Furan Resin as Potential Substitute for Phenol-formaldehyde Resin in Plywood Manufacturing

Anca Maria Varodi,* Emanuela Beldean, and Maria Cristina Timar

Replacement of phenol-formaldehyde with a mixed furan resin is considered in this work as a means to improving plywood properties made with urea-formaldehyde-based adhesive currently made with an addition of phenol-formaldehyde resin. Previous research showed that the furan resins can improve water resistance and can provide long stability for the glue line. Plywood was manufactured with modified adhesives and characterized in comparison with a reference product. Thickness, physical properties (moisture content, density, and total water absorption), mechanical properties (shearing strength, bending strength, and elasticity modulus in bending), and formaldehyde emission were determined according to standardized methods. The results indicated that the addition of furan resin enhanced the water resistance by 43% and formaldehyde emission is according to E1 class. Also, the mechanical properties were improved; the shear strength for the adhesive composition with furan resin was increased by 14 to 30% compared with the reference product, depending on the testing conditions.

Keywords: Bio-resources; Adhesives; Plywood; Water resistance; Mechanical properties

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INTRODUCTION

Urea-formaldehyde (UF), phenol-formaldehyde (PF), and other formaldehyde-based resins are the most used adhesives for the gluing of various wooden products (Pizzi and Mittal 2003; Zhang et al. 2014). As the urea-formaldehyde resins are the most widely employed adhesives for wood products, improvement of their properties is still an important research topic. For instance, recent studies refer to employment of inorganic nanoparticles for reducing water absorption (Djiporovic-Momcilovic et al. 2018). In the same context, phenol-formaldehyde resins are employed as additives in urea-formaldehyde adhesive mixtures to improve their water resistance in the production of plywood.

The development of eco-friendly binders made from natural bio-resources with improved mechanical properties and water resistance is of high interest for the wood-based industry (Pizzi 2016; Hemmilä et al. 2017). The use of tannin as bio-adhesive shows an increase of water resistance, but economically speaking the industrial usage of this kind of adhesive is not profitable (Hemmilä et al. 2017). A recent study regarding soy protein adhesives pointed out that this bioresource is suitable for gluing plywood for interior use (Hao and Fan 2018).

In the research presented in this paper, furan resins from furfural obtained by processing the agricultural wastes were investigated. This renewable bioresource is a subject of interest due to the potential environmental impact of wood gluing processes.
(Gosselink et al. 2011; Dong et al. 2014; Herold et al. 2014; Rivero et al. 2014). Dongre et al. (2015) proposed lignin-furfural resins as an alternative for phenol-formaldehyde resins. His study shows the capacity of furan resin to maintain the desired mechanical properties of wood panels and the possibility to lower the costs.

Historically speaking, Ponomarev (1960) was the first researcher who indicated that furan resins show good adhesion to wood but insufficient adhesion to metals. Different studies regarding the use of furan resins and furan-formaldehyde resins have shown an improvement in water resistance for particleboard and plywood (Schultz 1990; Kim et al. 1998; Schneider 2002; NPCS 2007; Abdullah and Pizzi 2013). Other studies suggested that the use of mixed furan resin condensed with different reagents will achieve improvements in wood-based products, such as particleboard, fibreboard, and OSB (Luckeneder et al. 2016; Pizzi 2016).

Zhang (2014) showed that plywood made with adhesives based on modified urea-formaldehyde resin, with furfural in the synthesis phase, revealed improved mechanical properties.

The furan formaldehyde resin was proposed in this work as a potential substitute for phenol-formaldehyde resin in UF-PF mixtures for plywood gluing, obtained by the polycondensation of furfuryl alcohol with formaldehyde.

Previous studies demonstrated that the furan resin, which cross-linked at 20 °C, can be used with good results as an adhesive for glue laminated timber (Zeleniuc et al. 2010) and can be rated as a Type I structural adhesive with good water resistance (Varodi et al. 2013).

