Properties of Pine Bark Tannin-based Adhesive Produced with Various Hardeners

Oktay Gonultas *

Tannin-based adhesives are alternative bio-based products that can be used in the wood panel industry instead of synthetic adhesives that contain formaldehyde. For the production of these adhesives, formaldehyde is utilized generally as a hardener as in its synthetic counterparts. In this study, adhesive formulations were prepared using eight different hardeners and tannin powder from Turkish red pine (*Pinus brutia*) barks. While the shortest gel time values in the adhesive formulations were identified in the samples prepared with formaldehyde and paraformaldehyde, the longest gel time was obtained in the formulation prepared with tris(hydroxymethyl)nitromethane. As a result of the dry bonding tests, the values closest to the commercial UF adhesive were found in descending order as paraformaldehyde, formaldehyde, hexamine glyoxal, and poly[(phenyl isocyanate)-co-formaldehyde] (pMDI). According to the wet bonding strength test results, the adhesive samples in which furfural, tris(hydroxymethyl)nitromethane, and benzaldehyde were used as hardeners did not achieve wet bonding strength. As a result of thermogravimetric analysis (TGA), commercial UF adhesive samples had dramatically lower thermal stability than all of the formulations prepared with tannin. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectral analysis revealed that new chemical bonds were established between the tannin and hardeners.

Keywords: Turkish red pine; Bark tannin; Formaldehyde, Bio-based adhesive; Shear strength; TGA; FTIR

*Contact information: Department of Forest Industry Engineering, Bursa Technical University, Yildirim, Bursa, 16310, Turkey; *Corresponding author: oktay.gonultas@btu.edu.tr*

INTRODUCTION

Turkish red pine has naturally spread in Turkey and is the most important pine species constituting 25% of the total forest area. The wood of this species is intensively used in the forest products industry, and its bark, which is abundant in terms of phenolic extractives consisting of catechin and taxifolin, has an important potential (Uçar *et al.* 2013). Because of the special chemical compounds found in their structure, tree barks are renewable raw materials with an ever-growing significance (Pasztory *et al.* 2016). Tannins that are found in barks and are extractive materials with a phenolic structure have been subject to numerous studies. These secondary compounds have various functions in biological activities, such as toxicity and hormonal structure, and they are known to protect the plant against herbivore animal damage, pathogens, and diseases (Hagerman 2002). In the past, tannins were used intensively to enable the raw leather to become non-degradable, flexible, and stable against bacterial degradation by tanning. Moreover, they are biocompounds used in medicine and pharmacology due to their antiviral, antimicrobial, and antioxidant features in formulations of various herbal medicines (Bisanda *et al.* 2003; Feng *et al.* 2013).

Apart from these areas of usage, tannins can be utilized in the paint industry, ink production, the coloring of textile products, for corrosion inhibition in metals, beer and wine clarification, and in chemical industry applications (Bisanda *et al.* 2003; Pizzi 2016). Tannins are natural phenolic substances that give a precipitation reaction with alkaloids, gelatin, and other proteins. Such reactions produce various colors ranging from light brown to white, and are in amorphous powder form with an interesting odor and acrid taste (Khanbabaee and Ree 2001; Gonultas and Ucar 2012). Especially in recent years, mimosa tannin obtained from the barks of the *Acacia* species and quebracho tannin obtained from the heartwood of the *Schinopsis* species have been the subjects of various research in different areas. In particular, after the 1970s, tannin-based bio-adhesives have been produced for the forest products industry, and currently these products have become commercial (Pizzi 2016). Recently, tannin-based biocomposites and rigid foams have started to be developed (Brosse and Pizzi 2017).

A big part of the adhesives used in the wood panel industry are being produced as a result of the reaction of formaldehyde with urea, phenol, and melamine (Pizzi and Mittal 2003). The panels produced with this type of adhesive cause carcinogenic formaldehyde emissions, which are known to have negative effects on human health in their service life. Tannin-based adhesives are systems generally formed with the polycondensation of tannin and formaldehyde. However, due to the high reactivity of tannins against formaldehyde, these adhesives are prepared with less formaldehyde with respect to their counterparts (Pizzi 1994). Therefore, adhesives with a fairly low formaldehyde emission can be produced by using tannin-based adhesive systems. Besides these, phloroglucinol-type pine tannins give fast reactions with formaldehyde when compared with resorcinol-type tannins. Hence, the gel time and shelf life of the obtained adhesive are rather short (Pizzi and Mittal 2003). Studies evaluating new hardeners that are nontoxic and do not contain aldehyde are being conducted to completely eliminate formaldehyde emission, achieve short gel time, and overcome shelf life problems in this type of adhesive (Kim and Kim 2003; Moubarik *et al.* 2010; Zhou and Pizzi 2014; Pizzi 2016; Brosse and Pizzi 2017; Tondi 2017; Zhang *et al.* 2017).

