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**INVESTIGATION OF INTERACTION BETWEEN WOOD BASIC COMPONENTS  
AND PHENOL FORMALDEHYDE RESIN BY IR SPECTROSCOPY**

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**ABSTRACT**

The interaction between wood and phenol formaldehyde resin was investigated. From beech wood (*Fagus sylvatica* from Central Balkan mountain, Bulgaria) cellulose, holocellulose and lignin were obtained. Mixtures with resol phenol formaldehyde resin (PFR) were made and after treatment at different temperatures and pressures their IR spectra were obtained. The hydrogen bond formation in these samples was characterized by shift of the bands, their peaks width at half height and ratios between absorbances. The efficiency of the treatment and activity of the wood derivatives in this process were determined. The changes in crystalline of cellulose and holocellulose were calculated by the crystalline index (CI).

**Key words:** beech wood, cellulose, holocellulose, lignin, hydrogen bonds, IR spectroscopy.

**1. INTRODUCTION**

The characteristics of the wood depend on its type and nature, the tree habitat and the raw material used for production of this wood. It is well known that the properties of the composite materials depend on all components of the wood. According to the data available in respective literature, there are six theories for adhesion between wood particles and synthetic resins, applied as adhesives in production of wood composites (Posius, 2002):

-Mechanical interlocking; Electronic or electrostatic theory; Adsorption (thermodynamic) or wetting theory; Diffusion theory; Chemical (covalent) bonding theory; Theory of weak boundary layers and interphases.

The existence of several theories depends on complicated processes of cure of resins in presence of wood. W.E. Johns in his book has reviewed 8 publications about curing processes with chemical bonding of wood, but exclusively from the point of view of the existence, or nonexistence, of structured covalent chemical bonding (Johns, 1989). Information for the interaction of wood with PFR (phenol formaldehyde resin) can be found in many works. Some authors reported that in presence of wood the activation energy of cure of PFR increased (Wang et al, 1995; He, Riedl, 2004). This fact can be explained by the formation of strong resin-wood bond at a higher energy level. The opposite results were given in several works (Lei, Wu, 2006; Furuno, Imamura, Kajita, 2004; Pizzi, 1994). Yong and co-authors confirmed that wood flour did not change the cure mechanism of the resin, but lowered its cure temperature and activation energy and increased its cure reaction order (Lei, Wu, 2006). The addition reaction happened at temperatures lower than 90°C and the condensation reaction was dominant at temperature higher than 110°C. A.Pizzi explained the decrease of activation energy by the catalytic activation induced by secondary interactions of dipole forces of hydrogen bonds between wood and phenol formaldehyde resin. In this work Pizzi cited the investigation of Kottes et al, that formaldehyde and formaldehyde based resins to a limited extent also react covalently with cellulose to form ether linkage and to crosslink cellulose fibres. The evaluation of hydrogen bonds formation usually was measured by the shift of the peaks in <sup>13</sup>C NMR and <sup>1</sup>H NMR or in IR spectra

and by the ratio of some absorbances (Kovalenko, Himina, 1991; Glavcheva, Kolev, Glavchev, 2001; Oh et al, 2005a; Oh et al, 2005b). For example Kovalenko et al. evaluated the hydrogen bonds in nitrocellulose by the absorbance ratio  $A$  of the bands at  $3500\text{ cm}^{-1}$  to  $3440\text{ cm}^{-1}$  (Kovalenko, Himina, 1991). Glavcheva et al. evaluated the hydrogen bond formation in the systems epoxy resin/ squaric acid by the shift of the bands ( $\Delta v$ ), by some bands ratio ( $A^*$ ) and by the increasing of the width of the bands at half of their height ( $\Delta h_{1/2}$ ). Sang Youn Oh and co-authors determined hydrogen bond index (HBI) from relative absorbance ratio  $A_{4000-2995} / A_{993}$  (Oh et al, 2005a). The reason for obtaining of hydrogen bonds were also reported (Oh et al, 2005b). The aim of this investigation is to determine the most available bands in IR spectra of wood and in all its components and their mixtures with PFR for evaluation of hydrogen bonds, to compare this information with other methods for evaluation of hydrogen bonds formation ( $\Delta v$ ,  $A^*$ ,  $\Delta h_{1/2}$ ) and to define the influence of the conditions of processing (temperature, time, pressure) on obtaining hydrogen bonds.