The water absorption, the mechanical properties (i.e., shear strength and bending strength modulus of elasticity), and the free formaldehyde emission of plywood manufactured with three types of adhesives were presented in this study. Based on the results, the plywood was further classified according to SR EN 636 (2004).

**EXPERIMENTAL**

**Materials and Methods**

Plywood made with seven layers of veneers was manufactured in two pilot series at S. C. Silva Carpat S. A., Braşov, Romania. The S.C. Silva Carpat S.A. is an economic agent specialized in producing elastic laminated veneer structures and beech (*Fagus sylvatica*) plywood for indoor applications. Each plywood panel was made from seven technical veneers of beech wood: two veneers as surface layers with a thickness of 1.00 mm and five veneers with a thickness of 1.20 mm for the middle layers. All veneers used were from the current production of the mentioned economic agent with a moisture content of 12% and the dimensions of 2100 × 1400 mm.

**Adhesive composition**

The characteristics for all three types of polycondensation resins employed in the mixture of the used adhesives are presented in Table 1 (the physical-chemical characteristics data provided by the producer S. C. Viromet SA, Victoria City, Romania). The data in this table show that the densities and the solid contents were nearly the same for all three resins. The most apparent difference was observed at free formaldehyde content data. The value registered for the URLEIT FC2 furan resin was much higher than the UF and PF resins employed.
Table 1. Physical and Chemical Characteristics of the Employed Resins

<table>
<thead>
<tr>
<th>Physical and Chemical Characteristics</th>
<th>UF Resin Adhesive G (AG)</th>
<th>PF Resin STERON (F4)</th>
<th>Furan Resin Mixed with Alcohol Furfurylic (URELIT FC2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect</td>
<td>Viscous liquid homogeneous</td>
<td>Homogeneous liquid</td>
<td>Viscous liquid homogeneous</td>
</tr>
<tr>
<td>Color</td>
<td>White</td>
<td>Red-brown</td>
<td>Yellow-white</td>
</tr>
<tr>
<td>Density at 20 °C (g/cm³)</td>
<td>1.280 to 1.295</td>
<td>1.170 ± 0.030</td>
<td>1.275 ± 0.015</td>
</tr>
<tr>
<td>Dynamic viscosity at 20 °C (mPa/s)</td>
<td>800 to 1200</td>
<td>400 to 2000</td>
<td>700 to 1250</td>
</tr>
<tr>
<td>Solid content (%)</td>
<td>66 ± 1</td>
<td>50 ± 2</td>
<td>68 ± 2</td>
</tr>
<tr>
<td>Free formaldehyde content (%), max</td>
<td>0.06 to 0.15</td>
<td>1.2</td>
<td>3.5</td>
</tr>
<tr>
<td>pH</td>
<td>8.8</td>
<td>8 to 10</td>
<td>6.5 to 7.5</td>
</tr>
<tr>
<td>Free phenol content (%), max</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Water miscibility (%), min</td>
<td>1:1 to 1:2</td>
<td>1:1 to 1:3</td>
<td>-</td>
</tr>
<tr>
<td>Reactivity (s), max</td>
<td>100 °C</td>
<td>50 to 65</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>160 °C</td>
<td>-</td>
<td>180</td>
</tr>
</tbody>
</table>

Three adhesives compositions based on the above presented resins were prepared and tested in order to improve the plywood properties. An adhesive composition based on UF resin, with 3.33% of PF resin, coded as AG-F4 was used as reference adhesive mixture. An adhesive composition based on UF resin with 3.33% of furan resin and mixed with URELIT FC2 was coded as AG-FC2/1. The last adhesive composition was also based on UF resin but with 6.66% furan resin FC2, coded as AG-FC2/2. The compositions for all adhesives used in this pilot experiment are summarized in Table 2.