The aim of this study was to prepare adhesive formulations by using Turkish red pine bark tannin that was obtained by hot water extraction and spray drying, and with various hardeners such as formaldehyde, paraformaldehyde, hexamethylenetetramine (hexamine), glyoxal, furfural, poly[(phenyl isocyanate)-co-formaldehyde] (pMDI), tris(hydroxymethyl)nitromethane (tris), and benzaldehyde. The bonding performance, thermal properties of the prepared adhesive formulations, and chemical (ATR-FTIR) behaviors were determined, and then results were compared with the formulation prepared with the mimosa tannin and commercial urea formaldehyde (UF) adhesive.

EXPERIMENTAL

Materials

In this study, Turkish red pine (*Pinus brutia*) barks obtained from the Mersin district (Mersin, Turkey) were utilized as the raw material. Bark samples were cleaned from the wood pieces inside and other impurities (stone and metal pieces, moss, leaves, and plastics) were kept at room temperature for a few weeks, and then they were dried to reach 10% to 12% moisture content.

Afterwards, the samples were cut into pieces in 3-cm thickness sizes appropriate for grinding. Later, they were ground in the Wiley mill with a 1 mm screen. The milled bark samples (without screening) were extracted with hot water for 1 h, at an extraction temperature of 70 °C in the ratio of 1:8, bark:water (w:w). Then, the water of the tannin solution was separated using a BUCHI B-290 mini spray dryer (BÜCHI Labortechnik AG, Flawil, Switzerland) and tannin powder was obtained. The tannin was obtained under the spray dryer conditions of 165 °C inlet temperature, 70 °C outlet temperature, and the solution feed was 0.5 L/h.

The commercial UF adhesive was provided from Balıkesir facilities of Kastamonu Integrated Wood Industry and Trade Company (Kastamonu, Turkey) and the mimosa tannin was obtained from Silva Chimica Italy (San Michele Mondovì, Italy). All of the chemicals used were of analytic grade.

Methods

Tannin analyses

After 1 h extraction, the suspension was filtered under reduced pressure, and the residue was repeatedly washed with water. The solid content of the extract (with water washings) was determined, and extraction yield was calculated as the percentage of the amount of extract recovered to initial mass of dry bark. The Stiasny number of the tannin samples was carried out through the precipitation of diluted tannin extract through its reaction with HCl (Yazaki and Hillis 1977). Methanol water solubility evaluation was carried out to demonstrate that the spray drayed tannin powder had completely soluble composition without wood and bark impurities.

The solubility test was executed in samples as stated by Balaban and Uçar (2001). The determination of the total phenol content in the samples was conducted according to the Folin-Ciocalteu method developed by Singleton and Rossi (1965). The condensed tannin amount was determined by the Butonal-HCl method, and the results were expressed in cyanidin equivalents (CyE) (Govindarajan and Mathew 1965). The tannin and non-tannin part in the samples were determined with the hide powder method (Roux 1951; Gordon-Gray 1957; Galvez *et al.* 1997).

The preparation of adhesives and determination of properties

The ratios of tannin/hardener in the adhesive formulation were determined as in previous works (Tondi 2001; Trosa and Pizzi 2001; Kim and Kim 2003; Zhou and Pizzi 2014). The tannin solution (40% solids) was placed in a glass reactor, and the hardener was added into the reactor. Then, the mixture was stirred at room temperature for 20 min. and another 20 min. at 60 °C. After that the mixture was cooled to 25 °C. The gel time in the bio-adhesive samples was determined in accordance with Pizzi and Stephanou (1994). The solid content was determined according to BS 5350-B2 (1976). The viscosity of the bio-adhesive produced was measured in a Brookfiled DV-II+pro (Middleboro, MA, USA) viscosimeter, CPE-52 cone spindle at 25 °C in an adhesive of 0.5 mL at a speed of 50 rpm. A Hanna 2211-05 pH meter (Hanna Instruments, Ann Arbor, MI, USA) was used for the determination of the bio-adhesive's pH assignment. The densities of the samples were determined by using a calibrated glass pycnometer (Isolab, Germany) at 25 °C.

