

SURFACE FREE ENERGY OF VISCOELASTIC THERMAL COMPRESSED WOOD AND ITS WETTABILITY BY THE PHENOL-FORMALDEHYDE ADHESIVE

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A SHORT TITLE: SURFACE ENERGY OF VTC WOOD

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Abstract—Surface free energy and its components of a viscoelastic thermal compressed (VTC) wood were evaluated by the Lifshitz - van der Waals/acid-base approach and the results compared to those calculated by the Owens-Wendt-Rabel-Kaelble method. We observed the decrease of the total surface free energy and its dispersive part as the consequence of VTC densification process. The surface free energy values were different from the results of the comparative method, so one has to consider them only relatively, to assess the influence of the densification process. In contrast to increased contact angles of water on VTC wood, the phenol-formaldehyde adhesive exhibited better wetting on VTC wood than on the untreated substrate.

Keywords: Poplar wood; viscoelastic thermal compression; Lifshitz - van der Waals/acid-base approach; surface free energy; phenol-formaldehyde adhesive; contact angle

1. INTRODUCTION

Wood is a valuable renewable resource, used in numerous applications. However, it has some less wanted properties, such as vulnerability against insect and fungi attack, dimensional instability, relatively low resistance against weathering, etc. There are many ways to overcome negative characteristics of wood. One possibility is to produce new wood-like materials using wood just as a raw material. For instance, there are numerous reports on production, characteristics and applications of chemically or thermally treated wood (e.g. [1] or [2]). In general, modified wood exhibits improved dimensional stability and increased resistance against wood pests. The poor mechanical properties of low-density wood can be modified and improved by wood densification processes. So, Kamke and Sizemore [3] developed a method for wood densification using a viscoelastic thermal compression (VTC) process.

All new wood-like materials are to be used in the same way as normal, unprocessed wood. That means that they should allow surface finishing with commercial wood coatings as well as bonding with common wood adhesives. However, surface characteristics (surface energy, surface morphology) of wood-based materials could be different from those of untreated wood and might affect bonding and surface finishing. Consequently, it is necessary to study influence of exposure of wood to heat, chemicals, compression, etc., on its wettability characteristics and surface free energy.

Wettability can be measured by contact angle measurements. The Wilhelmy plate method was shown to be especially appropriate for such a heterogeneous and porous material as wood is [4]. There are various approaches to determine the wood surface energy and its components. The most known ones are those of Zisman, Owens-Wendt-Rabel-Kaelble and Oss-Chaudhury-Good [5-7].

The objective of the present study was to evaluate influence of viscoelastic thermal compression of poplar wood on its surface free energy and its components, as calculated by the Lifshitz - van der Waals/acid-base approach and to assess wettability of VTC wood by a phenol-formaldehyde (PF) adhesive.

2. EXPERIMENTAL

Low density hybrid poplar wood (*Populus deltoides* x *Populus trichocarpa*), from a plantation in Northwest Oregon, was densified using the VTC process, as already described [8]. VTC specimens with three different degrees of densification (63 %, 98 % and 132 %) were prepared. The control and VTC specimens were examined without further surface preparation. All tested surfaces were one year old. The PF adhesive for contact angles measurements was a commercial product, supplied by Georgia-Pacific Resins (viscosity 330 mPa·s, around 50% solid matter). After conditioning to equilibrium at 20°C and 65% RH, the control samples had a moisture content (MC) of 12%, whereas the VTC specimens had 7% MC.

The apparent advancing contact angles of water (distilled in the laboratory), formamide (99+%, supplied by Kefo Slovenia), diiodomethane (99+%, supplied by Kefo Slovenia) and the PF adhesive were estimated by the Wilhelmy plate method (K100 Krüss Processor Tensiometer). The measurements with the wood plates (10 mm x 24 mm x (2.5 or 4) mm, longitudinal x tangential-radial x tangential-radial directions) were performed at the following conditions: 20°C, RH 40-50%, the immersion velocity of 12 mm/min.

The surface free energy of control and VTC wood (γ_{tot}) and its components (the dispersive part $\gamma_{\text{SV}}^{\text{LW}}$, the acid-base component $\gamma_{\text{SV}}^{\text{AB}}$ with its electron-accepting and electron-donating parts γ_{SV}^+ and γ_{SV}^-) were evaluated by the Lifshitz - van der

Waals/acid-base approach from contact angles of water, formamide and diiodomethane. The calculation procedure can be found elsewhere, for example in [9].

3. RESULTS AND DISCUSSION

3.1. SURFACE FREE ENERGY OF VTC WOOD

As can be seen from the Table 1 [8], modification of poplar wood due to the VTC densification process affects its surface wettability. The densification process increases its hydrophobic character.

Table 1.

