The Influence of Solvent Content in Liquefied Wood and of the Addition of Condensed Tannin on Bonding Quality

Utekućeno drvo (LW) je perspektivan prirodni materijal koji može biti upotrijebljen kao tvar za izradu ljepila. Međutim, vezivna ljepila napravljena samo od utekućenog drva imaju malu trajnost. Stoga je cilj provedenih istraživanja bio povećati trajnost vezivnih ljepila koja sadržavaju LW. U provedenim je istraživanjima LW dobiven u tekućenjem drva topole u etilen glikolu (EG) kao otapalu i sumpornoj kiselinom (SA) kao katalizatorom. Definiran je optimalno vrijeme utekućenja od 120 minuta i maseni omjer drvo:EG u iznosu 1:3 za utekućenje pri temperaturi 180 °C. Nakon utekućenja EG je ishlapljen da bi se postigao nizak sadržaj otapala u LW-u s konačnim masenim omjerom 1:1. Utvrđen je hidroksilni broj za LW s omjerom 1:1 i LW s added CT (LW1:1/CT) samples. No significant differences were observed between the cured LW1:1 and the LW1:1/CT samples.

Key words: adhesive, condensed tannin, FT-IR, liquefied wood, shear strength
Adhesives are an indispensable part of wood-based composites. They are mainly composed of oil-based derivatives, which make them dependent on an ever-increasing oil price. One of the basic constituents of a large number of synthetic wood adhesives is formaldehyde, which is, however, potentially carcinogenic (IARC, 2004). Due to the free formaldehyde emission, the increasing prices of oil-based derivatives, strict environmental requirements, and increasing ecological awareness, there have been many attempts to produce wood adhesives based on natural and renewable sources.

Liquefied wood is one of the naturally-based products that has been developed in recent years. Liquefied wood is a product of the thermochemical reaction between wood (wood residues), solvent, and added catalyst. Liquefied wood can be used for the production of various biocopolymers. These biocopolymers include coatings (Budija et al., 2009; Kurimoto et al., 2000), various polymers (Wang et al., 2008; Doh et al., 2005), carbon fibres (Xiaojun and Guangjie, 2010), foams (Alma and Shiraiishi, 1998; Lee and Ohkita, 2004), and adhesives.

Over the last 20 years there have been many attempts to use liquefied wood as a part of the adhesive formulation. In the earlier years, the development of liquefied wood adhesives was based on liquefied wood that was prepared with phenol and added formaldehyde (Alma and Bastürk, 2001, 2006; Li et al., 2004; Fu et al., 2006; Zhang et al., 2007). Many studies were performed in connection with the application of liquefied wood to epoxy resin systems (Kobayashi et al., 2000, 2001; Asano et al., 2007; Wu and Lee, 2010), and there have been some other attempts to blend liquefied wood with synthetic resins such as diisocyanates (Juhaida et al., 2010), urea-formaldehyde (Antonović et al., 2010), melamine-urea-formaldehyde (Kunaver et al., 2010) and phenol-formaldehyde resin (Ugovišek et al., 2010).

One of disadvantages of liquefied wood-based adhesives, besides low durability of the adhesive bond, is the low wood content in the final adhesive mixture. For example, if the wood/solvent mass ratio is 1:3, and later on 25 % of the liquefied product is incorporated into the adhesive mixture, the latter will only contain 6.25 % of wood (Ugovišek et al., 2010). Reducing the quantity of solvent in the final liquefied product was therefore the author’s fundamental goal. This could either be achieved by liquefying at different wood/solvent mass ratios, or with solvent evaporation after liquefaction. Due to the higher content of the non-liquefied residue when liquefying at lower mass ratios (1:2 or 1:1), solvent evaporation turned out to be more appropriate method.