Adhesive bonding tests

Within the scope of the study, the bonding performance of the bio-adhesive prepared using pine tannin and various hardeners was determined with the lap shear test as described previously (Moubarik *et al.* 2009; Zhao *et al.* 2010). As control samples, these were compared with lap shear samples prepared with commercial UF adhesive. The UF adhesive was catalyzed by 10% ammonium chloride in water. For this purpose, flawless beech (*Fagus orientalis*) veneer with 3 mm thickness, 25 mm width, and 115 mm length were used. Veneer samples were kept at a temperature of 20 °C and at 65% relative humidity for a week and were conditioned before their use. Lap shear test samples are given in Fig. 1.

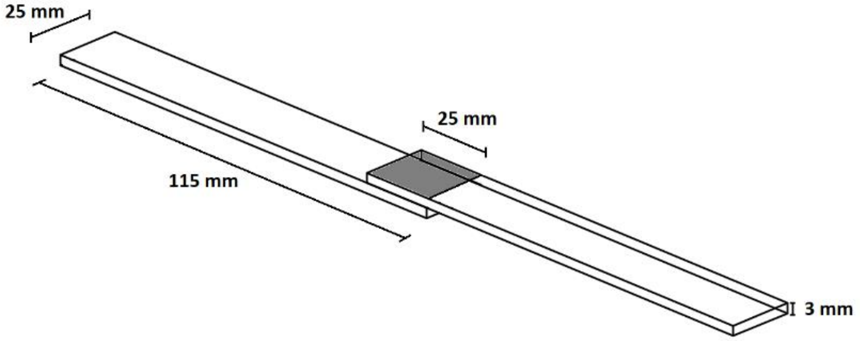

Fig. 1. Lap shear specimen dimensions

An adhesive of 0.019 to 0.024 g/cm^2 was applied to one side of the veneers in an area of 25 mm × 25 mm and was attached with the veneer that was not applied with adhesive. The obtained two-layered test sample was pressed (4 MPa) for 4 min. at a temperature of 140°C with metal thickness control rods with 4.5 mm thickness using a laboratory-type Carver (3639 Bench Top; Carver Inc., Wabash, IN, USA) hot press. At the end of the process, the samples were cooled and conditioned at a temperature of 20 °C at the relative humidity of 65% for two weeks. The tensile strength of the samples was determined using a universal test machine (Shimadzu AG-IC, Shimadzu Corporation, Kyoto, Japan) with a tensile speed of 3 mm/min. Prior to the wet tensile tests, the samples were soaked in water of 20 °C for 24 h. Samples were tested after drying the surfaces with paper towels at the end of the process. For each sample, the average values of 10 tests have been given.

Thermal analysis

Thermogravimetric analyses (TGA) were conducted to determine thermal degradation and stability properties of the adhesives produced by using Turkish red pine tannin (TP) and different hardeners. For this purpose, approximately 10 mg of adhesive was heated in a nitrogen gas atmosphere with a 5 °C/min heating speed from 30 °C to 600 °C through the use of a Hitachi STA 7200 TG/DTA (Hitachi, Tokyo, Japan) system.

ATR-FTIR analysis

The adhesive samples were dried at 50 °C for 12 h in a hot oven. Afterwards, FTIR spectrums of the ground powdered samples were conducted using the Bruker Tensor 37 device (Bruker Optik GmbH, Ettlingen, Germany) to examine the functional groups in their structures. It was performed at a wavelength between 4000 and 400 cm^{-1}, with a resolution of 4 cm^{-1} and 32 repeated measurements. The evaluation of the spectrums was carried out by using the Bruker OPUS software (Burker, Version 7.2, Ettlingen, Germany).

RESULTS AND DISCUSSION

Tannin Analysis

The properties of the tannin samples obtained from Turkish red pine bark are given in Table 1. The yield of tannin extraction from the bark was determined as 31.9%. The Stiasny number of the tannin was 88.7. The extraction yield of tannin from *Acacia* bark was 17.3% and the Stiasny number was 79.9 (Hoong *et al.* 2009). It is known that the Stiasny number should be over 65 for the bark tannins to be successfully used in adhesive applications (Yazaki and Collins 1994). According to these results, it was possible for TP to be utilized successfully in adhesive applications. The tannin solution obtained after the water extraction from Turkish red pine bark showed an acidic characteristic, and it was determined as high purity with 80.6% tannin content. In addition, TP samples were entirely soluble in the methanol-water solution.

