

Synthesis of Bio-Oil-phenol-Formaldehyde Resins under Alkali Conditions: Physical, Chemical and Thermal Properties of Resins and Bonding Performance

Sinteza bioulja s fenolformaldehidnim smolama u alkalnim uvjetima: fizička, kemijska i toplinska svojstva smola i svojstvo lijepljenog spoja

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ABSTRACT • In the present study, bio-oil produced from vacuum pyrolysis of woody biomass has been investigated as a source of chemical feedstock. Bio-based resins were produced using the bio-oil with phenol substitutions ranging from 10 to 30 wt%. The conventional GC/MS analysis was carried out for the evaluation of the chemical composition of bio-oil. TGA, DSC and FT-IR analyses were used in order to characterize the bio-oil-phenol-formaldehyde (BPF) resins. The bonding quality of wood samples bonded with the BPF resins was investigated under different pre-treatment conditions. The highest shear strength was observed for the control samples bonded with the laboratory PF resin. As the amount of bio-oil was increased up to 30 wt%, the shear strength of the samples decreased from 12.08 to 11.76 N/mm². The bonding performance was not negatively affected by the combination of bio-oil under dry conditions. According to TS EN 12765 standard, the relevant performance requirements for bonded samples under dry conditions must be at least 10 N/mm². Relating to the standard, all samples bonded with BPF resins obtained the requirements for durability class C1. Under wet conditions, the bonding performance was negatively affected by the addition of bio-oil. However, the BPF resins fulfilled the durability requirements for C1, C2, and C3 specified in EN 12765 (2002).

Keywords: bio-phenol; bonding performance; phenol formaldehyde resin; shear strength

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SAŽETAK • U radu je predstavljeno istraživanje mogućnosti upotrebe bioulja dobivenoga vakuumskom pirolizom drvene biomase kao izvora kemijske sirovine. Biosmole su dobivene zamjenom 10 – 30 % mase (ili težinskog udjela) fenola biouljima. Analiza kemijskog sastava bioulja provedena je GC/MS metodom. Za karakterizaciju biouljnih fenolformaldehidnih smola (BPF) primijenjene su TGA, DSC i FT-IR analiza. Kvaliteta spoja uzoraka drva slijepljenih BPF smolama ispitivana je pri različitim uvjetima predobrade. Najveća čvrstoća na smicanje postignuta je na kontrolnim uzorcima lijepljenim laboratorijskim PF smolama. S povećanjem udjela bioulja do 30 % mase (ili težinskog udjela), čvrstoća na smicanje smanjila se s 12,08 na 11,76 N/mm². Prema normi TS EN 12765, čvrstoća na smicanje u suhim uvjetima treba biti najmanje 10 N/mm². Kombinacija bioulja s fenolformaldehidnim smolama nije negativno utjecala na svojstva slijepljenog spoja u suhim uvjetima i svi uzorci lijepljeni BPF smolama zadovoljili su zahtjeve klase trajnosti C1. U vlažnim uvjetima dodatak bioulja negativno je utjecao na svojstva slijepljenog spoja. Međutim, BPF smole ispunile su zahtjeve trajnosti za klase C1, C2 i C3 propisane normom EN 12765 (2002).

Ključne riječi: biofenol; svojstva lijepljenog spoja; fenolformaldehidna smola; čvrstoća na smicanje

1 INTRODUCTION

1. UVOD

Currently, the global demand for chemicals is supplied largely from petroleum-based products. Because of the growing concern for the significant environmental problems and reduction of availability of fossil energy resources, researchers have been studying renewable feedstocks to replace petroleum. There are many similarities between biomass and crude oil in terms of their use as chemical feedstocks. Biomass offers viable greener, lower cost alternative feedstock to the chemical production (Gosselink *et al.*, 2004; Bozell, 2002; Yanik *et al.*, 2007; Connor and Piskorz, 1994).

Pyrolysis is thermal decomposition occurring in the nonexistence of oxygen to liquid, gaseous and solid fractions. Bio-oil acquired from pyrolysis includes phenols, aldehydes, alcohols and carboxylic acids that can be utilized for the production of adhesives, fertilizers, various chemicals, etc. (Bridgwater, 2003; Abu Bakar and Titiloye, 2013; Özbay, 2015; Rioche *et al.*, 2005; Yaman, 2004).

Phenol-formaldehyde resins (PF) are cross-linkable polymeric resins made from phenol and formaldehyde in the presence of a catalyst. Depending on the pH of the catalyst, these monomers react to form one of two main resin types: resol and novolac resins. A basic catalyst is generally used in formulating the resol type of resins. They are used successfully for the production of wood composites, because of their high bonding strength and extreme resistance to moisture (Junming *et al.*, 2010; Christjanson *et al.*, 2010; Moubarik *et al.*, 2009). They are, however, relatively expensive as regards the phenol price. Therefore, there have been many attempts to replace phenol with renewable resources, such as lignin, soybean, tannin or bio-oil, etc. in the production of phenol-formaldehyde (PF) resins (Alma *et al.*, 2001; Wang *et al.*, 2005; Tejado *et al.*, 2007; Moubarik *et al.*, 2009; Fan *et al.*, 2009; Jiang *et al.*, 2010; Hoong *et al.*, 2011; Lee *et al.*, 2011; Kouisni *et al.*, 2011; Shahid *et al.*, 2014; Aslan *et al.*, 2015).

In the present study, bio-oil produced from vacuum pyrolysis of woody biomass has been investigated as a renewable chemical feedstock. The chromatography-mass spectrometry (GC/MS) analysis was carried out for the evaluation of the chemical composition of bio-oil. The bio-oil was chemically synthesized with phenol

and formaldehyde at 10 wt%, 20 wt%, and 30 wt% phenol replacement levels under alkaline conditions. BPF resins were characterized by several thermal and chemical analyses such as TGA, DSC, and FT-IR. In addition, the shear strengths of wood samples were investigated under both dry and wet conditions.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

2.1 Biomass and chemicals

2.1. Biomasa i kemikalije

In this study, pine sawdust was used for the pyrolysis process as woody biomass. Prior to the experiments, the raw material was dried and ground. The particles with the size of 1-2 mm were selected for the experiments.

