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The influence of tannin on the improvement of adhesive properties of urea-formaldehyde resin

ABSTRACT

The aim of this study was to examine the properties of urea-formaldehyde (UF) adhesive with the addition of tannin, in order to determine whether it is possible to obtain so-called, bio-adhesives for wood with better mechanical properties compared to commercial UF. Tannin-based UF resins, with four different concentrations of tannin (5, 10, 15, and 20%), were prepared, and adhesive properties were tested and compared with properties of pure UF. Testing of tensile shear strength showed that the addition of tannin in UF adhesive formulation significantly increases its performance compared to pure UF adhesive. It was found that tensile shear strength increased with increasing concentration of tannin, while UF-tannin adhesives with tannin concentrations of 15% and 20% showed higher tensile shear strength than the corresponding pure UF adhesive. Therefore, it can be concluded that tannin-based UF adhesive can be a good candidate for application as an environmentally-friendly wood adhesive due to improvement in terms of adhesive and mechanical properties.

Keywords: *wood adhesive, UF resin, tannin, bio-adhesives***,** *wood-based composites*

1. INTRODUCTION

Phenolic resins are the first synthetic polymers whose industrial production started at the beginning of the 20th century [1]. Today, these resins have found their widest application in the wood industry. With the increase in the number of inhabitants on earth, the consumption of wood-based products is also increasing every day. Conventional wood adhesives based on formaldehyde (phenol-formaldehyde (PF), urea-formaldehyde (UF) and melamine–formaldehyde (MF)) have a wide use (even though formaldehyde is classified as highly carcinogenic), mostly because of their durability, moisture resistance, low cost, and gap-filling properties. This especially applies to urea-formaldehyde (UF) due to its characteristics such as good binding properties and high reactivity [2], but these resins also have certain disadvantages such as poor water resistance and formaldehyde emission (FE) [3].

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These synthetic resins are widely used in the production of wood-based panels thanks to their low cost and good reactivity, but their fossil origin and formaldehyde content have increased the interest in resin synthesis studies with the use of bio-based materials [4]. In recent years, the emphasis has been placed on the so-called "green" approach in the adhesive industry, so many plant sources, like tannins, have been used to make bio-based adhesives, even epoxies [5].

Tannins are polyphenols present in plant species and are widespread in nature [6], with a significantly higher extraction potential than lignin [7]. Tannins have an antibacterial and antifungal effect. Vegetable tannins have been used to tan leather for thousands of years [6]. Tannins are also used in enology (during winemaking) to give color stability, and protection against oxidation, odor, and flavor [8]. Due to their natural origin and broad availability, the application field of tannins is spreading from pharmacy and adhesives to solid biofuels. Tannin is one of the most studied raw materials to synthesize bio-based wood adhesives due to its chemical structure and availability [9]. Tannin-formaldehyde resins have been commercially available for several years and are characterized by very low formaldehyde emission (FE) and fast pressing times.

The term natural plant tannin refers to two broad classes of chemical compounds, condensed or polyflavonoid tannins and hydrolyzable tannins [6]. Although tannins have limitations, wood adhesives based on condensed tannins are intensively studied because of their moisture resistance [10], unlike hydrolyzable tannins.

Compared to hydrolyzable tannins, condensed tannins show greater reactivity with formaldehyde resulting in reduced formaldehyde emissions (FE), making them one of the most researched wood glue precursors [11]. Tannins applied with synthetic adhesives also act as formaldehyde scavengers in phenol-formaldehyde (PF), melamine-formaldehyde (MF), and UF resin [12].

Tannin is considered an additional component that can be mixed with typical UF resins in different ratios [14] to make bio-adhesives with very good adhesion and moisture tolerance [13]. The addition of tannin causes lower formaldehyde emission, even though too much tannin can cause gelation, but also improves the bonding properties and water resistance of conventional UF resin [15].

In this work, new adhesives based on UF resin and tannin were prepared and tested for application as wood adhesives. The influence of different concentrations of tannins on the properties of the commercial UF adhesive was examined by measuring the shear strength of the tested samples.