## 2. MATERIAL AND METHODS

Beech wood (*Fagus sylvatica*) from the Central Balkan, Bulgaria was milled so as to be used to prepare the mixtures with the FSF. The wood particles were fiber length between 50 and 100  $\mu\text{m}$ . The components of wood were prepared by methods previously described (Ajuong, 2001; He, Yan, 2005). After grinding, all hard materials were mixed by stirring them vigorously for 30 min. with 20 parts by weight of liquid resol FSF, produced in Troyan, Bulgaria. The obtained dry matter content of the resin was 50%. All samples were dried and ground again and were divided into 3 treatment groups: A - heating at  $180^\circ\text{C}$  for 20 min., B - heating at  $180^\circ\text{C}$  for 7 min., pressure 2MPa, C -under pressure 2MPa for 7 min. at  $25^\circ\text{C}$ . After cooling, the samples were powdered and prepared as pellets for IR analysis. The KBr pellets of samples were prepared by mixing (1.5–2.00) mg of samples, finely ground, with 200 mg KBr (FT-IR grade) in a vibratory ball mixer for 20 s. IR spectra were recorded on a Perkin Elmer spectrometer. IR spectra were used to determine values of  $\Delta v$ ,  $\text{cm}^{-1}$ ,  $\Delta h_{1/2}$ , index hydrogen bonds, crystalline index and  $A^*$ . Extraction of the non crosslinked resin in the samples was performed with ethanol, extra pure, Merck, using a Soxhlet apparatus for 2 h.

## 3. RESULTS AND DISCUSSION

The composition of the investigated beech wood was: cellulose- 46.6%, hemicelluloses- 25.3%, lignin- 23.3%, extractives in organic solvents- 3%, extractives in water- 1.8%, moisture- 5%. There is a lot of information in literature about the chemical structure of these materials and there are many discussions about their complexity and its dependence on the way of obtaining them, the type of the wood, etc. The composition of the extractives may be more complicated. According to IR spectra of extractives there are 12 bands: 3401.44, 2917.65, 2849.66, 1715.79, 1603.59, 1516, 1463.36, 1330.95, 1217.34, 1120.34, 1035.03 and  $729.65\text{ cm}^{-1}$  (Ajuong, 2001). Extractives are complex mixtures of tannins, flavonoids, stilbens, resin- and fatty-acids waxes, sterols and simple sugars. Although they are a minor contributor to the dry mass, extractives exercise decisive influence on many characteristics and possible use of wood. Many papers have described that extractives are deposited in cell cavities and infiltrated into cell wall structure, and during mixing the wood with liquid PFR they are the reasons for changing of pH of the mixtures (He, Yan, 2005). The structure of lignin is most complicated. There is information for alkaline activated hydrolysis of lignin with all functional groups in its molecules (Nenkova, Momchev, Vasileva, 2007). This structure of lignin can be changed after delignification procedure used to isolate these groups and the lignin reacts less readily. Holocellulose clearly shows a propensity to give condensation products with formaldehyde based resins (Mora, Pla, Gandini, 1987). It is evident that the data in literature gives an opposite point of view. The ratio 80: 20 between solid materials and PFR is applied in several cases for obtaining of thin resin layers on the surface of solid particles (He, Yan, 2005).

**Table 1.** Influence of treatment conditions on the IR spectra of wood and its mixtures with PFR

№	Characteristics	Wood	A	B	C
1	$\Delta v_{ev,1}, \text{cm}^{-1}$	-	18.25	13.17	11.4
2	$\Delta v_{ev,2}, \text{cm}^{-1}$	-	19.87	18.43	15.41
3	$\Delta v_1, \text{cm}^{-1}$	-	-7	-7	-5
4	$\Delta v_2, \text{cm}^{-1}$	-	+8	+1	-21
5	$A^*$	0.604	1 01.	0.506	0.3771
6	$\Delta h_{\frac{1}{2} \text{OH}}$	4.8	5	6	3.1
7	$\Delta h_{\frac{1}{2} \text{CH}_2}$	1.67	1.82	1.63	1.21
8	HBI	3.4377	3.2703	3.1692	2.008

A - heating at 180<sup>0</sup>C for 20 min.; B - heating at 180<sup>0</sup>C for 7 min., pressure 2Mpa; C -under pressure 2MPa for 7 min. at 25<sup>0</sup>C.