A commercial PF and laboratory PF resins were considered as reference resins in this work. The commercial PF adhesive was provided by POLİSAN chemical company in Izmit, Turkey. BPF resins were prepared by using phenol (liquid) and formaldehyde aqueous solution (37 %) supplied by GENTAŞ chemical company, İzmit, Turkey. Sodium hydroxide pellets were purchased from Sigma Aldrich.

2.2 Bio-oil production from biomass

2.2. Proizvodnja bioulja od biomase

The pyrolysis experiments were implemented in a vacuum pyrolysis reactor having 24 cm × 36 cm interior diameter and depth, respectively. The reactor was electrically heated externally. During the pyrolysis process, pyrolysis temperature was operated with a Proportional-Integral-Derivative controller. The total pressure was fixed at about 10 kPa. For the pyrolysis; 2000 g sample of biomass was placed into the reactor and the experiments were performed with a heating rate of approximately 15 °C/min to the final temperatures of 500 °C and held for 60 min. The bio-oil was collected by condensation in a condenser connected to the reactor exit. The bio-oil was filtered through the filter paper with a mesh size of 75 µm.

2.3 Chemical properties of bio-oil

2.3. Kemijska svojstva bioulja

The chromatography-mass spectrometry (GC/MS) analysis was carried out for the determination of

the chemical composition of bio-oil (Agilent 6890). Helium was used as the carrier gas. The oven temperature was set to start at 40 °C and gradually raised to the final temperature of 300 °C.

2.4 Chemical synthesis of resins

2.4. Kemijska sinteza smola

The reactions were performed in a glass reactor equipped with a stirrer, a reflux condenser, and a heating part. In a typical synthesis of a laboratory-made PF resin (lab. PF), the reactor was first filled with 1000 g of phenol and 1100 g formaldehyde (37 wt%). The temperature was increased to 60 °C and then 62.5 g of NaOH solution (50 wt%) was added to the process. The blend was mixed and heated up to 90 °C, and then held at that temperature for 90 min. Finally, the second part of NaOH (50 wt%) solution was charged at a temperature of 60 °C. After the reaction, the process was cooled to room temperature. The same procedure was applied for bio-oil/PF resins synthesis. By varying the amount of bio-oil in the reaction mixture, a series of phenol substitutions were synthesized ranging from 10 to 30 wt%.

2.5 Physical characterization of resins

2.5. Određivanje fizičkih svojstava smola

The pH and dynamic viscosity values were determined with a digital pH meter and a rotational viscometer at 25 °C, respectively. Gel times were calculated at 100 °C. The solid contents of the resins were determined by weighing 2 g of the resin in a glass plate. The glass plate was placed in an oven at 120 °C for 120 min and it was desiccated and weighed to find the weight of dry resin remaining.

2.6 Thermogravimetric analysis (TGA)

2.6. Termogravimetrijska analiza (TGA)

The thermal decomposition behavior of resins was analyzed by using a HITACHI STA 7300. For the thermogravimetric analysis (TGA), nearly 10 mg of

the sample was heated at a 5 °C/min heating rate up to the final temperature of 700 °C. The carrier gas was nitrogen with a flow rate of 25 ml/min.

2.7 Differential scanning calorimetry analysis (DSC)

2.7. Diferencijalna pretražna kalorimetrija (DSC)

DSC analyses were carried out using a DSC7000X. About 5 mg of samples (resin) was applied to a stainless-steel crucible. Scans were performed at a temperature of 50 – 550 °C at a 10 °C/min heating rate.

2.8 Fourier-transform infrared spectroscopy (FT-IR)

2.8. Fourierova transformacijska infracrvena spektroskopija (FT-IR)

FT-IR spectra were recorded on an Alpha FT-IR spectrometer by direct transmittance using KBr pellet technique. 10 scans were recorded for each sample with a resolution of 4 cm⁻¹ over a range from 4000 to 400 cm⁻¹.

2.9 Sample preparation and property testing

2.9. Priprema uzoraka i ispitivanje svojstava

The beech wood (*Fagus orientalis* Lipsky) planks provided from a commercial company in Karabuk, Turkey were used as wood material. The lamellas (5 mm × 20 mm × 150 mm) were prepared from the planks for shear strength tests. Prior to tests, the lamellas were conditioned (20 °C and 65 % relative humidity) to reach the equilibrium moisture content of 12 %. The resin was implemented on one surface of the lamella using a hand brush at a rate of 180 g/m² as suggested by the manufacturer. The pressure, temperature, and duration were set as 0.2 N/mm², 130 °C, and 15 min, respectively. Bonded samples were conditioned for 7 days in the standard climate room and then cut into samples. The dimensions and shape of a typical sample are shown in Figure 1.

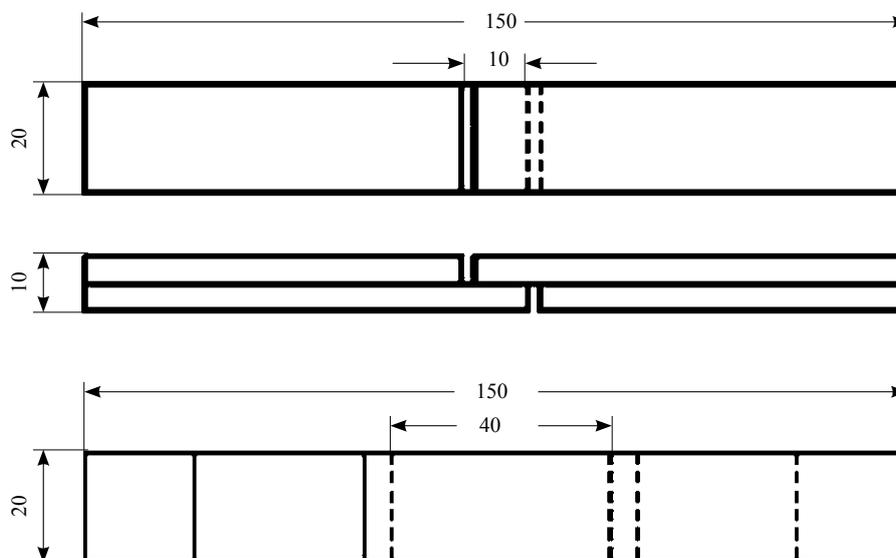


Figure 1 Shear strength test sample (size given in mm)