2. EXPERIMENTAL

2.1 Materials

In this study, we used a commercial UF resin provided by a domestic company (Serbia). Tannin sodium salt was purchased from CHIMAR HELLAS SA (Greece). Ammonium chloride was purchased from Centrohem (Serbia). Beech (*Fagus sylvatica*) logs were selected from a known locality and growth conditions (Goč Mountain, Serbia), and then primary boards (with the desired orientation of growth rings) were cut.

2.2. Tensile shear strength determination

2.2.1. Preparation of wood samples

The sawn timber was dried in a semi-industrial conventional kiln (Nigos MC 3000, capacity 0.8 m^3). The most homogeneous groups of testing samples were selected for further experiments.

2.2.2. Preparation of UF-tannin adhesive

At the beginning of this experiment, we determined the solid content of UF resin as important data for further adhesive formulations and analyses. Every formulation was prepared in concentration calculated using solid weight relative to UF resin solid content. A 20% ammonium chloride salt solution was used as a hardener for all samples (in the concentration of 1% w/w). One group of samples, with pure UF resin, was used as a control group while tannin was added to the others in concentrations of 5, 10, 15, and 20%, respectively, by weight.

2.2.3. Characterization of UF adhesive

Adhesives obtained in this research were performed according to the following standards: determination of pH (SRPS EN 1245:2012); determination of density (SRPS EN 542:2009); determination of conventional solids content and constant mass solids content (SRPS EN 827:2009); determination of tensile shear strength of lap joints for wood adhesives (SRPS EN 205:2017); and adhesives were classified according to the standard for the classification of thermosetting wood adhesives (SRPS EN 12765:2017).

The gel time of the resins containing ammonium chloride as hardener was determined by the boiling water test. The time measurement began when a test tube containing approximately 2.0 g of resin together with the hardener ammonium chloride (1 % based on the adhesive dry matter) was immersed in boiling water. The resin in the test tube was gently stirred throughout the test. The gel time was taken as the time elapsed from immersion of the test tube until hardening of the resin, when stirring was no longer possible.

The FTIR-ATR spectra were obtained with an FTIR spectrometer (iS20, Thermo Nicolet) with a resolution of 4 cm^{-1} in the wavelength region 4000–525cm^{-1}, using a diamond single reflection attenuated total reflectance (ATR). All spectra were obtained with 32 scans and the background measurement was made using air.

2.2.4. Determination and optimization of glue-line quality

The adhesive mixes were applied by a rubber roller onto one surface of the two wood specimens to be bonded (200 g/m^2). Assembling was always performed in a parallel grain direction. The ply without direct application of the adhesive mix was always in the bottom position to improve the penetration into its structure. Again, a special effort was made to have the taper as low as possible, guaranteeing equal penetration conditions for all samples. Ten joint samples were pressed in a hydraulic press at 120°C and 1.5 MPa for 15 minutes. Before testing, the single lap shear test specimens (150 mm × 20 mm × 5 mm) were conditioned at 20 ± 2°C and 65 ± 5% relative humidity for one week. The lap shear test was conducted according to SRPS EN 205 standard test on a hydraulic test machine (Wood tester WT4) with a measuring scale of 50 kN at a testing speed of 6 mm/min loading rate in tensile mode with the load direction always parallel to the grain in all tested specimens. The failure zone (shear area 20 mm × 10 mm) was examined using a light microscope to determine the proportion of wood failure and the thickness of the wood layer in the wood failure. Ten replications were performed for each set of parameters. An analysis of variance was applied to obtain centralized values and standard errors.

3. RESULTS AND DISCUSSION

For any type of bio-based wood adhesives, it is important to effectively evaluate their prospects for wood composite application and understand the adhesive/wood interaction to gain scientific insights to guide the adhesive development in terms of the mechanical strength, water resistance, thermal and rheological properties of the adhesives, as well as the adhesive penetration. To interpret the measured bonding strength of wood adhesives, it is also essential to take into consideration the type of failure or separation that occurred in the mechanical tests. There are four main types of failure modes for the adhesive bonded wood composites: (a) cohesive failure of the adhesive; (b) adhesive failure (c) mixed failure - a combination of (a) and (b), and (d) wood cohesive failure or wood failure.

