^{-2}$] | $\eta$ [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). The equilibrium state was matched with the moment when the liquid stopped spreading onto the surface, and started 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 displayed on a monitor. The measuring results were automatically loaded in a computer.

The values of contact angle $\theta_w$ 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)

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

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

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

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

## 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 previous text we defined this moment as the equilibrium state. The time $t_u$, necessary to reach the equilibrium state as well as the values of contact angles $\theta_0$, $\theta_u$, $\theta_w$ were variable.

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. At low wood moisture values, the time $t_u$ was near zero. With increasing moisture content of beech wood, the time necessary to reach equilibrium increased significantly. A similar trend we also observed for diiodomethane; in this case, the time necessary to attain the equilibrium was longer.

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 $\theta_u$, however, can ensure elimination of viscosity influence in liquids.

Also in case of wood wetting with apolar-polar liquids, the time $t_u$ extended with increasing wood equilibrium moisture content.

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. To spare the space, Table 2 contains the results for radial surfaces only.

Contact angles $\theta_0$ increased proportionally with increasing moisture content, in all cases (Table 2). The different performance of liquids at their phase boundary with wood was also reflected in the values of contact angles $\theta_0$, $\theta_u$ and $\theta_w$ (Table 2). The highest contact angle $\theta_0$ 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 (Liptáková *et al.* 1998). In this case, the values of $\theta_0$ were the results of interactions at the phase boundary between wood and liquid, the morphological and chemical properties of wood surface. This also explains the differences in contact angle $\theta_0$ of beech wood due to wood moisture content. The drop spreading rate decreased with increasing wood moisture content also due to the fact that more moisture means fewer free −OH groups, which results in reduced wood hydrophilicity (Kúdela and Wesserle 2013).

**Table 2** Basic statistical characteristics of equilibrium time, contact angles, surface free energy and its components for five probe liquids and for specific equilibrium wood moisture contents