Slika 1. Uzorci pripremljeni za ispitivanje čvrstoće na smicanje (dimenzije su u milimetrima)

Table 1 Proposed scale to evaluate the quality of bond lines based on their strength and durability
Tablica 1. Predložene vrijednosti za ocjenu kvalitete lijepljenog spoja na temelju čvrstoće i trajnosti

Test number <i>Broj tretmana</i>	Test conditions <i>Uvjeti tretmana</i>	Scale / Strength, N/mm ² <i>Razred / Čvrstoća, N/mm²</i>			
		C1	C2	C3	C4
Pre-treatment 1 <i>predobrada 1.</i>	7 days in standard conditions <i>7 dana u standardnim uvjetima</i>	≥10	≥10	≥10	≥10
Pre-treatment 2 <i>predobrada 2.</i>	7 days in standard conditions / 7 dana u standardnim uvjetima 24 h in cold water at (20±5) °C / 24 h u hladnoj vodi pri (20±5) °C	-	≥7	≥7	≥7
Pre-treatment 3 <i>predobrada 3.</i>	7 days in standard conditions / 7 dana u standardnim uvjetima 3 h in boiled water / 3 h u kipućoj vodi 2 h in cold water at (20±5) °C / 2 h u hladnoj vodi pri (20±5) °C	-	-	-	≥4

Classified samples were divided into three sub-groups for different pre-treatments, prior to the evaluation according to TS EN 12765 standard. Table 1 summarizes the proposed criteria for evaluating the quality of bonds according to this standard. The first sample groups (pre-treatment 1) was evaluated in dry conditions after conditioning for 7 days (65±5 % relative humidity, 20±5 °C standard climate); the second group of samples (pre-treatment 2) was soaked in cold water (20 °C) for 24 h; the third group of samples (pre-treatment 3) was boiled for 3 h, then cooled in water (20 °C) for 2 h. The determination of shear strength was performed in a universal testing machine, according to BS EN 205.

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

3.1 Chemical composition

3.1.1. Kemijski sastav

Table 2 presents the chemical characterization of the bio-oil. The bio-oil consists mainly of oxygenated organics (aldehydes, ketones, phenols, benzenes, alcohols, and polycyclic aromatic hydrocarbon). It was

found that phenols were the main component in the bio-oil. The most abundant phenols in the bio-oil include phenol, 2-methyl-phenol, 4-methyl-phenol, 2-methoxy-phenol, 2,5-dimethyl-phenol, and 2-methoxy-4-methyl-phenol. The compounds found in the bio-oil correspond well to the literature (Ingemarsson *et al.*, 1998; Kang *et al.*, 2006; Ren *et al.*, 2012; Kim *et al.*, 2014; Fukuda, 2015; Özbay *et al.*, 2015).

3.2 Characterization of resins

3.2. Karakterizacija smola

The results of the physical properties of the resins are displayed in Table 3. The pH values of all resins were similar due to the fact that pH values were continuously adjusted during the synthesis process. The viscosities of the BPF resins were higher than those of reference resins, and also, gradually increased with the increasing addition of bio-oil. This result may be due to the fact that high molecular weight compounds in the bio-oil cause high viscosity in bio-based resins. The solids content of 10-30 % BPF resins were 44.32 wt%, 46.61 wt% and 46.76 wt%, respectively. The solid content of the laboratory PF resin (40.67 wt%) was lower than that of BPF resins and the solids content increased as the bio-oil per-

Table 2 GC/MS characterization of bio-oil
Tablica 2. GC/MS karakterizacija bioulja

RT, min	Name of compound / <i>Naziv spoja</i>	Area, % / <i>Površina, %</i>	Category / <i>Kategorija</i>
14.65	5-Methyl-2-furancarboxaldehyde	2.00	Aldehyde
15.86	Phenol	7.33	Phenol
18.92	2-Methyl-phenol	4.15	Phenol
19.75	4-Methyl-phenol	9.82	Phenol
20.10	2-Methoxy-phenol	3.40	Phenol
20.72	1-Methoxy-3-methyl-benzene	0.16	Benzene
22.25	2,5-Dimethyl-phenol	3.16	Phenol
23.22	Naphthalene	4.09	Benzene
23.67	2-Methoxy-4-methyl-phenol	6.66	Phenol
23.88	1,2-Benzenediol	4.34	Alcohol
25.73	4-Methyl 1,2-benzenediol	2.06	Alcohol
26.30	Pyrazine	2.93	PAH
26.58	4-Methyl 1,2-benzenediol	3.85	Alcohol
26.63	1-Methyl-naphthalene	1.18	Benzene
28.77	2-Methoxy-4-propenyl-phenol	0.78	Phenol
29.15	4-Ethyl-1,3-benzenediol	2.74	Alcohol
30.81	Biphenylene	2.04	Benzene
32.96	1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	0.52	Ketone
34.11	Fluorene	1.96	Benzene
38.50	Cyclopropanone	2.70	Ketone
40.99	3-Methyl-phenanthrene	0.99	Benzene

Table 3 Physical properties of PF resins

Tablica 3. Fizička svojstva PF smola

Properties <i>Svojstva</i>	Reference resins <i>Referentne smole</i>		BPF resins <i>BPF smole</i>		
	Com. PF	Lab. PF	10 wt% bio-oil	20 wt% bio-oil	30 wt% bio-oil
pH at 20 °C / <i>pri 20 °C</i>	11.90	11.96	11.83	11.78	11.75
Viscosity at 25 °C, cPs <i>viskoznost pri 25 °C, cPs</i>	310	240	340	366	398
Gel time at 100 °C, s <i>vrijeme želiranja pri 100 °C, s</i>	185	172	160	142	117
Solids content, % <i>sadržaj suhe tvari, %</i>	48.84	40.67	44.32	46.61	46.76

centage in the resin increased. This could be due to the lower reactivity of bio-oil when compared to phenol. Commercial PF resin had the highest solid content (48.84 wt%). Fan *et al.* (2010) reported that faster curing PF resins can be produced by the addition of urea during or after the resin synthesis process. The highest solids content might be caused by urea in the commercial PF resin. BPF resins had the shortest gel time when compared with the reference PF resins. These results were in good agreement with the literature data of the properties of the bio-based adhesives (Sarkar and Adhikari, 2000; Tejado *et al.*, 2007; Wang *et al.*, 2009; Zhao *et al.*, 2010; Wang *et al.*, 2011; Cheng *et al.*, 2012; Yi *et al.*, 2012).