The above mentioned problem – low durability of liquefied wood based adhesives – could be potentially alleviated with the incorporation of a chemical substance that would help to crosslink the components of the liquefied wood. Based on the aim of creating an environmentally-friendly adhesive, the authors tried to use natural substances that are used as a part of adhesive mixtures. Tannins have been one of the most useful natural sources for wood adhesives (Gornik et al., 2000; Vázquez et al., 2002; Moubarik et al., 2009). They can be divided in two different classes, based on their chemical structure: hydrolyzable and condensed tannins. Almost all tannin-based wood adhesives are made from condensed tannins, due to their widespread availability and higher reactivity. The most reactive part of condensed tannin is resorcinol or the phloroglucinol A-ring of the flavonoid unit. The resorcinol A-rings of mimosa (Acacia sp.) and quebracho (Schinopsis sp.) tannins show reactivity toward formaldehyde that is comparable to that of resorcinol (Pizzi, 2008). In this study spruce condensed tannin was used, and it was found that it contained approximately 60 % procyanidin and 40 % prodelphinidin (Behrens et al., 2003). Condensed tannins can thus be added to liquefied wood due to their high reactivity at elevated temperatures, so that they can react with the free phenolic and alcoholic hydroxyl groups that are present in the liquefied wood.

The objective of this study was to optimize the liquefaction of black poplar (Populus nigra L.) using ethylene glycol (EG) as the solvent, and the preparation of liquefied wood with a low content of EG. Additionally, the properties of adhesive mixtures using liquefied wood with different solvent contents and added condensed tannin (hydroxyl number and infrared spectroscopy) were studied. Finally the shear strength of adhesive bonds that were produced with different adhesive mixtures was tested.
h). Ethylene glycol (p.a. grade) was used as the solvent, and sulphuric acid (p.a. grade) was used as a catalyst. 3% of SA based on the EG mass was added. Liquefaction was carried out in a 1000 mL three-neck glass reactor equipped with mechanical stirrer. The reactor was immersed in an oil bath that was preheated to 180 °C.

2.2 Temporary amount of residue and liquefaction yield determination

2.2.1. Determination of liquefaction yield

Different mass ratios between wood and EG (1:1, 1:2, 1:3, 1:4, 1:5) and different liquefaction times were investigated in order to achieve the optimum results. By calculating the temporary amount of the residue (TAR), (Eq (1)) the optimum liquefaction time was assessed. During liquefaction, the samples of liquefied wood were dispossessed, diluted with a mixture of 1.4-dioxane/water, and filtered through filter disks (Sartorius filter disks 388 grade/84/mm²) every 15 minutes. The insoluble parts were dried in a laboratory oven (103 °C, 24 h), and weighed in order to calculate the TAR according to Eq (1).

\[
TAR = \left(1 - \frac{W_3 - W_2}{W_1}\right) \times 100\% \quad (1)
\]

\(W_1\) represents the mass of the filter paper with the dry residue (g), \(W_2\) is the mass of the filter paper (g), \(W_3\) is the mass of the dispossessed sample (g), and TAR represents the temporary amount of the residue (%).

After the optimum liquefaction time, the reactor was immersed in cold water in order to quench the reaction. The liquefied product was then diluted with a mixture of 1.4-dioxane and water (4/1, v/v), and filtered through filter disks (Sartorius filter disks 388 grade/84/mm²) every 15 minutes. The insoluble parts were dried in a laboratory oven (103 °C, 24 h), and weighed in order to calculate the TAR according to Eq (1).

\[
TAR = \left(1 - \frac{W_3 - W_2}{W_4}\right) \times 100\% \quad (2)
\]

\(W_4\) represents the mass of the filter paper with the dry residue (g), \(W_1\) is the mass of the filter paper (g), \(W_2\) is the mass of wood (g) and \(LY\) represents the liquefaction yield (%).

2.2.2. Determination of hydroxyl number of liquefied wood

The hydroxyl (OH) numbers of liquefied wood with wood/EG ratios of 1:3 (LW₁:₃) and 1:1 (LW₁:₁) were determined according to standard ASTM D 4274-05, test method C – reflux phthalation. 0.45 g of sample LW₁:₃ and 0.85 g of sample LW₁:₁ was dissolved in 25 mL of a phthalic anhydride-pyridine reagent (115 g phthalic anhydride and 700 mL pyridine) and heated at 115 ± 2 °C, for 1 h, under reflux. After esterification, 50 mL of pyridine was added through a condenser, and a phenolphthalein solution in pyridine was added. The mixture was titrated with 0.5 M sodium hydroxide. Due to the dark colour of the solution and the severe difficulty in perceiving the colour change to pink, the titration end point was determined with a pH meter (Mettler Toledo, SevenEasy, pH meter S20). The end titration point was determined when a significant change in the mV value occurred.