The hydrogen bonds formation usually shifted the bands (3000 - 4000  $\text{cm}^{-1}$ ) to higher wave number by several  $\text{cm}^{-1}$  and the bands 600 - 2900  $\text{cm}^{-1}$  to lower wave numbers (Opinion 1). Oh et al reported different information (Opinion 2)- many of the FTIR bands including 2901,1431, 1282, 1236, 1202, 1165, 1032 and 897 were shifted to higher wave number (by 2 - 13  $\text{cm}^{-1}$ ), (Oh et al, 2005b). However, the bands at 3355, 1373 and 983 were shifted to lower wave number (by 3 - 95  $\text{cm}^{-1}$ ). Tables 1 - 4 give the results obtained from IR spectra of the mixtures with PFR. These results showed that there is not information for a new band appeared after treatment of the mixtures, because in the IR spectra there is not a new band. All shifts were calculated as differences between the wave numbers of the basic materials (PFR and wood, cellulose, hemicelluloses or lignin) and the corresponding bands in spectra of the materials after different treatments. The  $\Delta v_{ev,2}$  were obtained as average values of the shifts of all bands (Opinion 2), and  $\Delta v_{ev,1}$  - only from the shifts of the bands corresponding with opinion 1.  $\Delta v_1$  are the shifts of the band for -OH group around 3400  $\text{cm}^{-1}$  and  $\Delta v_2$  - of the band for -CH<sub>2</sub>- group around 2900  $\text{cm}^{-1}$ .  $\Delta h_{\frac{1}{2} \text{OH}}$  and  $\Delta h_{\frac{1}{2} \text{CH}_2}$  are the peak width at half height of their bands, divided with  $h_{\frac{1}{2}}$  of band internal standard. The increase in the number of conformations of macromolecules with the formation of H - bonds leads to increasing of their peak width at half height. (Sanders, Taylor, 1991).  $A^*$  is ratio between the absorbances for -OH group, like it was made for nitrocellulose by the equation  $A^* = A_{3440} / A_{\text{max}}$  (Kovalenko, Himina, 1991). In IR spectra of wood its derivates also have the band with maximal absorbance at 3434  $\text{cm}^{-1}$ , and in their mixtures with PFR after different treatment this band shifted to 3417  $\text{cm}^{-1}$ . The values of  $A^* = A_{3427-3417} / A_{3434}$ . The values of HBI were calculate by the equation  $\text{HBI} = A_{4000-2995} / A_{993}$  (Oh et al, 2005b).

**Table 2.** Influence of treatment conditions on the IR spectra of cellulose and its mixtures with PFR

№	Characteristics	Cellulose	A	B	C
1	$\Delta v_{ev,1}, \text{cm}^{-1}$	-	15	20	9.43
2	$\Delta v_{ev,2}, \text{cm}^{-1}$	-	18.38	25.64	14.43
3	$\Delta v_1, \text{cm}^{-1}$	-	-14	-7	-7
4	$\Delta v_2, \text{cm}^{-1}$	-	+7	+3	-
5	$A^*$	0.7276	0.7807	0.6497	0.7623
7	$\Delta h_{\frac{1}{2} \text{OH}}$	9.27	10.5	16.11	7
8	$\Delta h_{\frac{1}{2} \text{CH}_2}$	2.67	2.5	4.28	1.3
9	HBI	2.6077	2.5849	2.3976	2.0206

**Table 3.** Influence of treatment conditions on the IR spectra of holocellulose and its mixtures with PFR

№	Characteristics	Holocellulose	A	B	C
1	$\Delta v_{ev.1}, \text{cm}^{-1}$	-	10.83	13.14	
2	$\Delta v_{ev.2}, \text{cm}^{-1}$	-	7.78	9.33	4.5
3	$\Delta v_1, \text{cm}^{-1}$	-	-7	-13	-42
4	$\Delta v_2, \text{cm}^{-1}$	-	+13	+5	-3
5	A*	0.5808	0.5978	0.8509	0.8618
7	$\Delta h_{1/2}$	3.87	5.67	6.11	1.57
8	$\Delta h_{1/2}$	2.23	2.05	4.28	4
9	HBI	4.7743	4.7687	2.2415	2.1288

**Table 4.** Influence of treatment conditions on the IR spectra of lignin and its mixtures with PFR

№	Characteristics	Lignin	A	B	C
1	$\Delta v_{ev.1}, \text{cm}^{-1}$	-	24	7.6	4.5
2	$\Delta v_{ev.2}, \text{cm}^{-1}$	-	17.86	25.18	14.83
3	$\Delta v_1, \text{cm}^{-1}$	-	-14	-17	-17
4	$\Delta v_2, \text{cm}^{-1}$	-	-35	-	-
5	A*	0.6291	0.8854	0.8516	0.7167
6	$\Delta h_{1/2}$	6.63	9.4	15.83	6.17
7	$\Delta h_{1/2}$	1.75	2.6	3.89	1.27
8	HBI	5.1503	5.0416	5.612	4.3792

The values of A\* were calculated from corresponding ratios, given in tab. 5.