The TGA curves of the resins (i.e. the bio-oil modified/commercial/lab.) are presented in Figure 2. The thermal behavior of the commercial PF resin was different from that of the laboratory PF resins and the BPF resins after the temperature was higher than approx. 150 °C. This higher thermal degradation is due to the fact that commercial PF resin contains an amount of urea decomposing easily at high temperatures. It was observed that the lab. PF resin and all of the BPF resins had a similar trend of thermal behavior. The highest thermal degradation of the BPF resins was determined in the 30 % bio-oil PF resin. In the literature, thermal degradation of bio-based PF resins obtained from the different renewable feedstocks were a rough match to our results (Wang *et al.*, 2009; Domínguez *et al.*, 2013; Zhao *et al.*, 2013).

Figure 3 shows the DSC thermograms obtained at a heating rate of 10 °C/min for all resins from 50 to 550

°C. As shown in Figure 3, the DSC thermograms of all resins had a multiple peak structure. The main endothermic peak was detected between 125 and 136 °C for all resins. The formation of these peaks might be connected to the condensation of phenol or bio-oil with methylol groups in order to create a methylene bridge and the condensation of two methylol groups in order to create dibenzyl ether bridges and the cross-linking condensation of the methylene bridges (Christiansen and Gollob, 1985; Gabilondo *et al.*, 2007; Wang *et al.*, 2009). All modified resins showed the second peak at a lower temperature than commercial PF. DSC thermograms obtained in this study were consistent with the earlier research of thermal behavior of bio-based adhesives (Khan *et al.*, 2004; Cheng *et al.*, 2012; Lin *et al.*, 2014).

BPF resins were fractionally and structurally characterized by FT-IR spectroscopy; the 4000-400 cm⁻¹ infrared spectral region is shown in Figure 4. The reference resins (commercial and lab. PF resins) were also analyzed as a comparison.

The O–H stretching vibrations between 3600 and 3200 cm⁻¹ represent the existence of phenols. The peak around 1600 cm⁻¹ was assigned to the aromatic ring vibrations, indicating the existence of phenols in resins. A new peak was observed at around 1650 cm⁻¹, attributed to C=O stretching, indicating carbonyl compounds in the BPF resin. All the resins have the aromatic rings around 1450 cm⁻¹, phenolic C–O stretching around 1200 cm⁻¹, C–O stretching around 1000 cm⁻¹. The peaks around 900 cm⁻¹, 800 cm⁻¹, and 750 cm⁻¹