UF adhesive is the most important adhesive in the wood industry, especially in the production of wood-based panels, primarily because of its relatively good characteristics and low price. However, considering that it has poor water resistance and high formaldehyde emission, it is necessary to make some modifications to the chemistry of the glue itself in order to make it more environmentally friendly. Herein, we prepared modified adhesive formulations based on commercial UF resins (UF), cured alone (cUF) and with tannin (labels UFT5, UFT10, UFT15, and UFT20 correspond to samples with 5, 10, 15 and 20% of tannin added to UF). The maximum tannin concentration of 20% was chosen because in the case of higher tannin concentration, it was hard to achieve homogeneity of the adhesive system due to its high viscosity, and consequently, the application on the wood surface was difficult. Their adhesive properties were evaluated following the change in shear strength of samples with different tannin content.

Commercial UF resin was characterized and its technical specifications are given in Table 1. Properties, such as solid content, density, pH, viscosity, free formaldehyde content, and gel time were determined (Table 1).

Table 1. The technical properties of UF resin

Sample	Property					
	Solid content (wt%)	Density (g/cm^3)	Gel time (s)	pH	Free-F (wt%)	Viscosity, F^4_{20} (s)
UF	68	1.290	71	8.0	0.14	84

3.1. FTIR analysis

Fourier transform infrared (FTIR) spectroscopy was used to characterize the chemical structures of the resins. The obtained FTIR spectra of commercial UF adhesive emulsions examined in this work are given in Figure 1 for UF adhesive emulsion and for cured cUF resin. The following four spectra given in Figure 2 are for cured resin with tannin addition of different concentrations, respectively: a) 5%, b) 10%, c) 15%, and d) 20%.

The wide bands at 3321 cm^{-1} are related to the stretching vibration of O–H and N–H and originate from the presence of by-products such as water and excess formaldehyde that can hydrogen bond to the CH_2OH, NH_2, and NH functional groups present in the UF resins and their intensities decreased in cured samples, as it was expected. A sharp but small peak occurring at 2959 cm^{-1} arising from the stretching C–H vibrations originated from dimethylene ether bonds (CH_2–O–CH_2), hydroxymethyl (CH_2OH) and methylene bonds (N–CH_2). The characteristic bands that appear at 1629, 1531, and 1243 cm^{-1} represent amide I (C=O stretching vibration in –CONH), amide II (stretching vibration of C-N and deformation of vibration of N-H in NH-CO), and amide III and all amide bands become broader after curing. The peak at 1457 cm^{-1} of methylene bonds (–CH_2–) which appear only as a shoulder in UF emulsion broadens and becomes stronger after curing leading to the conclusion that the resulting resin contains more methylene bridges liberating formaldehyde for further crosslinking. The methylene ether bridge (–CH_2–O–CH_2–) characteristic absorption peak at 1129 cm^{-1} ascribed to the C–O stretching vibration of hydroxymethyl decreases after curing compared with UF resin, as well as the peak at 1011 cm^{-1}, assigned to v(C–O–C) of ether linkage indicated additional crosslinking probably due to the transformation of unstable ether bridges (–CH_2–O–CH_2–), initially formed, to methylene ones (–CH_2–). On the contrary, the weak band at 1361 cm^{-1} in UF emulsion, broaden after curing. This area of UF polymer spectra is usually assigned to C–H vibrations in CH_2 and CH_3 structures. A small peak at 767 cm^{-1} which appears in cured samples is the characteristic absorption peak of the uronic structure that is formed.