Table 1. Properties of *Pinus brutia* Bark Tannin

Extraction Yield (%)	31.86
Staisny Number	88.70
pH	3.74
Total Phenol Content (Ether Phase) (mg/g)	29.89
Total Phenol Content (Aqueous Phase) (mg/g)	20.07
Butanol: HCl Assay (mg/g CyE)	153.59
Hide Powder Method (Tannin / Non-tannin, %)	80.61/19.39
Methanol-water Solubility (%)	100

The Preparation of Adhesives and Determination of Properties

The adhesive formulations prepared with the use of pine tannin and the adhesive formulation prepared by using commercial mimosa tannin are given in Table 2.

Table 2. Experimental Design of Adhesive Formulation

Group	Formulation
PT1	40% Red Pine Tannin Solution + 8% Formaldehyde
PT2	40% Red Pine Tannin Solution + 8% Paraformaldehyde
PT3	40% Red Pine Tannin Solution + 5% Hexamethylenetetramine
PT4	40% Red Pine Tannin Solution + 12% Glyoxal
PT5	40% Red Pine Tannin Solution + 10% Furfural
PT6	40% Red Pine Tannin Solution + 10% PMDI-Poly[(phenyl isocyanate)-co-formaldehyde]
PT7	40% Red Pine Tannin Solution + 12% Tris(hydroxymethyl)nitromethane
PT8	40% Red Pine Tannin Solution + 10% Benzaldehyde
MT1	40% Mimosa Tannin Solution + 8% Formaldehyde
UF1	Commercial Urea Formaldehyde Adhesive
	*Hardeners Based on Oven-dry Tannin

The properties of the bio-adhesive prepared with various hardeners and pine bark tannin and the properties of the commercial UF adhesive and the formulation prepared with commercial mimosa tannin can be seen in Table 3. It was determined that the 40% tannin solution had 98 cP viscosity, 3.82 pH and 1.183 g / cm^3 density values. The shortest gel time for pine tannin was obtained with formaldehyde (52 s) while the longest was with tris(hydroxymethyl)nitromethane (1083 s). The reactivity of pine tannins with the phloroglucinol A ring is known to be rather high (Pizzi and Mittal 2003). The short gel time that occurred in the PT1 sample exposes this situation. Another problem in the adhesive production from the bark tannins is that the viscosity comes out very high for tannin concentrations over 40% (Pizzi and Mittal 2003). Therefore, a tannin solution concentration of 40% was used in the study. The solid content of the adhesive samples prepared was between 40.7% and 44.9%. The solid content was determined as 56.1% in the commercial UF1 sample. The tannin-based bio-adhesives are able to work with adhesives with lower solid content because of its high viscosity at high solid content. Viscosity is another important parameter for tannin-based bio-adhesives. The high viscosity limits the usage area of the adhesive in question. The highest viscosity values were obtained through the use of formaldehyde as a hardener. While the use of hexamine and tris as a hardener resulted in higher values than the commercial UF1 sample, the use of other hardeners showed values similar to the UF sample. The tannin adhesive prepared at pH 7 with radiata bark tannin and 5% hegzamine have 186 cP viscosity and 95 s gel time values (Santos *et al*. 2018). It is also known that there is an inverse relationship between the viscosity value and the gel time in bio-based adhesives (Pizzi 1994). In this study, the samples of PT 1 (52 s) and MT1 (126s) had the lowest gel time values, while the samples had the highest viscosity values (339 cP and 311 cP, respectively). It was reported that the tannin-based adhesives with low gel time and high viscosity has a short shelf life too (Pizzi 1994). While the PT7 sample showed slight alkaline character (pH 8.72), all other adhesive samples were acidic character. When the density values of the samples were examined, the lowest value (1.17 g/cm^3) was found in the formulation prepared with the mimosa tannin. The density in all formulations prepared with pine bark tannin was lower than the commercial UF1 adhesive.

Table 3. Properties of Adhesives

Group	Gel Time (s)	Solid Content (%)	Viscosity (cP)	pH	Density (g/cm3)
PT1	52	41.66	339	6.12	1.191
PT2	133	44.08	197	5.90	1.207
PT3	248	44.89	204	6.75	1.206
PT4	461	42.36	152	5.49	1.215
PT5	556	44.51	127	6.67	1.205
PT6	387	44.71	278	5.93	1.194
PT7	1083	44.48	252	8.72	1.203
PT8	929	43.42	133	6.94	1.193
MT1	126	40.74	311	5.43	1.169
UF1	158	56.13	152	6.11	1.233