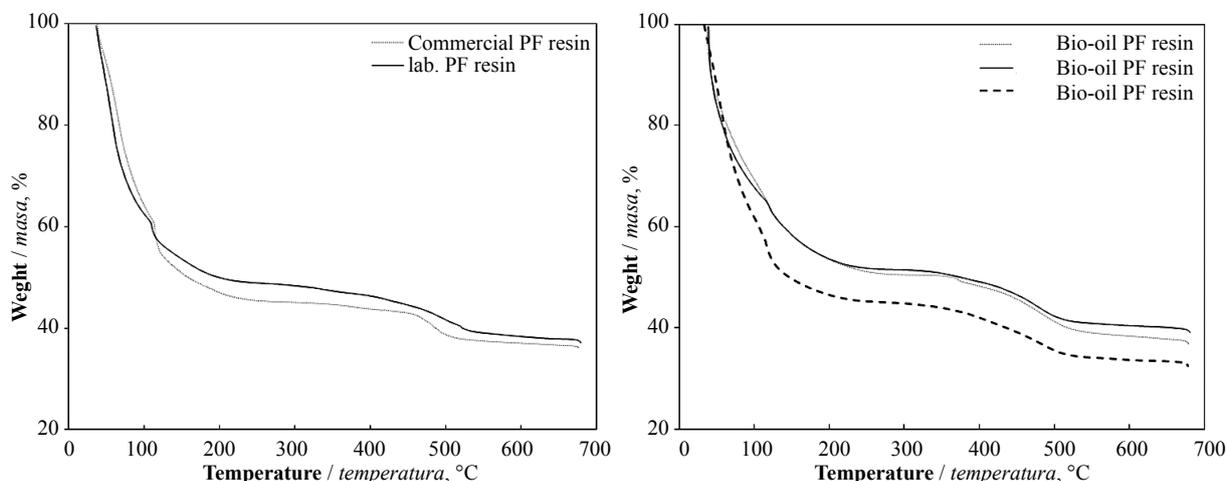


Figure 2 TGA analysis of resins

Slika 2. TGA analiza smola

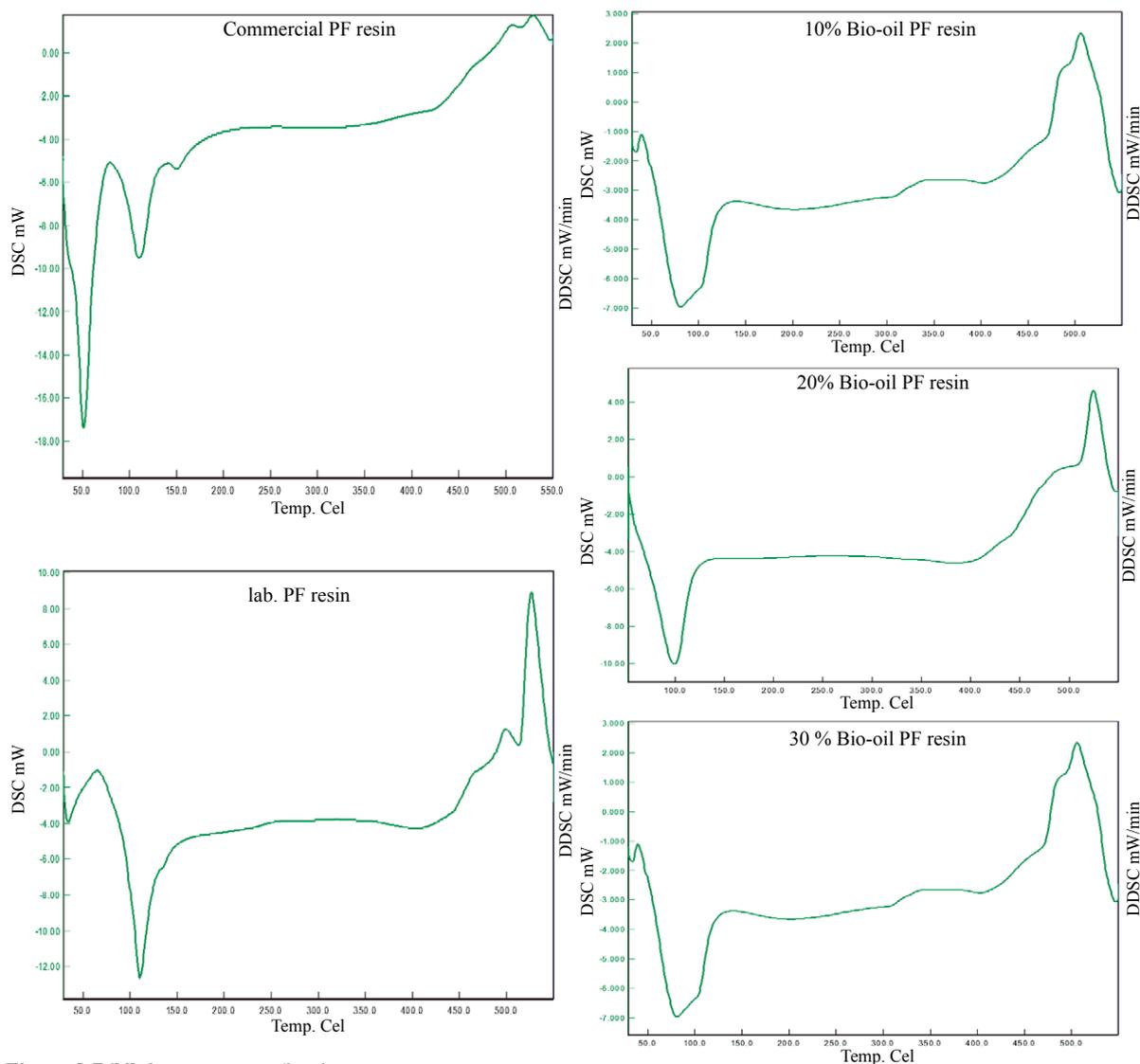


Figure 3 DSC thermograms of resins
Slika 3. DSC termogrami smola

were related to the bending vibration of C–H in the aromatic rings. Cui and co-workers reported that the BPF resins have similar FT-IR spectra as PF resin. This indicates that the BPF resins display a similar molecular structure as the PF resin (Cui *et al.*, 2016). According to FT-IR analysis, it can be claimed that bio-based resins were successfully produced by polymerization of phenol, bio-oil and formaldehyde.

3.3 Bond performance

3.3.1 Svojstva lijepljenog spoja

The shear strength and wood failure of the samples bonded with the BPF, lab. PF and commercial PF resins are given in Table 4. Under dry conditions, the percentage of wood failure was almost 100 %, except for 30 wt% modified BPF resin that was a bit lower (97 %). According to Table 4, the bonding performances of all resins are satisfying. The highest shear strength was observed for the control samples bonded with the lab. PF resin. As the amount of the bio-oil was increased up to 30 wt%, the shear strength of the samples decreased from 12.08 to 11.76 N/mm². The bonding performance was not negatively affected by the combination of bio-

oil under dry condition. According to TS EN 12765 standard, the relevant performance requirements for bonded samples under dry condition must be at least 10 N/mm². Relating to the standard, all samples bonded with BPF resins obtained the requirements for durability class C1.

The shear strength and wood failure values of all samples after 24 h soaking in water (pre-treatment 2) are presented in Table 4. The shear strength of wood bonded with the reference PF resins was higher than that of BPF resins. The shear strength was gradually decreased with increasing concentration of the bio-oil. For pre-treatment 2, the reference resins had the highest percentage of wood failure (100 % - 97 %). All the BPF samples showed a lower percentage of wood failure (especially samples bonded with 30 wt% BPF resin). The BPF resins containing 10-30 wt% bio-oil fulfilled the requirements for durability class C2 (EN 12765).

For pre-treatment 3, similar trends were observed as for pre-treatment 2. The strength values of the samples decreased after pre-treatment 3 as compared with pre-treatment 1 and 2. The bond line was more or less negatively affected by the presence of the bio-oil. As