Average (n=10) advancing contact angle on poplar wood, obtained with the different test liquids (the standard deviation is shown in parentheses) [8]

Sample	Contact angle (°)		
	Water	Formamide	Diiodomethane
Control	71.6 (7.6)	38.7 (19.6)	5.4 (9.2)
VTC 63%	90.9 (5.7)	79.2 (6.6)	48.5 (6.5)
VTC 98%	93.6 (10.3)	75.4 (3.7)	60.9 (7.0)
VTC 132%	93.1 (6.2)	81.8 (5.0)	58.0 (5.17)

It appears that the hydrophobic character of the VTC wood samples is the consequence of the chemical changes in wood due to hydrothermal conditioning during the densification process and the related reduction of the surface energy of densified wood, as suggested by Jennings *et al.* [10]. In addition, it has to be taken into account that the contact angle can be also influenced by the wood surface's morphology [11-14]. Namely, the VTC process significantly changes the morphology

of the VTC wood [15]. Densification to a higher degree is achieved by a larger reduction in the void spaces of the wood.

Indeed, the surface free energy of VTC densified poplar wood decreased from the original value of 53.3 mJ/m² to around 26-30 mJ/m² due to the densification process, as calculated by the Lifshitz-van der Waals/acid-base approach (Table 2). The total surface free energy of the control wood was relatively close to the data in the literature [16].

Table 2.

Surface free energy components of the control and VTC poplar wood specimens obtained by Lifshitz - van der Waals/acid-base approach

Sample	Surface free energy [mJ/m ²]				
	γ_{sv}^{LW}	γ_{sv}^{AB}	γ_{sv}^{+}	γ_{sv}^{-}	γ_{tot}
Control	50.6	2.75	5.4	0.4	53.3
VTC 63%*	35.1	5.55	7.1	1.1	40.7 (29.6)
VTC 98%	28.1	0.33	3.2	0.0	28.4
VTC 132%*	29.7	3.81	6.4	0.6	33.6 (25.9)

*The corrections, as described later in the text, were used in the evaluation.

For all groups of specimens, the Lifshitz-van der Waals (γ_{sv}^{LW}) was the major surface free energy component. It has to be noted that when the surface free energy of the VTC 63% and VTC 132% was evaluated, the square root of the electron-acceptor component γ_{sv}^{+} became negative, which is the consequence of the mathematical formalism of the LW-AB theory. Shalel-Levanon and Marmur [17] analyzed the validity and accuracy of the LW-AB equation from a mathematical point of view. The study determined the conditions for an infinite number of solutions and for no mathematical solution, when $\gamma_{sv}^{+} < 0$ and $\gamma_{sv}^{-} < 0$. The infinite number of

solutions was obtained if liquids with similar properties were used. The allowed range of contact angles that results in physical meaningful solutions (positive values of square roots of the surface tension components of the solid) was determined. Furthermore, the research found that the allowed range becomes significantly narrower when the chosen liquids have more similar properties.

Experimental determination of surface free energy of solids and the problem of negative square roots was discussed by many studies [17-22]. Volpe and Siboni [18] proposed the best-fit approach. The method considers large sets of liquid/solid pairs with a corresponding large system of algebraic equations which is solved by means of a best-fit algorithm. Furthermore, Greiveldinger and Shanahan [19] inverted the method and used the accepted solid surface characteristics to “redeliver” surface free energy parameters of probe liquids. Based on the obtained inconsistencies, which indicate insufficiencies in the mathematic determination of the LW-AB method the study suggested that theoretical developments are required.

Michalski et al. [20] discussed negative square roots in the LW-AB method and interpreted them based on the literature review. The study disagrees with the consideration of Good and van Oss [21] that a negative value γ_{sv}^+ was allowable, if the total surface free energy was positive. Also, the study did not find suitable the suggestion of Good [22], who affirmed that the negative values can be considered as an artefact and simply assume that they should be zero. Therefore the study chose to handle these electron-acceptor component data simply by taking them as the square of the negative square root.

Also in the present study, the γ_{sv}^+ was taken as the square of the negative square root (which always yields positive values). De Meijer *et al.* [16] considered this negative γ_{sv}^+ value as negative contribution to the total surface free energy and his

proposal was applied also in our calculations. The surface free energies obtained by proposal of de Meijer et al. [16] are shown in parentheses in table 2.

Kutnar *et al.* [8] reported data on the surface free energy of VTC wood, obtained by the Owens-Wendt-Rabel-Kaelble (OWRK) approach using contact angle data of formamide and diiodomethane. Similarly to the results presented herein, they stated that the densification process considerably lowered the total surface free energy of the VTC specimens. Both the dispersive and the polar components of the surface free energy were higher in the case of the control wood than of the VTC wood. Previous studies of the surface free energy of heat treated wood have, however, reported a slight increase in the dispersive component after heat treatment [9,10]. The decrease of the dispersive component of the surface free energy of the VTC wood is most likely the result of surface ageing, as mentioned earlier.