Adhesive Bonding Strength

The wet and dry bonding strength values of the test samples belonging to the adhesives prepared with different hardeners are given in Fig. 2. The dry bonding strength in the samples prepared with the commercial UF adhesive (UF1) was 5.28 MPa. For the formulations prepared with Turkish red pine bark tannin, the highest dry bonding strength values were obtained in the PT2 sample with 4.69 MPa and in the PT1 with 4.66 MPa. The dry bonding strengths in samples PT5, PT7, and PT8 were the lowest values for pine tannin and they were 2.42, 2.44, and 2.40, respectively. The dry bonding strength (4.36 MPa) of the MT1 sample prepared using commercial mimosa tannin and 8% formaldehyde was close to the PT1 sample prepared with the pine tannin and 8% formaldehyde. The pyrogallol type A ring of the pine tannin reacts better with formaldehyde. Furthermore, the average polymerization degree of pine tannin (6 to 8) is higher than that of the mimosa tannin (4-5), consequently pine tannin has high reactivity (Pizzi 1994).When the wet bonding strength values of the samples, after soaking in water for 24 h, were examined, the best result was found in the UF control sample (UF1) as 2.63 MPa. The wet bonding strength of the MT1 sample (2.09 MPa) was higher than all of the samples prepared with the pine tannin. The best wet bonding strength value in the adhesives prepared with the pine tannin was determined as 1.89 MPa in the PT1 sample, where 8% formaldehyde was used as a hardener. This value was 1.56 MPa in the PT2 sample (8% paraformaldehyde). Moreover, the wet bonding strength was 1.15 MPa in the sample PT6 (10% pMDI). The wet bonding strengths were 0.26 and 0.14 MPa in the PT3 (5% hexamine) and the PT4 samples (12% glyoxal), respectively. In the wet bonding strength samples prepared using PT5 (10% furfural), PT7 (12% tris), and PT8 (10% benzaldehyde), beech veneers were separated from each other after 24 h.