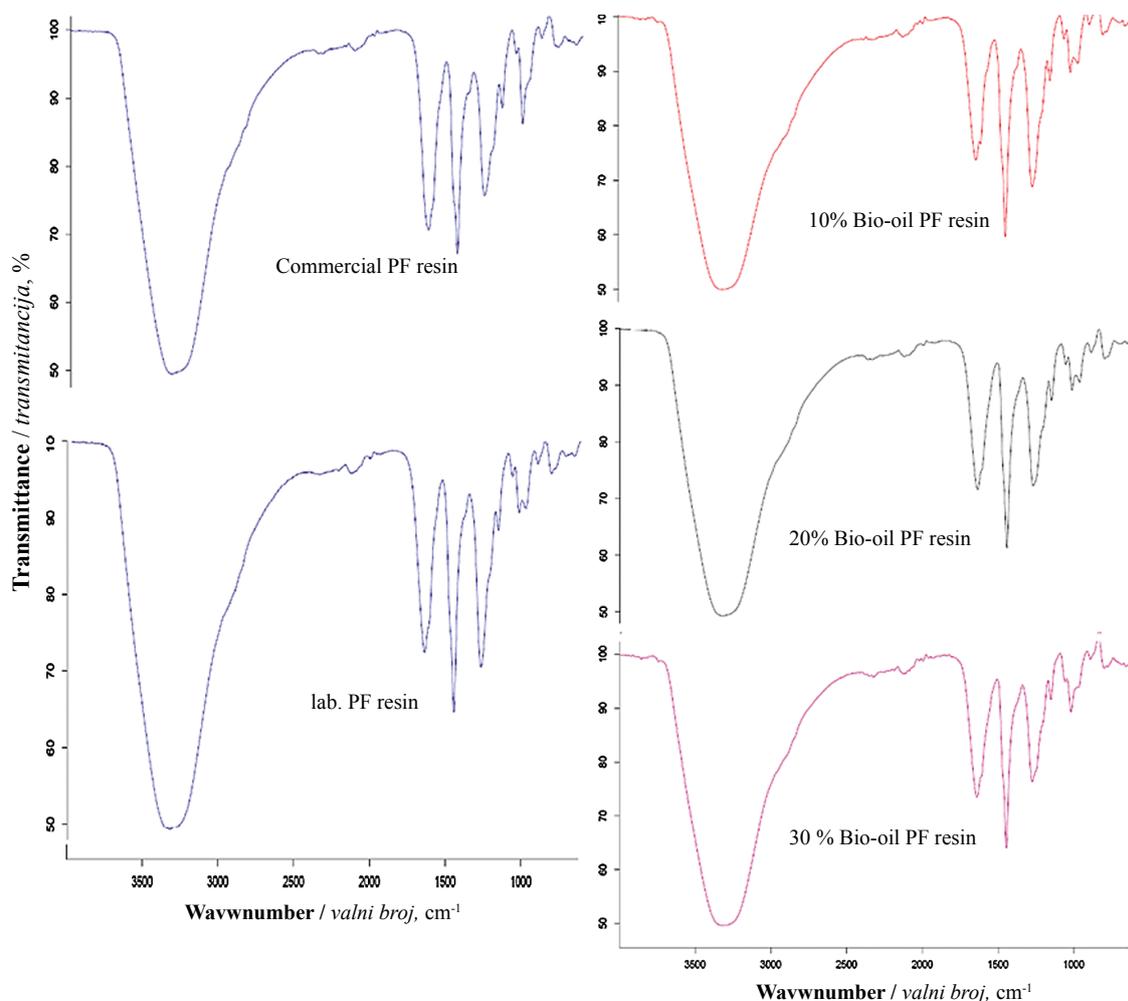


Figure 4 FT-IR spectra of resins

Slika 4. FT-IR spektri smola

Table 4 Shear strength and wood failure (%)

Tablica 4. Čvrstoća na smicanje i lom po drvu (%)

Type of resin <i>Vrsta smole</i>	Shear strength, N/mm ² / wood failure, % <i>Čvrstoća na smicanje, N/mm² / lom po drvu, %</i>	Conditions / <i>Uvjeti</i>		
		Dry condition (Pre-treatment 1) / St. Dev <i>Suhi uvjeti (predobrada 1.) / standardna devijacija</i>	24 h submersion in water (Pre-treatment 2) / St. Dev <i>24 h potapanja u vodi (predobrada 2.) / standardna devijacija</i>	3 h boiling and then 24 h submersion in water (Pre-treatment 3) / St. Dev <i>3 h kuhanja i 24 h potapanja u vodi (predobrada 3.) / standardna devijacija</i>
Commercial PF resin <i>Komercijalna PF smola</i>	Shear strength / <i>čvrstoća na smicanje, N/mm²</i>	11.94 ± 0.13	8.17 ± 0.23	5.65 ± 0.39
	Wood failure / <i>lom po drvu, %</i>	100	100	96
Lab. PF resin <i>Laboratorijska PF smola</i>	Shear strength / <i>čvrstoća na smicanje, N/mm²</i>	12.04 ± 0.26	7.91 ± 0.31	5.78 ± 0.24
	Wood failure / <i>lom po drvu, %</i>	100	100	94
10 wt% bio-oil PF resin <i>PF smola s 10 wt% bioulja</i>	Shear strength / <i>čvrstoća na smicanje, N/mm²</i>	11.90 ± 0.11	7.73 ± 0.19	5.43 ± 0.21
	Wood failure / <i>lom po drvu, %</i>	100	96	85
20 wt% bio-oil PF resin <i>PF smola s 20 wt% bioulja</i>	Shear strength / <i>čvrstoća na smicanje, N/mm²</i>	11.88 ± 0.23	7.47 ± 0.21	5.37 ± 0.33
	Wood failure / <i>lom po drvu, %</i>	100	92	74
30 wt% bio-oil PF resin <i>PF smola s 30 wt% bioulja</i>	Shear strength / <i>čvrstoća na smicanje, N/mm²</i>	11.76 ± 0.19	7.12 ± 0.33	4.43 ± 0.36
	Wood failure / <i>lom po drvu, %</i>	97	84	70

the amount of bio-oil in the PF resin was increased by 30 wt%, the shear strength of the samples after pre-treatment 3 decreased from 5.78 to 4.43 N/mm². However, these samples exceeded the minimum requirements for the durability class C3 (EN 12765). Cheng *et al.* (2012) reported that the methylolated bio-oil-phenol formaldehyde (MBPF) adhesives were more sensitive to water than the PF adhesive. They could be used as adhesives for the production of interior wood products. It can be concluded that renewable resources such as bio-oil have potential as a substitute for PF resin.

4 CONCLUSIONS

4. ZAKLJUČAK

In this work, bio-based PF resins were produced by substitution of phenol with the bio-oil at varying ratios (from 10 wt% to 30 wt%) in the synthesis of phenol-formaldehyde resins under alkaline condition. The following conclusions can be obtained:

The bio-oil produced from woody biomass was composed mainly of phenols, aldehydes, ketones, alcohols and, benzenes. The phenols accounted for the largest amount of compound in the bio-oil.