Table 2. Adhesives Composition

<table>
<thead>
<tr>
<th>Adhesives Composition</th>
<th>Units of Measurement</th>
<th>Indicatives of Adhesive Compositions (Resin Type/Catalyst Type)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AG-F4</td>
</tr>
<tr>
<td>UF resin Adhesive G (AG)</td>
<td>kg</td>
<td>60</td>
</tr>
<tr>
<td>PF resin STERON (F4)</td>
<td>kg</td>
<td>2</td>
</tr>
<tr>
<td>Furan Resin Mixed with Alcohol furfurylic type URELIT FC2 (FC2)</td>
<td>kg</td>
<td>-</td>
</tr>
<tr>
<td>Solid ammonium chloride (NH₄Cl)</td>
<td>kg</td>
<td>0.7</td>
</tr>
<tr>
<td>Rye flour</td>
<td>kg</td>
<td>8</td>
</tr>
<tr>
<td>Water</td>
<td>l</td>
<td>5</td>
</tr>
</tbody>
</table>

As filler-extender, a constant amount of 12.33% rye flour (the mass percentage was reported for the UF resin) was employed. The catalyst used, was the same amount of solid ammonium chloride, 1.17% (mass percentage reported to the UF resin) for all adhesive compositions. This type of catalyst is currently used in production and is in accordance with other studies that have involved furan resins (Zhang et al. 2014).

The physical-chemical properties of the used adhesives compositions are presented in Table 3.
The data presented in Table 3 show that the two adhesive compositions modified with furan resin URELIT FC2 had a lower final pH after gel formation, compared to the reference adhesives. The viscosity, expressed as flowing time through a standard flow viscosity cup FORD type, with a nozzle diameter of 8 mm at 20 °C, decreased by approximately 16% to 20% compared to the reference.

The gelling time at 100 °C of the two adhesive modified compositions was also smaller. For adhesive composition coded AG-FC2/1, the gelling time was 78 s and for AG-FC2/2 the gelling time was 62 s. The difference between the reference and tested furan resin was 12 s for AG-FC2/1 and 28 s for AG-FC2/2. The shorter gelling time can be correlated with the more acidic pH. With increasing of the percent of furan resin the gelling time decreased, which was in accordance with Abdullah and Pizzi (2013) who developed tannin-furfuryl alcohol adhesives for wood panels.

The curing time was considered as the time between gel phase until cured resin is finished. Zhang (2014) reported the same effect of increasing the curing time of adhesives based on some urea-formaldehyde furfural co-condensed resin using the same catalyst. In the same study, the researchers indicated that if another type of catalyst was used, the reaction can be sped up.

The adhesive compositions were applied with a roller gluing machine (Karl Tränklein GmbH, Schönaich, Germany), and the pressing of veneer packages was achieved in a flat press SIWO type (SIWO GmbH, Hamburg Germany). The gluing parameters used on the industrial scale were the same for all cases when the pressing temperature was 110 °C, specific pressure 1.7 N/mm², at a pressing time of 9 min. The adhesive application rate ranged from 130 g/m² to 150 g/m² and was applied on a single side of veneers.

After the flat press, the plywood was conditioned for 7 days and sized to a final format of 2100 mm × 1300 mm. Six plywood sheets were manufactured with each of the three adhesive mixtures.

The costs of 1 m³ of glued plywood, for an average value of 150 g/m² as adhesive consumptions were slightly reduced for the adhesive composition mixed with the same amount of furan resin (AG-FC2/1) compared with reference (AG-F4). However, by increasing the quantity of furan resin (AG-FC2/2), the cost will also increase, and the properties will be improved as well (water resistance and mechanical properties).
FTIR investigation of used adhesives

FTIR spectra were recorded using an ALPHA Bruker spectrometer equipped with ATR (attenuated total reflection) module in the range 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹ and 24 scans/spectrum. The spectra were registered for the cured adhesives (reference and modified adhesive AG-FC2/2). Spectra from three randomly chosen measuring areas were registered for each sample and further processed for baseline correction and smoothing. An average spectrum of the three individually recorded spectra was computed. Average spectra were further normalised (Max-Min normalisation) and compared. Assignment of characteristic absorption bands was based on literature references. The OPUS software was employed for all spectra processing and calculations.