The data in tab. 5 shows complicated processes in the interaction between components- the wave number of most available bands is different after shifting.

From tables 1-4 it is evident that for the mixtures based of cellulose and holocellulose the efficiency of the treatment conditions, measured by the shifts of the bands, decreased in the order B > A > C. From the data of HBI, the influence of the treatment of mixtures with lignin is the same, but for the others the order is A > B > C. The influence of the pressure and temperature are evident. All applied characteristics, calculated from the IR spectra are available for showing the hydrogen bond formation. Several differences in the orders of the values of the applied characteristics confirm the complicity of the processes. From the spectra of the mixtures, 5 bands were divided with maximal shifting for obtaining information for the most sensitive bands to these processes (tab. 6).

**Table 5.** The wave number of the bands for calculation of A\* values

№	Mixtures base - PFR	Base	A	B	C
1	Beech wood - PFR	3299/ 3434	3250/ 3427	3284/ 3427	3145/ 3419
2	Cellulose - PFR	3284/ 3434	3319/ 3436	3248/ 3427	3284/ 3427
3	Holocellulose - PFR	3284/ 3434	3276/ 3427	3292/ 3421	3280/ 3392
4	Lignin - PFR	3284/ 3434	3212/ 3420	3254/ 3417	3296/ 417

Many of the bands in tab. 6 were part of hydrogen bond intensity (Oh et al, 2005b). The explanation of the kind of hydrogen bonds is possible to be made. For example, the band at  $3352 \text{ cm}^{-1}$  was related to the sum of valence vibration of the hydrogen bonded -OH group and an intermolecular hydrogen bond of 3 -OH .O- 5. It is impossible to explain all bands, but it is evident that several have appeared in all IR spectra. This is the reason to determine these bands as the most available for characterization of hydrogen bond formation in wood mixtures or its derivatives and PFR. For

quantitative analysis of this data it is necessary to have additionally another analytical result, as it was done by some authors (Glavchev, Petrova, Devedjiev, 2000; Ganey, Glavchev, 2004).

It is well known that the degree of crystalline - crystalline index (CI) is the ratio of crystalline and amorphous bands. According to Oh et al. the crystalline band is at  $1430\text{ cm}^{-1}$  (Oh et al, 2005b). The amorphous bands are at  $987 - 893\text{ cm}^{-1}$ . The values of CI of the mixtures cellulose – PFR decreased in the order of treatments: A (0.5463) > B (0.4838) > C (0.4641). In the mixtures holocellulose – PFR the dependence was the same: A (1.104) > B (0.8116) > C (0.7342). The explanation of this order is better to be given after X- ray analysis. The same order was given for cellulose after treatment with sodium hydroxide and  $\text{CO}_2$  (Oh et al, 2005b).

**Table 6.** Wave numbers of the bands with maximal shifting in IR spectra of mixtures

№	Mixtures	A	B	C
1	Wood - PFR	3250,2960, 3352,1371, 1599	1636,1381, 3284, 1161 3427	1377, 2897, 1119 3419, 1595
2	Cellulose - PFR	1335, 897, 3284, 3434, 3319	3338, 1371, 3248, 897	1375, 899, 3427, 1057, 1164
3	Holocellulose - PFR	1370, 897, 3287, 3427, 1059	1379, 897, 3365,3421, 2912	3392, 1375, 897,1452, 1479
4	Lignin - PFR	3212, 902, 1372 1057, 2902	3417, 849, 914, 1423, 1375,	3417, 914, 1421, 1221, 1375

#### 4. CONCLUSIONS

The activity of different materials in hydrogen bond formation can be made if the values of the applied characteristics from IR spectra were compared. The activity of the applied materials decreased in the order: holocellulose > cellulose > lignin.

The results obtained confirmed the formation of hydrogen bonds in the mixtures beech wood or its derivatives – PFR after different treatments.

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