The viscosities of the BPF resins were higher than those of reference resins and gradually increased with the increasing addition of bio-oil.

The laboratory PF resin and all of the BPF resins had a similar trend of thermal behavior.

FTIR spectra demonstrated that bio-based resol resins were successfully produced by polymerization of phenol, bio-oil, and formaldehyde.

The shear strength values of the BPF resins were similar to the commercial PF and the lab. PF resins under dry condition. Under wet conditions, the shear strength and wood failure values of the samples bonded with BPF resins exhibited poorer performance as compared to samples bonded with the reference resins. However, the BPF resins fulfilled the requirements for C1, C2, and C3 specified in EN 12765.

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5 REFERENCES

5. LITERATURA

1. Abu Bakar, M. S.; Titiloye, J. O., 2013: Catalytic pyrolysis of rice husk for bio-oil production. *Journal of Analytical and Applied Pyrolysis*, 103: 362-368. <https://doi.org/10.1016/j.jaap.2012.09.005>.
2. Alma, M. H.; Basturk, M. A.; Shiraishi, N., 2001: Cocondensation of NaOH-catalyzed liquefied wood wastes, phenol, and formaldehyde for the production of resol-type adhesives. *Industrial & Engineering Chemistry Research*, 40: 5036-5039. <http://dx.doi.org/10.1021/ie000858x>.
3. Aslan, M.; Özbay, G.; Ayırlımış, N., 2015: Adhesive characteristics and bonding performance of phenol formaldehyde modified with phenol-rich fraction of crude bio-oil. *Journal*

- of Adhesion Science and Technology, 29 (24): 2679-2691. <https://doi.org/10.1080/01694243.2015.1080474>.
4. Bridgewater, A. V., 2003: Renewable fuels and chemicals by thermal processing of biomass. *Chemical Engineering Journal*, 91: 87-102. [https://doi.org/10.1016/S1385-8947\(02\)00142-0](https://doi.org/10.1016/S1385-8947(02)00142-0).
5. Bozell, J. J., 2002: Green chemistry in practice. In: *Handbook of Green Chemistry and Technology*, Clark, J.; Macquarrie, D. (eds.). Blackwell, Oxford, 338-365. <https://doi.org/10.1002/9780470988305.ch14>.
6. Cheng, S.; Yuan, Z.; Anderson, M.; Leitch, M.; Xu, C., 2012: Synthesis of biobased phenolic resins/adhesives with methylolated wood-derived bio-oil. *Journal of Applied Polymer Science*, 126: 430-440. <https://doi.org/10.1002/app.35655>.
7. Christiansen, A. W.; Gollob, L., 1985: Differential scanning calorimetry of phenol-formaldehyde resols. *Journal of Applied Polymer Science*, 30: 2279-2289. <https://doi.org/10.1002/app.1985.070300601>.
8. Christjanson, P.; Pehk, T.; Paju, J., 2010: Structure and curing mechanism of resol phenol-formaldehyde prepolymer resins. *Proceedings of the Estonian Academy of Sciences*, 59 (3): 225-232. <http://dx.doi.org/10.3176/proc.2010.3.05>.
9. Connor, M. A.; Piskorz, J., 1994: Workshop report: Chemical from biomass. In: *Advances in Thermo-Biomass Conversion*, Bridgewater, A. V. (ed). Blackie, New York, 1502-1504.
10. Cui, Y.; Chang, J.; Wang, W., 2016: Fabrication of glass fiber reinforced composites based on bio-oil phenol formaldehyde resin. *Materials*, 9: 886-896. <https://doi.org/10.3390/ma9110886>.
11. Domínguez, J. C.; Oliet, M.; Alonso, M. V.; Rojo, E.; Rodríguez, F., 2013: Structural, thermal and rheological behavior of a bio-based phenolic resin in relation to a commercial resol resin. *Industrial Crops and Products*, 42: 308-314. <https://doi.org/10.1016/j.indcrop.2012.06.004>.
12. Fan, D. B.; Chang, J. M.; Li, J.; Mao, A.; Zhang, L. T., 2009: ¹³C NMR study on the structure of phenol-urea-formaldehyde resins prepared by methylolureas and phenol. *Journal of Applied Polymer Science*, 112 (4): 2195-2202. <https://doi.org/10.1002/app.29532>.
13. Fan, D.; Chang, J.; Gou, J.; Xia, B.; Ren, X., 2010: On the cure acceleration of oil-phenol-formaldehyde resins with different catalysts. *The Journal of Adhesion*, 86: 836-845. <https://doi.org/10.1080/00218464.2010.498730>.
14. Fukuda, S., 2015: Pyrolysis investigation for bio-oil production from various biomass feedstocks in Thailand. *International Journal of Green Energy*, 12: 215-224. <https://doi.org/10.1080/15435075.2014.891519>.
15. Gabilondo, N.; López, M.; Ramos, J. A.; Echeverría, J. M.; Mondragon, I., 2007: Curing kinetics of amine and sodium hydroxide catalyzed phenol-formaldehyde resins. *Journal of Thermal Analysis and Calorimetry*, 90 (1): 229-236. <https://doi.org/10.1007/s10973-006-7747-3>.
16. Gosselink, R. J. A.; Snijder, M. H. B.; Kranenbarg, A.; Keijsers, E. R. P.; De Jong, E.; Stigsson, L. L., 2004: Characterisation and application of NovaFiber lignin. *Industrial Crops and Products*, 20: 191-203. <https://doi.org/10.1016/j.indcrop.2004.04.021>.
17. Hoong, Y. B.; Paridah, Md. T.; Loh, Y. F.; Jalaluddin, H.; Chuah, L. A., 2011: A new source of natural adhesive: Acacia mangium bark extracts co-polymerized with phenol-formaldehyde (PF) for bonding Mempisang (*Annonaceae* spp.) veneers. *International Journal of Adhesion & Adhesives*, 31: 164-167. <https://doi.org/10.1016/j.ijadhadh.2010.12.002>.