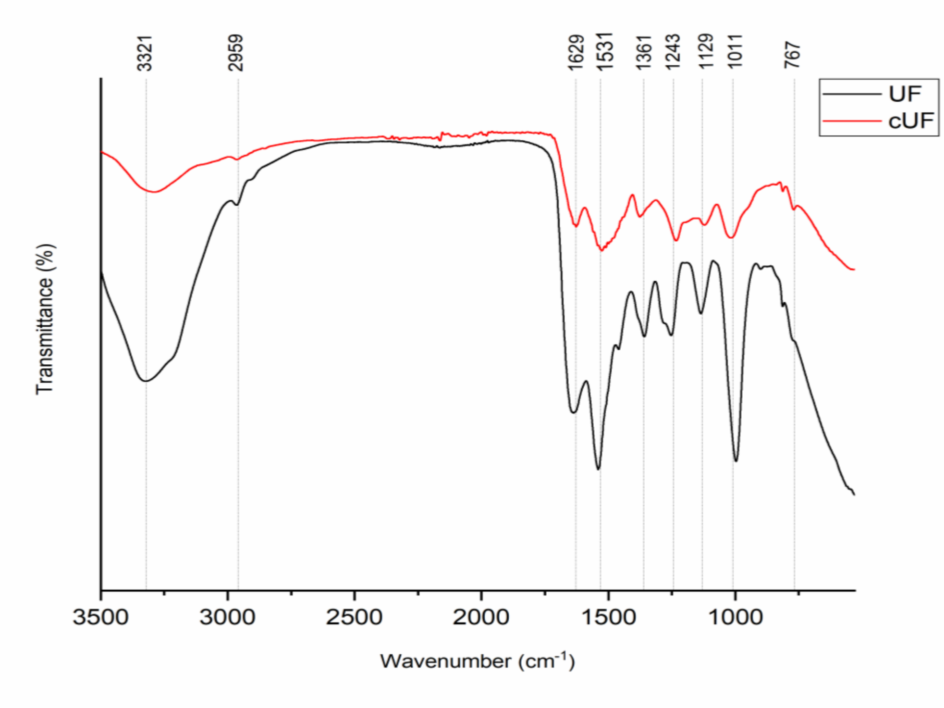

Figure 1. FTIR spectra of pure commercial UF resin and cured adhesive (cUF)