Physical-mechanical characteristics

Before testing the plywood panels, they were conditioned for 72 h at 20 °C ± 2 °C and with a relative humidity of 65% ± 5%.

The determination of the plywood thickness was made in accordance with SR EN 324 1 (1993), the moisture content was performed in accordance with SR EN 322 (1996), and the density was determined in accordance with SR EN 323 (1996).

Although the total water absorption is not a compulsory property for interior plywood, it was considered useful to highlight the effect of furan resin addition on the water resistance of the glued products. Thus, test samples of plywood with dimensions of 100 mm × 100 mm × 7 mm were immersed for 24 h in water at 20 °C ± 1 °C (STAS 10913 - 1977).

The total water absorption is symbolized by $A_t$ (%) and was calculated by using Eq. 1,

$$A_t \%(\%) = \left( \frac{m_2 - m_1}{m_1} \right) \times 100$$

where $A_t$ is the total water absorption of the plywood (%), $m_1$ is the weight of the conditioned samples before immersion in water (g), and $m_2$ is the weight of the samples after immersion in water for 24 h at 20 °C (g).

The following standards were used to determine the mechanical properties: SR EN 3141 (2005) for shear strength, and SR EN 310 (1996) for the bending strength and modulus of elasticity in bending (MOE). A universal testing machine Zwick Roell Z 250 (Zwick GmbH &Co.KG, Ulm, Germany) with a testing rate of 2 mm/min was used. The percentage of wood failure in the bonding area was measured in accordance with SR EN 3141 (2005).

The determination of the shear strength was made on three types of samples, as presented in Fig. 1. These samples were coded as Long 1, Long 2, and Long 3. Ten replicates were tested for each type of sample, representing a total of 30 samples/types of plywood.

![Fig. 1. The schematic representation of the three types of samples for shear strength testing, according to SR EN 314-1 (2005)](image-url)
The formaldehyde emissions of the plywood boards were determined by the gas analysis method. A Timber test equipment by Stephen Young and Associates (New Plymouth City, New Zealand) was used in accordance with SR EN 7172 (1995).

All of the obtained experimental data were statistically analyzed with a one-way ANOVA test to find out the significant difference between the reference sample and tested samples. The analyses of variance were performed with Excel 2010 (Microsoft Corporation, Microsoft Office 2010, Albuquerque, NM, USA).

RESULTS AND DISCUSSION

FTIR spectra

The FTIR features of the cured adhesives compositions, with common and differentiating aspects, are presented in Fig. 2.

![FTIR spectra](image)

**Fig. 2.** The FTIR spectra registered for the cured adhesives compositions: reference (AG-F4) and the mixture composition with furan resin (AG-FC2/2)

Absorbance in the range 3000 to 3600 cm\(^{-1}\) can be associated with both O-H and N-H bonds; therefore the band is common and cannot provide much information. Absorption at 2928 cm\(^{-1}\) can be assigned to C-H vibration in methylene groups. This band is larger for the cured adhesives modified with furan resins, which is expected, as methylene bridges are characteristic structural features for these condensation resole resins and more methylene bridges are formed by curing, which is consistent with proposed structures in the literature (e.g. Zhang et al. 2014). The absorption bands at 1632 cm\(^{-1}\) and 1597 cm\(^{-1}\), common to both spectra, are assignable to carbonyl bonds in amides (amide I) and N-H bonds (amide II). According to Tian et al. 2009, the presence of furan rings can be associated with the characteristic absorption bands at ~1509 cm\(^{-1}\) (C=C in furan ring), 1154 cm\(^{-1}\) (C-O in furan ring), and 1032 cm\(^{-1}\) (furan ring vibration). These bands were present only in the FTIR spectra of the adhesives mixtures modified...
with furan resins. The absorption band at 1730 cm\(^{-1}\), assignable to saturated unconjugated carboxyls, was present only in the spectrum of the adhesive mixture modified with furan resins.