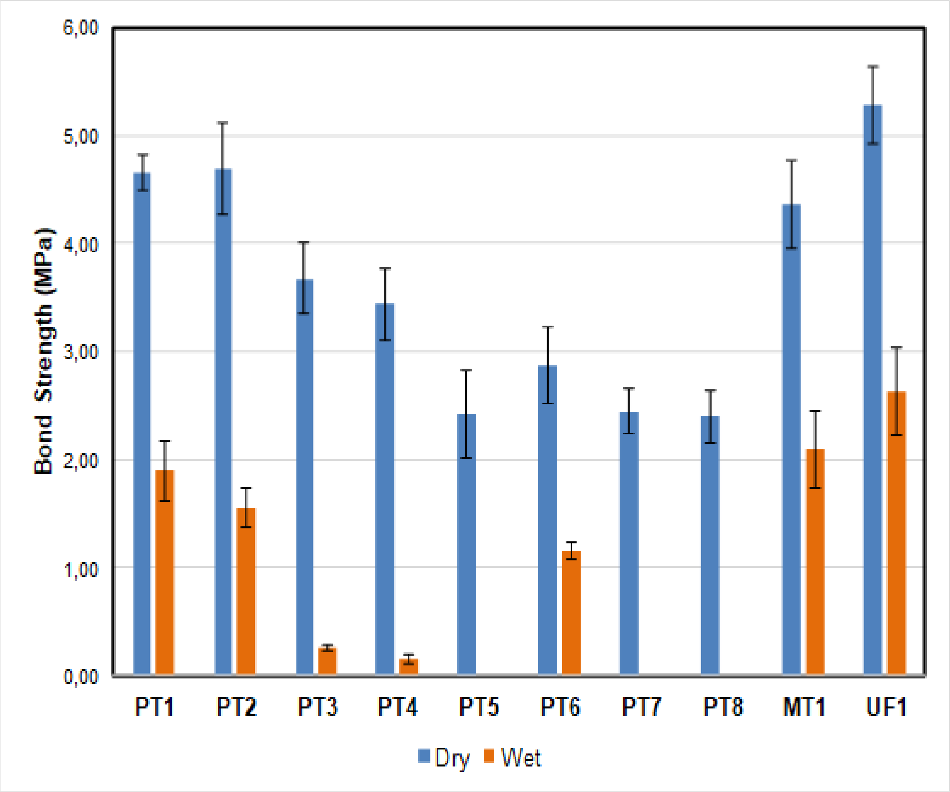

Fig. 2. Bond strength of lap shear specimens

Thermal Analysis

The TGA analysis was conducted for the determination of the thermal degradation and stability properties of the adhesive samples. The TGA curve and its derivative (DTG) were determined in the nitrogen atmosphere in a heating speed of 5 °C/min and are given in Figs. 3 (TGA curves) and 4 (DTG curves). The DTG curves, derivative of mass loss percentage, were used because they showed different degradation processes better in the samples. When the DTG curve was examined, the thermal degradation of the UF1 control sample occurred in three steps at temperatures of 180 °C, 270 °C, and 310 °C, while this event occurred in the adhesive formulations with tannin in two steps. Zanetti *et al.* (2014) have stated similar degradation properties for the UF adhesive and mimosa tannin. The mass loss for the UF1 sample was approximately 70% in 310 °C and mass loss for other samples was approximately 30% to 35%.