2.4 Preparation of adhesive mixtures

The adhesive mixtures were prepared according to Table 1. Condensed tannin (CT) (Tanin Sevnica, Slovenia) from the Norway spruce (Picea abies L.) was used to prepare mixtures with different proportions of CT and LW.

2.5 Bonding and testing of specimens

Solid beech wood lamellas were used as a substrate for the preparation of two-layered test specimens, which were bonded according to EN 12765 by using conventional hot-pressing. Prior to the bonding, all of the beech wood lamellas were planed in order to ensure...
smooth and flat surfaces. Two lamellas were then bonded together with different adhesive mixtures (Table 1). Each of the adhesive mixtures was applied by means of a roller, using an application rate of 200 g/m². The press temperature was 200 °C, and the press time was 900 seconds. The specific press pressure was 1.5 MPa. The bonded specimens were tested immediately after bonding (n=12), and later on after 7, 30 and 50 days of conditioning in a standard climate (20±2 °C, relative humidity 65±5 %). All the shear tests were carried out on a ZWICK/Z005 universal testing machine according to the standard EN 205.

2.6 FT-IR analysis
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Fourier transform infrared spectroscopy (FT-IR) was used to investigate and compare the samples of LW1:1 and LW1:1/CT (85/15) in their uncured state. Both samples were later on placed on aluminium foil and cured in an oven for 600 seconds at 200 °C. The cured LW1:1 and LW1:1/CT (85/15) specimens were also investigated using a Perkin-Elmer Instruments Spectrum One, FT-IR spectrometer. All the spectra were compared using Perkin-Elmer Spectrum 6.3.5 software. The spectra were recorded by the ATR technique, using a HATR ZnSe Trough Plate 45°, over the 4000-650 cm⁻¹ wave number range. The spectral resolution of the spectrometer was 1 cm⁻¹.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Preparation of the liquefied product
3.1. Priprema utekućenih proizvoda

The temporary amounts of residue versus the reaction time at different wood/EG ratios are shown in Figure 1. By calculating the TAR, the optimal liquefaction time was assessed. The optimum liquefaction time was assessed when the TAR was the least. The figure shows that the optimum liquefaction time for the ratios 1:3, 1:4 and 1:5 is above 120 min. With the aim of achieving the lowest possible (and optimal) wood/EG ratio, the 1:3 ratio turned out to be optimal. In the case of the ratio 1:2 the lowest TAR was at 135 minutes. After 135 minutes the TAR increased and re-condensation of the liquefied product occurred. In the case of 1:1 ratio, wood liquefaction did not occur, and the stirring in the reactor was aggravated. The ratio 1:1 turned out to be inappropriate for wood liquefaction. The optimal time for liquefying black poplar wood at 180°C was therefore 120 minutes.

The LY was determined for LW with wood/EG mass ratios of 1:2, 1:3 and 1:4. The highest LY was attained at a mass ratio of 1:3 (91 %) and the lowest LY at a mass ratio of 1:2 (84 %). LY for LW with a mass ratio of 1:4 was similar to LW with a mass ratio of 1:3. Due to the above mentioned purpose of achieving the lowest wood/EG ratio, the LY for 1:5 ratio was not investigated. At 1:1 ratio, liquefaction did not occur. A wood/EG mass ratio of 1:3 was therefore the most appropriate for the liquefaction of black poplar with EG, and 120 minutes at 180°C was required for the highest liquefaction yield.

The liquefaction process at the optimal conditions and the preparation of low-solvent liquefied product is shown in Figure 2. As can be seen, a theoretical wood/EG mass ratio of 1:1 was obtained. The exact mass ratio of the final product was actually 1.05:1.0. The evaporation of EG also contributed to the suitable viscosity of the LW when applying it to the wood surface.