| Moisture content [%] | Time | | Contact angle | | | | | | Surface free energy | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\bar{t}_u$ | s | $\bar{\theta}_0$ | s | $\bar{\theta}_u$ | s | $\bar{\theta}w$ | s | $\bar{\gamma}_s$ | s | $\bar{\gamma}_s^d$ | s | $\bar{\gamma}_s^p$ | s |
| | [s] | | [°] | | | | | | [mJ·m$^{-2}$] | | | | | |
| Water | | | | | | | | | | | | | | |
| 3.9 | 37.7 | 25.6 | 60.9 | 7.6 | 18.0 | 7.3 | 20.5 | 8.4 | 67.1 | 3.2 | 27.8 | 4.1 | 39.3 | 7.0 |
| 9.7 | 53.5 | 24.5 | 64.5 | 12.5 | 21.1 | 5.6 | 24.7 | 7.2 | 67.9 | 2.6 | 31.4 | 2.3 | 36.5 | 4.8 |
| 12.9 | 65.7 | 25.3 | 70.0 | 9.2 | 20.1 | 9.1 | 23.9 | 10.1 | 68.0 | 5.1 | 30.8 | 2.0 | 37.2 | 6.3 |
| 19.4 | 66.7 | 27.4 | 72.0 | 9.1 | 21.8 | 7.1 | 26.5 | 9.0 | 67.1 | 3.9 | 31.8 | 2.2 | 35.4 | 5.6 |
| 24.0 | 67.0 | 26.7 | 74.7 | 14.7 | 36.5 | 8.7 | 43.7 | 11.9 | 58.8 | 6.5 | 34.6 | 1.4 | 24.2 | 7.5 |
| 26.1 | 103.3 | 46.0 | 82.7 | 14.6 | 36.8 | 9.6 | 46.1 | 12.2 | 57.4 | 6.9 | 34.7 | 1.4 | 22.7 | 7.5 |
| Ethylene glycol | | | | | | | | | | | | | | |
| 3.9 | 3.0 | 5.0 | 23.8 | 7.6 | 12.9 | 4.9 | 13.1 | 5.1 | 46.6 | 1.0 | 29.0 | 0.02 | 17.6 | 1.0 |
| 9.7 | 3.3 | 5.1 | 28.3 | 5.5 | 15.2 | 6.2 | 15.5 | 6.2 | 46.1 | 1.3 | 29.0 | 0.05 | 17.0 | 1.3 |
| 12.9 | 9.9 | 14.6 | 34.0 | 11.0 | 11.9 | 8.8 | 12.4 | 9.0 | 46.4 | 2.0 | 29.0 | 0.18 | 17.4 | 1.9 |
| 19.4 | 18.1 | 24.2 | 40.6 | 6.3 | 18.1 | 7.1 | 19.0 | 7.4 | 45.2 | 1.9 | 29.0 | 0.17 | 16.2 | 1.8 |
| 24.0 | 37.0 | 18.8 | 44.6 | 6.4 | 21.0 | 6.5 | 22.3 | 6.8 | 44.4 | 2.1 | 28.9 | 0.27 | 15.4 | 1.9 |
| 26.1 | 39.4 | 64.8 | 50.2 | 8.2 | 27.0 | 6.5 | 29.0 | 6.8 | 42.3 | 2.3 | 28.7 | 0.38 | 13.5 | 2.0 |
| Formamide | | | | | | | | | | | | | | |
| 3.9 | 1.9 | 2.4 | 27.1 | 11.1 | 14.8 | 8.1 | 15.1 | 8.2 | 55.6 | 2.5 | 39.2 | 0.29 | 16.4 | 2.4 |
| 9.7 | 3.2 | 5.2 | 30.9 | 8.6 | 13.0 | 5.9 | 13.4 | 6.0 | 56.2 | 1.6 | 39.3 | 0.12 | 17.0 | 1.7 |
| 12.9 | 3.5 | 4.9 | 31.6 | 9.4 | 15.4 | 6.9 | 15.8 | 7.0 | 55.6 | 1.9 | 39.3 | 0.14 | 16.3 | 2.0 |
| 19.4 | 6.8 | 8.0 | 41.6 | 10.3 | 17.6 | 5.8 | 18.6 | 5.9 | 54.9 | 1.7 | 39.4 | 0.12 | 15.5 | 1.7 |
| 24.0 | 8.4 | 15.2 | 43.2 | 9.8 | 16.5 | 7.1 | 17.6 | 7.4 | 55.1 | 2.1 | 39.3 | 0.15 | 15.7 | 2.1 |
| 26.1 | 17.1 | 38.6 | 53.7 | 12.6 | 19.9 | 8.4 | 22.1 | 9.1 | 53.6 | 2.8 | 39.3 | 0.21 | 14.3 | 2.7 |
| α-Bromonaphtalene | | | | | | | | | | | | | | |
| 3.9 | 0.4 | 0.7 | 12.8 | 4.7 | 11.1 | 4.6 | 11.1 | 4.6 | 43.1 | 0.6 | 43.0 | 0.6 | 0.0 | 0.01 |
| 9.7 | 0.4 | 0.5 | 13.0 | 4.1 | 11.3 | 4.6 | 11.3 | 4.6 | 43.0 | 0.7 | 43.0 | 0.7 | 0.0 | 0.01 |
| 12.9 | 0.8 | 1.0 | 15.6 | 4.8 | 13.4 | 5.6 | 13.5 | 5.6 | 42.6 | 1.0 | 42.6 | 1.0 | 0.0 | 0.03 |
| 19.4 | 6.3 | 6.9 | 42.3 | 9.9 | 16.3 | 5.6 | 7.3 | 5.7 | 41.9 | 1.3 | 41.8 | 1.4 | 0.0 | 0.05 |
| 24.0 | 6.4 | 7.9 | 43.2 | 9.7 | 17.0 | 6.7 | 18.1 | 7.1 | 41.6 | 1.6 | 41.6 | 1.6 | 0.1 | 0.07 |
| 26.1 | 7.9 | 14.4 | 54.4 | 11.3 | 22.3 | 12.1 | 24.1 | 11.4 | 39.5 | 4.2 | 39.3 | 3.8 | 0.2 | 0.30 |
| Diiodomethane | | | | | | | | | | | | | | |
| 3.9 | 6.4 | 8.1 | 32.9 | 5.6 | 30.5 | 7.2 | 30.6 | 7.2 | 44.1 | 2.4 | 43.7 | 2.6 | 0.4 | 0.24 |
| 9.7 | 8.6 | 9.1 | 34.8 | 4.0 | 33.4 | 4.1 | 33.5 | 4.0 | 43.1 | 1.6 | 42.6 | 1.7 | 0.5 | 0.17 |
| 12.9 | 8.8 | 12.3 | 38.5 | 4.3 | 37.9 | 4.4 | 38.0 | 4.4 | 41.3 | 1.9 | 40.5 | 2.1 | 0.8 | 0.25 |
| 19.4 | 9.0 | 10.1 | 38.5 | 6.5 | 37.9 | 6.8 | 37.9 | 6.7 | 41.3 | 3.0 | 40.5 | 3.4 | 0.8 | 0.41 |
| 24.0 | 14.0 | 13.5 | 43.3 | 5.2 | 41.8 | 4.7 | 42.0 | 4.8 | 39.5 | 2.2 | 38.5 | 2.5 | 1.0 | 0.30 |
| 26.1 | 14.5 | 13.8 | 50.4 | 5.4 | 36.5 | 5.9 | 36.7 | 5.9 | 41.8 | 2.5 | 41.1 | 2.7 | 0.7 | 0.30 |

s – standard deviation, measuring set size n = 40

The lower wood hydrophilicity due to higher wood moisture content was also reflected in bigger values of equilibrium contact angle $\theta_u$, influenced equally as the angle $\theta_0$, by the same factors. At the same time, the equilibrium contact angle was noticeably lower than the contact angle $\theta_0$ within the entire investigated range.