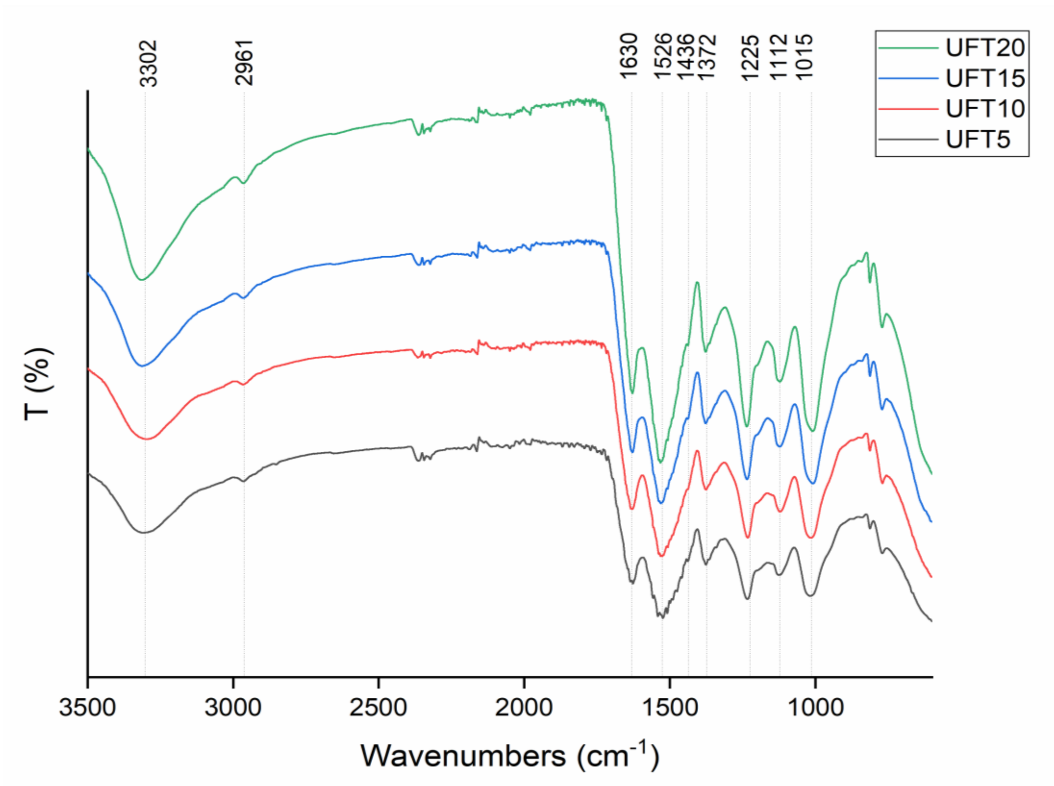

Figure 2. FTIR spectra of cured UF adhesive with different tannin concentrations: 5%, 10%, 15%, and 20%

According to FTIR analysis of UF resin cured after tannin addition, all amid bands did not show significant change. The peak at 1436 cm^{-1} indicates the presence of methylene linkages and increases with tannin percentage. However, characteristic absorption peaks at 1112 cm^{-1} (–C–O stretching vibrations) and 1015 cm^{-1} originated from the methylene ether bridge ($–CH_2–O–CH_2$) that belong to the C–O stretching vibration of hydroxymethyl increased with increasing tannin concentration indicating the reaction of UF resin and tannin and formation of new ether linkages. Similarly, the weak band at 1361 cm^{-1} (–C–H vibrations in CH_2 and CH_3 structures), broadens with increased tannin concentration. This area of UF polymer spectra is usually assigned to C–H vibrations in CH_2 and CH_3 structures. The spectra of all UFT samples indicated a greater amount of ether and methylene linkages compared to pure UF resin which increased with the addition of tannin.

3.2. Tensile shear strength determination

The tensile shear strengths of examined adhesives are shown in Figure 3. The tensile test results of the samples demonstrated that the resin mixed with tannin (10, 15, and 20% by weight) had better performance than the corresponding pure UF resin. Compared to pure UF resin, shear strength was slightly lower in the case with 5% tannin addition but increased with every higher content of tannin. Some authors showed that the addition of tannin to UF resins in particleboards appears to decrease formaldehyde emission over some time proportional to the amount of tannin added but the improvement of the strength performance caused by the denser cross-linking was offset by the decrease of the amount of UF resin [16]. In that case, the formaldehyde emission of tannin-UF resin decreased but the bonding strength was also decreased compared with pure UF resin. Additionally, Zanetti et al. [17] used condensed tannins to improve the heat resistance of UF resins and the result showed that a high percentage of tannin in a UF-tannin blend improves the overall UF thermal resistance to a great extent. However, in this study, tannin was used to substitute some of the UF resin, to reduce formaldehyde emission and to produce an environmentally friendly wood adhesive along with enhanced adhesive properties. The higher shear strength of UFT compared to UF might be the result of better water resistance of the product arising from the reaction between tannin and UF resin.

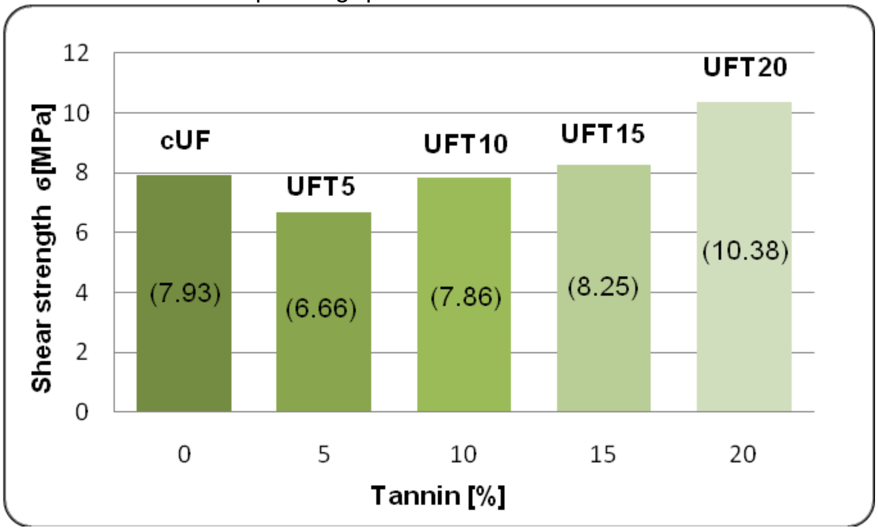

Figure 3. Tensile shear strength of beech wood samples with cured pure UF adhesive (cUF) and samples with added tannin in different concentrations (UFT)