**Physical Characteristics**

The physical characteristics and the formaldehyde emission of the experimental beech plywood with seven layers of veneer are presented in Table 4.

**Table 4. Thickness, Physical Properties, and Formaldehyde Emission of Plywood**

<table>
<thead>
<tr>
<th>Indicative of Adhesives Composition</th>
<th>Plywood Thickness (mm)</th>
<th>Moisture Content (%)</th>
<th>Density (g/cm(^3))</th>
<th>Total Water Absorption (%)</th>
<th>Formaldehyde Emission (mg/m(^2)h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG-F4/NH(_4)Cls</td>
<td>7.13</td>
<td>6.55</td>
<td>0.784</td>
<td>30.84</td>
<td>3.01</td>
</tr>
<tr>
<td>AG-FC2/1/NH(_4)Cls</td>
<td>7.38</td>
<td>6.31</td>
<td>0.715</td>
<td>26.70</td>
<td>3.32</td>
</tr>
<tr>
<td>AG-FC2/2/NH(_4)Cls</td>
<td>7.29</td>
<td>6.21</td>
<td>0.773</td>
<td>17.60</td>
<td>3.40</td>
</tr>
</tbody>
</table>

The experimental data from Table 4 indicate that the plywood glued with modified resin had approximately the same moisture content and density as the reference, while the total water absorption was reduced. The water absorption decreased as furan resin amount increased. In this case, the water absorption was lower, approximately 43% compared to the plywood manufactured with the reference adhesive mixture.

Esmaeili *et al.* (2017) reported the same effect of reducing the water absorption and the thickness swelling for wood-based panels made with adhesives based on a urea-hydroxymethyl furfural-formaldehyde resin. Although the formaldehyde emission slightly increased for the plywood manufactured with the adhesive mixture modified with furan resin, it still remained in the E1 class of emission.

**Mechanical Properties**

*Shear strength*

The results of shear strength tests were expressed as an average of 10 replicates. The graphs shown in Fig. 3 present the mean shear strength and standard deviation determined for Long 1 (Fig. 3a), Long 2 (Fig. 3b), and Long 3 (Fig. 3c) samples. Each adhesives composition was tested in the dry state, after 24 h immersion in water at 20 °C temperature, and after 3 h immersion in water at 67 °C temperature.

The shear strength for the plywood made with modified adhesive was higher regardless of the testing conditions. When the addition of furan resin was increased, the shear strength also increased, which demonstrated the positive effect of furan resin on plywood properties. The samples Long 1 and Long 2 exhibited nearly the same type of milling process. The shape of Long 3 samples was specialized for the bonding strength of the inner plywood layers. The values of Long 3 were higher than the Long 1 and Long 2 values for all three adhesive mixtures. A comparison between the average shear strength (Long 1, Long 2, and Long 3) of the three types of manufactured plywood is presented in Table 5. These values showed that the shear strength of the plywood manufactured with UF resins modified with furan resin was higher than the reference adhesive mixture, based on UF resin modified with PF resin.
Fig. 3. Average of shearing strength of Long 1 (a), Long 2 (b), and Long 3 (c) samples
Table 5. Shear Strength Value Obtained by Average Calculation of Experimental Data for Studied Plywood