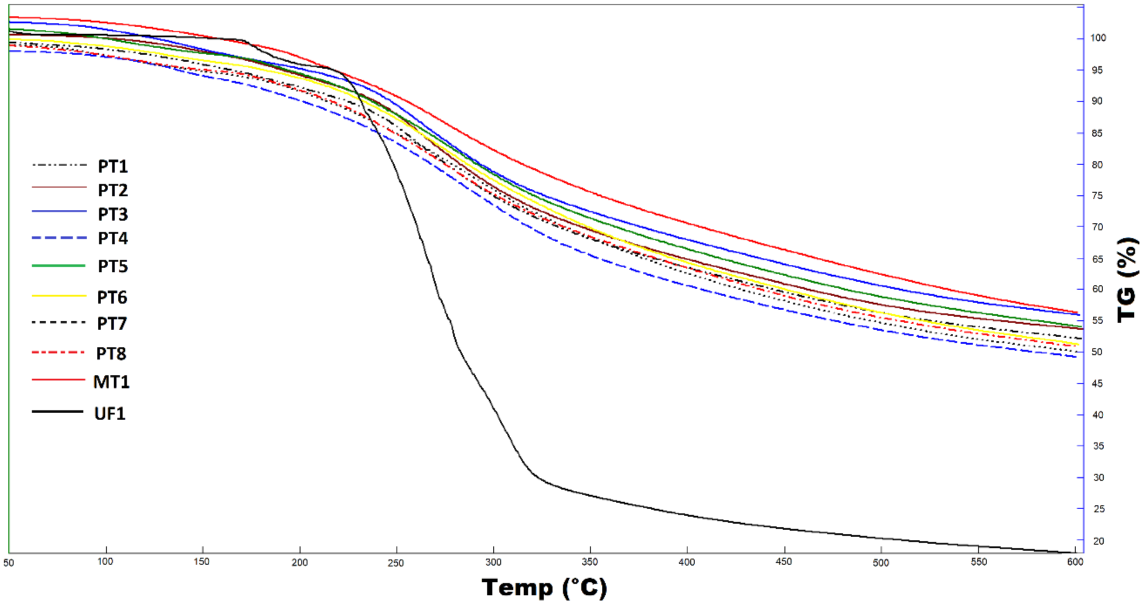

Fig. 3. Thermogravimetric curves of cured adhesives

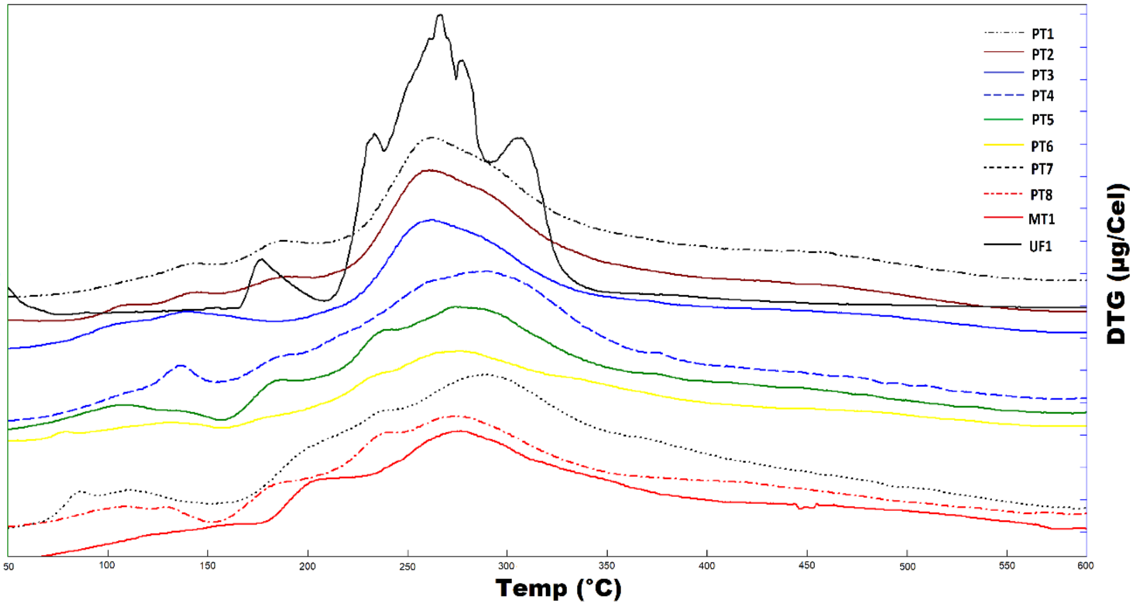

Fig. 4. Corresponding derivative curves of cured adhesives

It was observed that the mimosa tannin had a lower mass loss than all of the samples prepared with TP. This situation could have originated because of the low carbohydrate content of the mimosa tannin sample (Gaugler and Grigsby 2009). Pizzi (1994) reported that the mimosa tannin has 3 to 6% hydrocolloid carbohydrate content while it is 5 to 8%

of pine tannin. For adhesives prepared with the pine tannin, the lowest mass loss values were determined in PT3 and PT5 samples, while the highest mass loss was observed in PT4 sample. The UF1 sample was observed to have a lower onset temperature for degradation than the other samples. With the tannin-based adhesives beginning to degrade over 300 °C, catechols, which are characteristic components, were stated as being formed, and other phenolic compounds originated from the lignified tissues (Moubarik *et al.* 2009). The adhesive samples prepared with tannin showed dramatically better thermal stability than the UF control sample. Additionally, the pressing temperature of 140 °C does not pose a risk of degradation in adhesive formulations with tannin.

ATR-FTIR Analysis

Infrared spectra belonging to the tannin-based bio-adhesive samples, UF control sample, and TP are shown in Fig. 5. The ketone peak was only determined in the PT4 and PT8 formulations at 1730 cm^{-1} (Li *et al.* 2016). While the tension of aromatic C=C bonds gave absorption bands in the region of 1607 to 1448 cm^{-1}, the vibration deformation of C-C bonds in phenolic groups was in the range of 1500 to 1400 cm^{-1} (Özacar *et al.* 2006; Li *et al.* 2016; Tondi 2017).