The diverse types of failure after completion of the adhesion tests i.e., cohesive, adhesive, and substrate failure, were considered by analysing the surface of both specimens through high-resolution imaging. Cohesive failure was considered when both samples presented adhesive on the overlapping surfaces; adhesive failure means that only one of the overlapping surfaces had adhesive, whereas substrate failure indicates breakage of the substrate itself so that the bonding surface was not altered. Examination of the failure showed that all samples had a 100% fracture through the wood (Figure 4). The mode of failure is important to take into consideration when discussing the strength of wood adhesives. If the adhesive is stronger than the wood itself, the wood fibers in contact with the adhesive are ripped off. Thus, regarding wood adhesives, wood failure is preferred to obtain well-bonded and high-performance wood composites.

Figure 4. The failure zone of all sample groups: (a) cured pure UF, (b) UF cured with 5% tannin, (c) UF cured with 10% tannin, (d) UF cured with 15% tannin and (e) UF cured with 20% tannin

4. CONCLUSION

Wood adhesives based on UF resin and tannin were prepared (using different concentrations of tannin – 5, 10, 15, and 20%) and characterized and their adhesion properties were investigated to determine their potential as wood adhesives. The main goal of this study was to determine if natural adhesive materials, presented above, can significantly reduce the negative environmental impact of formaldehyde emissions and provide better performance of the adhesive. FTIR results confirmed the reaction between UF resins and tannin due to increased content of ether and methylene linkages. The addition of tannin improved crosslinking in UF resins. Based on characterization results, it was found that tensile shear strength increased with increasing concentration of tannin, while UF-tannin adhesives with tannin concentrations of 15% and 20% showed higher tensile shear strength than the corresponding pure UF adhesive. It was shown that a tannin content of 20% in UF adhesive formulation gave the best performance compared to the one with 5, 10, and 15%, even compared to pure UF adhesive. Therefore, the general conclusion after the experiment is that UF adhesives with the addition of tannin could be used as "green", environmentally-friendly wood adhesives that can show much better characteristics than pure UF in terms of adhesion and mechanical properties.

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IZVOD

UTICAJ TANINA NA POBOLJŠANJE ADHEZIVNIH SVOJSTAVA UREA-FORMALDEHIDNIH ADHEZIVA

Cilj ovog rada je bio da se ispitaju svojstva urea -formaldehidnog (UF) adheziva sa dodatkom tanina, kako bi se utvrdilo da li je moguće dobiti bioadheziv sa poboljšanim mehaničkim svojstvima u poređenju sa komercijalnim UF. Pripremljene su UF smole na bazi tanina, sa četiri različite koncentracije tanina (5, 10, 15 i 20%), a adhezivna svojstva su ispitana i upoređena sa svojstvima čistog UF. Ispitivanje zatezne čvrstoće na smicanje pokazalo je da dodavanje tanina u formulaciju UF adheziva značajno povećava njegove performanse u poređenju sa čistim UF lepkom. Utvrđeno je da se zatezna čvrstoća na smicanje povećava sa povećanjem koncentracije tanina, dok su UF-taninski lepkoviadhezivi sa koncentracijom tanina od 15% i 20% pokazali veću zateznu čvrstoću na smicanje od odgovarajućeg čistog UF adheziva . Stoga se može zaključiti da UF adheziv na bazi tanina može biti dobar kandidat za primenu kao ekološki prihvatljiv adheziv za drvo sa poboljšanim adhezivnim i mehaničkim svojstvima.

Ključne reči: *adheziv za drvo, UF smola, tanin, bioadhezivi, kompoziti na bazi drveta*

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