<table>
<thead>
<tr>
<th>Indicative of Adhesives Composition</th>
<th>Shear Strength (N/mm²)</th>
<th>Dry State</th>
<th>After 24 h Immersion in Water at 20 °C</th>
<th>After 3 h Immersion in Water at 67 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG-F4</td>
<td>4.30</td>
<td>4.07</td>
<td>1.88</td>
<td></td>
</tr>
<tr>
<td>AG-FC2/1</td>
<td>4.92</td>
<td>4.67</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>AG-FC2/2</td>
<td>5.65</td>
<td>4.97</td>
<td>2.65</td>
<td></td>
</tr>
</tbody>
</table>

The data presented in Table 5 show that the shear strength for the adhesive composition AG-FC2/1 increased compared to the reference AG-F4 as follows: 14.4% in dry state, 14.7% in wet state after 24 h immersion in water at 20 °C, and with 30.8% in wet state, after 3 h immersion in water at 67 °C. When the addition of furan resin was increased, the shear strength was much higher than the reference sample with 31.3% in dry state, with 22.1% after 24 h immersion in water and with 40.9% after 3 h immersion in water at 67 °C.

The percentage of wood failure of the tested samples is presented in Fig. 4.

Fig. 4. Percentage of wood failure after shear strength test

In Fig. 4, the percentage of wood failure estimated as the percent of wood fibers in the breaking area is presented to highlight the good resistance of furan resin in the glued layers. For example, for the reference adhesive composition, the surface covered with wood fiber is approximately 70%, while 30% was covered with adhesive film. For the adhesive compositions modified with furan resin, the clear glue film area had a smaller percentage of surface covered with wood fibers after breaking, being approximately 80% from the total glued area. According to SR EN 3141 (2005) is not compulsory to evaluate the wood failure when the shear strength is higher than 1N/mm². The results correlated with the requirement of SR EN 3142 (2004) regarding the bonding quality indicated that the experimental plywood panels can be classified in Class 1 (the imposed limit is a minimum shear strength of 0.2 N/mm²). However, it can be seen
that the addition of furan resin significantly increased the shear strength of glued joints in the obtained plywood (based on ANOVA statistical analysis, the P value was 0.001).

**Bending strength and modulus of elasticity in bending**

The results of these tests were expressed as an average of five test pieces for each type of plywood and are presented in Fig. 5 (MOR - Fig 5a and MOE - Fig. 5b) with the corresponding standard deviations.

![Fig. 5](image)

**Fig. 5.** The bending strength (a) and the modulus of elasticity (b) registered for the manufactured plywood

The data presented in Fig. 5 show that the bending strength of plywood obtained with the adhesive composition modified with furan resin was higher than for the reference plywood. The increasing in the bending strength on the longitudinal direction was approximately 4% to 16% in the transversal direction.

Esmaili (2017) obtained some similar results performed on the particleboards glued with adhesives based on a urea-hydroxymethyl furfural-formaldehyde resin. He also mentioned the water resistance improvement of these wood-based products with the addition of furfural in adhesive synthesis.
The modulus of elasticity in bending increased for modified plywood with approximately 10% to 17% in the longitudinal direction and 1.7% to 5.4% in the transversal direction, compared to the reference.

Therefore, the plywood made with the adhesive mixture based on urea-formaldehyde resin modified with furan resin was more rigid and more resistant to rupture.

CONCLUSION

1. The adhesive compositions based on the urea-formaldehyde resin in addition with furan resin improved the properties of plywood.

2. The cured adhesives modified with furan resins investigated by FTIR, revealed that the peak for methylene bridges is higher, being characteristic for condensation resole resins with more methylene bridges formed by curing.

3. The beech plywood for interior use made with UF adhesives modified with furan resin, showed a better resistance to water and superior mechanical properties, compared to those of similar products glued with a similar addition of phenol-formaldehyde resin.

4. The manufactured plywood can be classified as Class 1, according to the requirements of bonding quality, and classified in the E1 class of formaldehyde emission.

5. The results indicated that the furan resins could be a substitute for the phenol-formaldehyde resins, which are commonly employed in plywood manufacturing for improving the water resistance of plywood made with UF resins.

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