There was also evident a qualitatively similar course of contact angle $\theta_w$ changing with moisture content over the bound water range (Table 2). Liptáková *et al.* (1998) state that the contact angle $\theta_w$ values are completely controlled by the chemistry of the interface. The variability of contact angle $\theta_w$ values should, according to these authors, reflect exclusively the variability of the chemical composition of randomly cut cell elements. Accordingly, the contact angle $\theta_w$ changing with increasing moisture content indicates chemical changes to the wood surface due to the changes in the wood moisture content. Therefore, the differences between $\theta_0$ and $\theta_w$ values manifest the different character of wood interface with apolar and apolar-polar liquids.

Further we determined the surface free energy and its components (Table 2). The surface free energy values varied in quantity and quality, according to the liquid used. The results assembled in Table 2 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.

The surface free energy of beech wood determined based on wood wetting with redistilled water was higher than with the other probe liquids, decreasing with increasing wood moisture content over the whole moisture range. As the disperse component of surface free energy of beech wood increased with increasing wood moisture content, the surface free energy drop was due to the significant jump down in the polar component of this energy.

It was also found that the ratio of the disperse and polar component varied with wood moisture content. For the moisture content range of 0–19 %, the disperse share was significantly lower than the polar one. The difference between the disperse and polar component was diminishing with increasing wood moisture content, but the wood surface mostly displayed a polar nature. Beyond the beech wood moisture content of 20 %, the disperse component was clearly dominant and the wood surface was apolar. Similar moisture-dependent changes in surface free energy of beech wood have been reported in our previous work KÚDELA and WESSERLE (2013). There was observed more pronounced decrease in surface free energy of beech wood from 12–14 %.

The moisture-dependent changes in surface free energy values of beech wood determined with ethylene glycol and formamide were qualitatively similar, but the surface free energy of beech wood in this case was considerably lower. Inn both cases, the disperse component was dominant and almost without changes over the whole moisture range. This means that the decrease of surface free energy with increasing moisture content was only to the decrease in its polar component.

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 (KÚDELA 2014).

According to this author, to determine the polar share of surface free energy of wood, there are needed liquids whose surface free energy has additive properties. The differences between the values $\gamma_L^p$ (Table 1) and the determined values $\gamma_S^p$ (Table 2) 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 apolar and 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 $\gamma_{SV}$ and the values of its disperse and polar components $\gamma_S^d$ and $\gamma_S^p$ obtained in this way are higher (Fig. 2). These values are also 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.