3.2 Determination of hydroxyl number of liquefied wood
3.2. Određivanje hidroksilnog broja za utekućeno drvo

The OH numbers of the liquefied wood with different wood/EG ratios are shown in Figure 1. By calculating the TAR, the optimal liquefaction time was assessed. The optimum liquefaction time was assessed when the TAR was the least. The figure shows that the optimum liquefaction time for the ratios 1:3, 1:4 and 1:5 is above 120 min. With the aim of achieving the lowest possible (and optimal) wood/EG ratio, the 1:3 ratio turned out to be optimal. In the case of the ratio 1:2 the lowest TAR was at 135 minutes. After 135 minutes the TAR increased and re-condensation of the liquefied product occurred. In the case of 1:1 ratio, wood liquefaction did not occur, and the stirring in the reactor was aggravated. The ratio 1:1 turned out to be inappropriate for wood liquefaction. The optimal time for liquefying black poplar wood at 180°C was therefore 120 minutes.

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LW1:3 OH value. The reduction of free OH groups to almost one half of the number of OH groups to evaporation of EG to obtain a mass ratio of 1:1 lowered (Budija number is also the consequence of solvent evaporation.)

Condensation reactions between the glycol and wood components, such as cellulose, hemicelluloses and lignin (Kunaver et al., 2010). The reduction of the OH number is also the consequence of solvent evaporation (Budija et al., 2009). It can be seen that the additional evaporation of EG to obtain a mass ratio of 1:1 lowered the number of OH groups to almost one half of the LW1:3 OH value. The reduction of free OH groups could potentially affect the durability of the bond-line. This is because free OH groups are potentially reactive locations, which interact with other functional groups, but are also possibly weak points for water deterioration if the adhesive bond is inadequately cured.

3.3 Shear strength of tested specimens
3.3. Smičajna čvrstoća ispitivanih uzoraka

The initial shear strength values of the specimens bonded with EG liquefied wood adhesive mixtures were low (Table 3), and also, they did not exceed the requirements of the standard for any of the durability classes. It is interesting that they did not decrease drastically over the following period of time, which is typically the main problem of bonding only with LW (Ugovšek et al., 2010). It can also be seen that the shear strength values of the adhesive mixtures with a wood/EG ratio of 1:1 exhibited higher shear strength values than those with a ratio of 1:3. This was probably due to the more suitable viscosity of the sample LW1:1, which contributed to the appropriate flow and penetration of the adhesive and wetting of the wood surface (Marra, 1992). The durability of the LWx adhesive bonds was also better compared to those corresponding to LWx. The unreacted EG in the LW1:3 influenced negatively the shear strength durability. The latter could be correlated to fewer free OH groups in the LW1:3 than in the LWx, which has more OH groups from the excessive EG. The free OH groups could be potential locations for water deterioration.

The addition of condensed tannin to the EG liquefied wood adhesive mixtures did not contribute significantly to higher shear strength values of the adhesive bond. This could be due to the high viscosity of the adhesive mixture containing tannin, and, consequently, poor penetration and anchoring. It could also be due to the low solubility of the tannins in the liquefied wood, which has a very low pH value (less than 1).

As the curing mechanism and the rate of crosslinking at the given curing conditions (200 °C, 900 s) of the liquefied wood adhesive mixtures is not known, it should be investigated in the future.

The wood surface was considerably deteriorated in the area where the adhesive had been applied, which was probably the consequence of either liquefaction of the wood tissue due to very low pH of the adhesive mixture. The wood surface had, therefore, much lower shear strength values than normal (unaffected) wood,
and a higher percentage of wood failure (Figure 3). The latter is, apart from poor water resistance, the main problem that needs to be worked on.

3.4 FT-IR analysis

Fourier transform infrared spectroscopy (FT-IR) was used to investigate and compare samples of LW1:1 and LW1:1/CT (85/15). Both samples were also cured (cured LW1:1 and cured LW1:1/CT (85/15)) and their spectra were investigated. A comparison of all four spectra is shown in Figure 4. It can be seen that spectra corresponding to LW1:1 and LW1:1/CT (85/15) are almost indistinguishable, which is proof that there were no new functional groups in the LW1:1/CT (85/15) adhesive mixture.