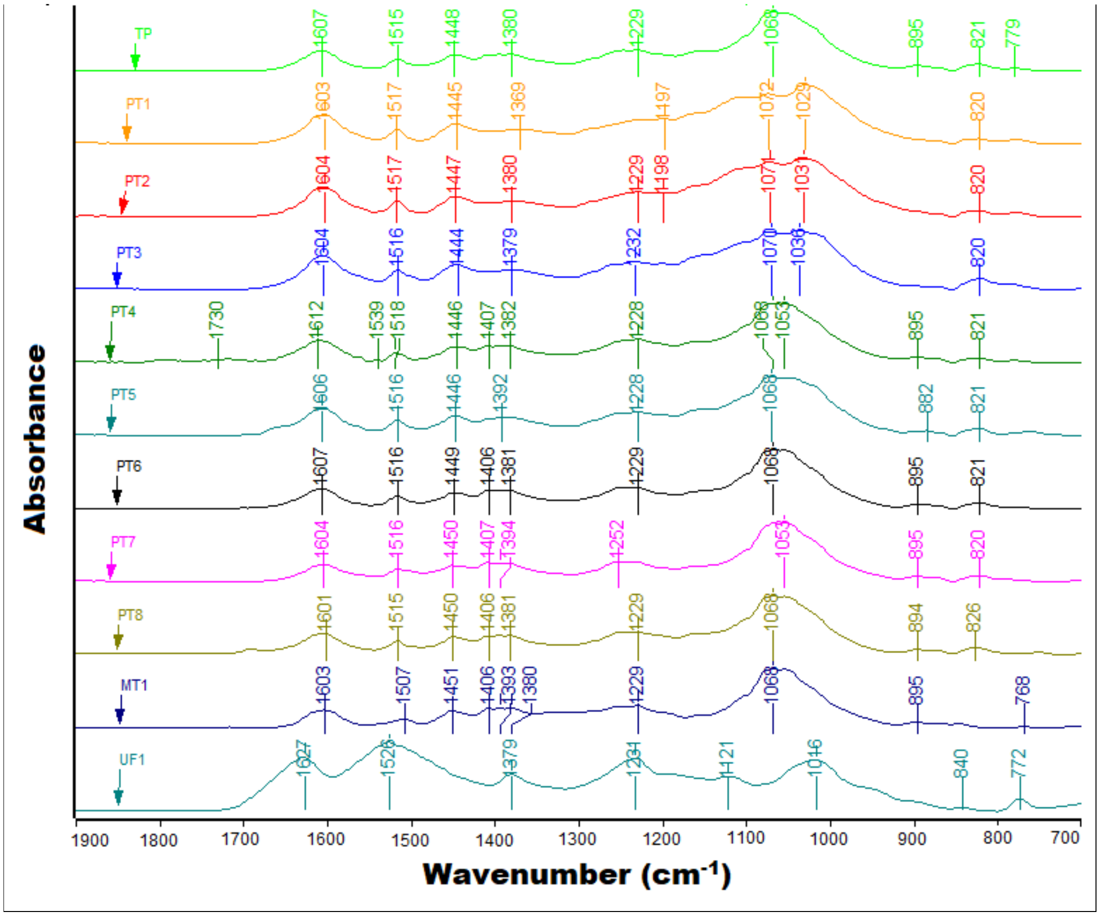

Fig. 5. FTIR spectra of pine tannin and cured adhesives

While the peak strength that occurred at 1607 cm^{-1} in the tannin samples caused a noticeable increase and shift to low wavelength in PT1, PT2, PT3, and PT5 samples, the increases in PT7 and PT8 formulations were limited. This situation was thought result from the polycondensation process of tannin with hardeners (Kim and Kim 2003; Li *et al.* 2016; Zhang *et al.* 2017). The peak, which can be seen in all TP and red pine-based adhesive formulations at 1515 cm^{-1}, showed that the structure of procyanidin was predominant in the tannin in question. This peak can be seen in the MT1 formulations prepared with mimosa tannin. The 1448 cm^{-1} peak observed in the TP sample decreased in the other adhesive formulations and expanded to shift to a high wavelength. This situation is known to be due to formations of CH_2 bridges (Kim and Kim 2003; Li *et al.* 2016). The strength of the peak in the C-O bond at 1603 cm^{-1} increased in the PT1, PT2, PT3, and PT5 adhesives and shifted to a low wavelength. It was stated that this change in peaks may have originated due to the formation of the CH_2-O-CH_2 bonds (Li *et al.* 2016; Zhang *et al.* 2017). The 1038 cm^{-1} peak determined in the PT1, PT2, PT3, PT5, and MT1 samples was thought to be related to the CH_2OH bridges that occurred after the methylation reaction (Li *et al.* 2016; Tondi 2017). It was stated that the deformation tension of C-H bonds exists in the benzene ring at the 910 to 740 cm^{-1} region and this area was lost as a result of the polymerization process of tannin-based adhesive formulations (Kim and Kim 2003; Tondi 2017). This area disappeared to a considerable extent in the PT1, PT2, PT4, PT6, and MT1 samples.

CONCLUSIONS

1. While very short gel time (52 s) and high viscosity (339 cP) were obtained using formaldehyde as a hardener in the adhesive formulations prepared with TP, the gel time was long (1083 s) in the formulation prepared with tris(hydroxymethyl)nitromethane and the lowest viscosity value was identified in the formulation where furfural was used as the hardener. All adhesive formulations showed a slight acidic characteristic except PT7.
2. With regard to the result of the lap shear tests, the results closest to the (MT1) adhesive prepared with commercial mimosa tannin and commercial UF were determined in a descending order in formulations prepared with paraformaldehyde, formaldehyde, hexamine, glyoxal, and pMDI. The only lap shear samples prepared with formulations of furfural, tris(hydroxymethyl)nitromethane, and benzaldehyde did not have wet bonding strength. Additionally, only the formulations in which formaldehyde, paraformaldehyde, and pMDI were used as hardeners exhibited a satisfactory wet bonding strength property.
3. When the Turkish red pine bark tannin and commercial mimosa tannin were compared, formulations of both tannins prepared with formaldehyde possessed similar wet and dry bonding strength properties.
4. At the end of the TGA analysis, all tannin-based adhesive formulations had a higher onset degradation temperature, low mass loss values, and much better thermal resistance properties when compared to the UF control sample.
5. As a result of the FTIR analyses, it was observed that the tannin samples could form new bonds by having reactions with other hardeners as well as their high reactivity against formaldehyde and para formaldehyde.

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