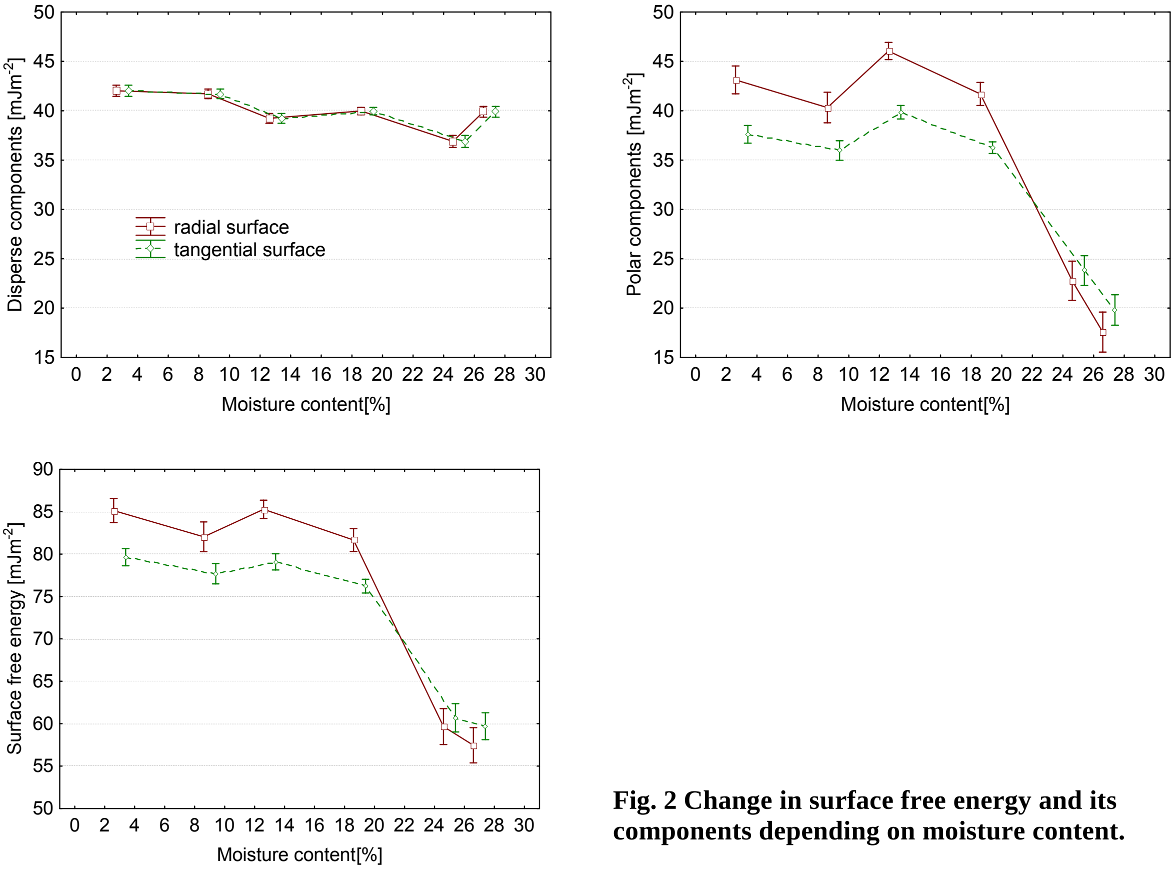

**Fig. 2 Change in surface free energy and its components depending on moisture content.**

Our results show that the values of surface free energy of wood $\gamma_{SV}$ as well as the values of its disperse and polar components $\gamma_{SV}^d$ and $\gamma_{SV}^p$ 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 (Kúdela 2014). 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).

## CONCLUSIONS

Based on the results and their analysis we can derive the following conclusions:

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 $\theta_u$. The contact angle $\theta_u$ and the derived value of the contact angle corresponding to the ideally smooth wood surface $\theta_w$ grow proportionally with growing polar share of the surface free energy $\gamma_{LV}^p$.

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 $\gamma_{SV}^d$ there were found suitable the results obtained at the phase boundary between wood and α-bromonaphtalene and diiodomethane; for determining $\gamma_{SV}^p$, 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 $\gamma_{SV}$ is the sum of the determined disperse and polar shares $\gamma_{SV}^d$ and $\gamma_{SV}^p$.

The experimental results have also confirmed that wood moisture content has a significant influence on wood wetting characteristics as well as on the values of wood surface free energy values and its polar and disperse component. It has been shown that the time $t_u$, needed for reaching the equilibrium, expanded with increasing moisture content in case of all probe liquids. The $t_u$ values for these liquids primarily depended on their polar share and viscosity.

The influence of wood moisture content was also evident in the case of contact angle values. All contact angles $\theta_0$, $\theta_u$, $\theta_w$ for all liquids increased with increasing wood moisture content over the bound water range. The differences between $\theta_0$ and $\theta_w$ manifest the different character of the phase boundary of wood with apolar and apolar-polar liquids. Our results suggest that wood hydrophilicity decreases with increasing wood moisture content over the bound water range. The wood hydrophilicity is the result of its chemical composition, it follows that changes in wood moisture content entail changes to its chemical structure. This has also been confirmed with the contact angle $\theta_w$ values increasing with increasing wood moisture content.

The free surface energy values were decreasing with increasing moisture content over the whole moisture range. This trend was very strong from a moisture content of 20 %. Proportionally with moisture content, there also decreased the disperse and polar component of surface free energy of wood. More distinct changes were observed in the case of polar component. The changes in wood moisture content induced changes in the shares of its polar and disperse component, with the disperse one dominating with increasing wood moisture content.

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## Addresses of authors

Prof. Dr. Jozef Kúdela
Dr. František Wesserle
Technical University in Zvolen
Faculty of Wood Sciences and Technology
Department of Wood Science
T.G. Masaryka 24
Sk-960 53 Zvolen
Slovakia
kudela@tuzvo.sk

Dr. Ján Bakša
Technical University in Zvolen
Faculty of Wood Sciences and Technology
Department of Mathematics and Descriptive Geometry
T.G. Masaryka 24
Sk-960 53 Zvolen
Slovakia