After curing, the spectra of the LW1:1 and LW1:1/CT (85/15) mixtures changed. If the focus is placed on changes in peaks, then the most evident changes was at 1120 cm⁻¹, which could correspond to the reduction of \(-OH\) groups after curing (evaporation and reaction of the solvent) (Budija et al., 2009) or \(C-O\) stretch in the cellulose (Pandey and Pitman, 2003). Reduction of the peak at 1050 cm⁻¹ can be associated with \(C-O\) stretch in the cellulose (glucose) (Morohoshi, 1991; Ibrahim et al., 2006; Gierlinger et al., 2008), and reduction in the peak at 883 cm⁻¹ can be linked to antisymmetric out-of-phase stretching of cellulose (Morohoshi, 1991). All three peak reductions correspond to changes in the cellulose, or a reduction in the number of hydroxyl groups, which is a reasonable explanation and the consequence of curing.

New peaks around 1090 cm⁻¹ and 1020 cm⁻¹ correspond to \(C-O\) ether vibrations (Budija et al., 2009). This indicates the presence of new compounds after curing. A comparison of the spectra of the cured LW1:1 and LW1:1/CT (85/15) is shown in Figure 5. It explains the possible differences due to the addition of condensed tannin. Both spectra are rather similar, but with three differences in the fingerprint region. Reduction of the peak at 1242 cm⁻¹ could either be associated with a syringyl ring and C-O stretch in the lignin and xylan (Pandey and Pitman, 2003), or C-H and \(-OH\) deformation and \(C-O-C\) stretching vibration of the cellulose (Morohoshi, 1991; Gierlinger et al., 2008). The peak around 1065 cm⁻¹ is attributed to pyranose ring stretching (Bouchard, 1990). The absorption at 853 cm⁻¹ is associated with C-H out-of-planes in positions 2, 5 and 6 of the G lignin units (vanillin) (Faix, 1991). It can be clearly seen that the latter absorption peak and the peak at 1242 cm⁻¹ disappeared during the LW1:1/CT (85/15) curing. This means that during the curing of the LW1:1/CT (85/15) sample, vanillin and syringyl units of lignin, xylan or parts of cellulose could interact with the other functional groups or molecules. Despite the mentioned changes in the FT-IR spectra of the cured LW1:1 and LW1:1/CT (85/15) samples, the effect of the addition of tannin to LW cannot be confirmed, which also coincides with the results of the shear strength test.

4 CONCLUSIONS

The bonding properties of low solvent content liquefied wood, with the addition of condensed tannin, have been investigated. It was determined that the mass...
The influence of solvent content in liquefied wood was investigated. A ratio between the solvent and wood of 1:3 during liquefaction for 120 minutes at 180 °C was optimal in terms of the highest liquefaction yield achieved. The preparation of this low solvent liquefied wood was performed with ethylene glycol evaporation at 120 °C and at reduced pressure. The final mass ratio obtained between the solvent and wood was 1:1. The hydroxyl group number of the low solvent LW1:1 was reduced to almost one half of the LW1:3 hydroxyl number after the evaporation of ethylene glycol. The specimens bonded with
liquefied wood (LW$_{1:1}$ and LW$_{1:3}$), and the liquefied wood with added condensed tannin, were tested for shear strength. It was found that the evaporation of ethylene glycol contributed to better durability of the adhesive bonds. The addition of condensed tannin did not contribute essentially to better durability or higher adhesive bonds. The addition of condensed tannin did not contribute to an improvement in shear strength. The specimens did not fulfill the requirements of the standard EN 12765 for any of durability classes. FT-IR spectra of the low solvent content LW, with and without the addition of condensed tannin, were investigated. Some minor differences among spectra were observed. The presence of new functional groups was not confirmed. The results of this study indicated that LW containing less EG (a mass ratio of 1:3), and that the addition of condensed tannin, were tested for durability of the liquefied wood (LW$_{1:1}$ and LW$_{1:3}$), and the liquefied wood with added condensed tannin, were tested for shear strength. It was found that the evaporation of ethylene glycol contributed to better durability of the adhesive bonds. The addition of condensed tannin did not contribute essentially to better durability or higher adhesive bonds. The addition of condensed tannin did not contribute to an improvement in the bonding quality.

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