When the surface free energy data in the Table 2 are compared with the values obtained by the OWRK approach [8], we can see some differences in calculated surface free energies of the VTC 63% and VTC 132% specimens. When the proposal of de Meijer et al. [16] was used, the OWRK data were higher (higher OWRK values of 35.5 mJ/m² and 29.8 mJ/m², respectively, were reported). On the contrary, when the negative γ_{sv}^+ values were not considered as negative contribution to the total surface free energy, the OWRK data were lower. On the other hand, the determined surface free energies of the control and VTC 98% specimens were independent of the evaluation theory used. Furthermore, the γ_{sv}^{LW} was found to be the same as γ_{sv}^d determined by OWRK theory for all groups of specimens. The observed differences highlight an importance of the theory, applied to calculate the surface free energy and its components. We strongly believe that in the case of such a heterogeneous and porous material as wood is, one should not take the calculate values as the

absolute ones. Wood exhibits enormous variability due to the difference in its composition [23]. Hence also the magnitude of surface free energy and its components is highly variable. De Meijer et al. [16] delivered an overview of the literature on the surface energy data obtained for various wood species and methods. The reported data, variations in the surface free energy, can be explained by the complex nature of the wood surface, which is the result of porous structure of wood, surface roughness and chemical heterogeneity of wood. Furthermore the contact angle measurements are influenced by the water adsorbed onto the cell wall, which is always present in significant amounts, depending on the wood species and the relative humidity of the environment [16]. It is much more important therefore, to study and interpret the changes of surface free energy as a consequence of a process to which the specimens were submitted.

Additionally, there is a problem of experimental determination of the equilibrium contact angle that results from minimum free energy in the investigated solid/liquid/air system at constant conditions. The equilibrium contact angle, which is expressed by the Young equation, should lie between those of the advancing and receding contact angles [24,25,26]. However, the utilization of the Wilhelmy method on wood determines only the advancing contact angles, while the receding contact angles are usually zero due to the liquid soaking into the wood. Rodriguez-Valverde and co-authors [27] who measured contact angles on stone and wood, stated that a sessile drop on a real surface shows different contact angle values due to its lack of symmetry or to the loss of volume by capillary action. That is why they conducted measurements by the dynamic technique of the so called captive bubble method. Wålinder [28] also showed that, because of the intricate nature of wood (e.g. the porosity, hygroscopicity, anatomic complexity, heterogeneity, and the extractive

content) and its surfaces, wetting measurements on wood may be inherently difficult. The direct measurement of the contact angle of a drop deposited on the wood surface is according to Wålinder an unsatisfactory approach from both an experimental and a statistical point of view. Therefore, he showed a successful application of the Wilhelmy method. To conclude this part of our discussion, we believe that it is correct to use dynamic contact angles instead of the static (thermodynamic) ones for surface free energy assessment of wood, for the purpose of comparisons within the same set of wood samples.

3.2. CONTACT ANGLE OF PF ADHESIVE ON VTC WOOD

Since the wettability study with the Wilhelmy plate method showed that the VTC wood surface exhibited hydrophobic behaviour, a concern on potential increase of contact angle of certain adhesive types appeared. Therefore, we measured contact angles of the liquid PF adhesive in dependence of the degree of densification of VTC poplar wood (Table 3)

Table 3.

Average (n=5) advancing contact angle of the PF adhesive on poplar wood (the standard deviation is shown in parentheses)

Contact angle (°)	
Sample	Water
Control	133.7 (7.8)
VTC 63%	126.3 (5.6)
VTC 98%	127.8 (3.0)
VTC 132%	126.2 (3.0)

In spite of our expectations, based on the increase of water contact angles on VTC wood, a slight decrease of contact angles of the PF adhesive was observed. This is a promising and interesting result, opening possibilities of using the adhesive normally, just as in the case of normal, unprocessed wood. Although heat-treated wood is a different material than the VTC wood we used, it is interesting to note, that a similar observation with waterborne wood coatings on heat-treated wood was reported in [29]. Contact angles of water on surfaces of oil heat-treated Scots pine wood were substantially higher than on unmodified specimens. On the contrary, various waterborne acrylic stains revealed much lower contact angles on the modified samples as on the untreated ones. The authors did not elucidate the phenomenon, stating that due to complex formulations of commercial wood finishes further investigations are needed to clarify the mentioned observation. Apparently, we should continue with additional studies on wetting of VTC wood, as well.

4. CONCLUSIONS

Viscoelastic thermal compressed poplar wood exhibited increased hydrophobicity in comparison with the unprocessed wood. Calculations of the surface energy and its components of VTC wood, by the Lifshitz - van der Waals/acid-base approach, revealed the decrease of the total surface free energy and its dispersive part as the result of VTC densification process. In contrast to increased contact angles of water on VTC wood, the phenol-formaldehyde adhesive exhibited better wetting on VTC wood than on the untreated substrate.

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