18. Ingemarsson, A.; Nilsson, U.; Nilsson, M.; Pedersen, J. R.; Olsson, J. O., 1998: Slow pyrolysis of spruce and pine samples studied with GC/MS and GC/FTIR/FID. *Chemosphere*, 36 (14): 2879-2889. [https://doi.org/10.1016/S0045-6535\(97\)10245-4](https://doi.org/10.1016/S0045-6535(97)10245-4).
19. Jiang, H.; Wang, J.; Wu, S.; Wang, B.; Wang, Z., 2010: Pyrolysis kinetics of phenol-formaldehyde resin by non-isothermal thermogravimetry. *Carbon*, 48: 352-358. <https://doi.org/10.1016/j.carbon.2009.09.036>.
20. Junming, X.; Jianchun, J.; Wei, L., 2010: Preparation of novolacs using phenolic rich components as partial substitute of phenol from biomass pyrolysis oils. *Bulletin of the Chemical Society of Ethiopia*, 24(2): 251-257. <http://dx.doi.org/10.4314/bcse.v24i2.54754>.
21. Kang, B.-S.; Lee, K. H.; Park, H. J.; Park, Y. K.; Kim, J. S., 2006: Fast pyrolysis of radiata pine in a bench scale plant with a fluidized bed: Influence of a char separation system and reaction conditions on the production of bio-oil. *Journal of Analytical and Applied Pyrolysis*, 76: 32-37. <https://doi.org/10.1016/j.jaap.2005.06.012>.
22. Kim, J. W.; Lee, H. W.; Lee, I.-G.; Jeon, J.-K.; Ryu, C.; Park, S. H.; Jung, S.-C.; Park, Y.-K., 2014: Influence of reaction conditions on bio-oil production from pyrolysis of construction waste wood. *Renewable Energy*, 65: 41-48. <https://doi.org/10.1016/j.renene.2013.07.009>.
23. Khan, M. A.; Ashraf, S. M.; Malhotra, V. P., 2004: Development and characterization of a wood adhesive using bagasse lignin. *International Journal of Adhesion and Adhesives*, 24(6): 485-493. <https://doi.org/10.1016/j.ijadhadh.2004.01.003>.
24. Kouisni, L.; Fang, Y.; Paleologou, M.; Behzad, A.; Jalal, H.; Zhang, Y.; Wang, X., 2011: Kraft lignin recovery and its use in the preparation of lignin-based phenol formaldehyde resins for plywood. *Cellulose Chemistry and Technology*, 45 (7-8): 515-520. <http://dx.doi.org/10.4067/S0718-221X2014005000013>.
25. Lee, J.-H.; Jeon, J.; Kim, S., 2011: Green adhesives using tannin and cashew nut shell liquid for environment-friendly furniture materials. *Journal of the Korea Furniture Society*, 22 (3): 219-229.
26. Lin, R.; Sun, J.; Yue, C.; Wang, X.; Tu, D.; Gao, Z., 2014: Study on preparation and properties of phenol-formaldehyde-chinese fir liquefaction copolymer resin. *Maderas Ciencia y tecnología*, 16 (2): 159-174. <http://dx.doi.org/10.4067/S0718-221X2014005000013>.
27. Moubarik, A.; Pizzi, A.; Ahmed, A.; Charrier, F.; Charrier, B., 2009: Cornstarch and tannin in phenol-formaldehyde resins for plywood production. *Industrial Crops and Products*, 30: 188-193. <https://doi.org/10.1016/j.indcrop.2009.03.005>.
28. Özbay, G., 2015: Catalytic pyrolysis of pine wood sawdust to produce bio-oil: Effect of temperature and catalyst additives. *Journal of Wood Chemistry and Technology*, 35: 302-313. <https://doi.org/10.1080/02773813.2014.958240>.
29. Özbay, G.; Kilic Pekgozlu, A.; Ozcifici, A., 2015: The effect of heat treatment on bio-oil properties obtained from pyrolysis of wood sawdust. *Eur. J. Wood Prod.*, 73 (4): 507-514. <https://doi.org/10.1007/s00107-015-0911-3>.
30. Ren, S.; Lei, H.; Wang, L.; Quan, Q.; Chen, S.; Wu, J.; Julson, J.; Ruan, R., 2012: Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet. *Journal of Analytical and Applied Pyrolysis*, 94: 163-169. <https://doi.org/10.1016/j.jaap.2011.12.004>.
31. Rioche, C.; Kulkarni, S.; Meunier, F. C.; Breen, J. P.; Burch, R., 2005: Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts. *Applied Catalysis B: Environmental*, 61: 130-139. <https://doi.org/10.1016/j.apcatb.2005.04.015>.
32. Sarkar, S.; Adhikari, B., 2000: Lignin-modified phenolic resin: synthesis optimization, adhesive strength, and thermal stability. *Journal of Adhesion Science and Technology*, 14 (9): 1179-1193. <https://doi.org/10.1163/156856100743167>.
33. Shahid, S. A.; Zafar, M. A.; Zafar, I., 2014: Characterization of phenol-formaldehyde resins modified with crude bio-oil prepared from ziziphus mauritiana endocarps. *BioResources*, 9 (3): 5362-5384. <https://doi.org/10.15376/biores.9.3.5362-5384>.
34. Tejado, A.; Pena, C.; Labidi, J.; Echeverria, J. M.; Mondragon, I., 2007: Physico-chemical characterization of lignins from deferent sources for use in phenol-formaldehyde resin synthesis. *Bioresource Technology*, 98: 1655-1663. <https://doi.org/10.1016/j.biortech.2006.05.042>.
35. Wang, J.; Jiang, H.; Jiang, N., 2009: Study on the pyrolysis of phenol-formaldehyde (PF) resin and modified PF resin. *Thermochimica Acta*, 496: 136-142. <https://doi.org/10.1016/j.tca.2009.07.012>.
36. Wang, M.; Leitch, M.; Xu, C., 2009: Synthesis of phenol-formaldehyde resins using organosolv pine lignins. *European Polymer Journal*, 45 (12): 3380-3388. <https://doi.org/10.1016/j.eurpolymj.2009.10.003>.
37. Wang, M.; Wei, L.; Zhao, T., 2005: Cure study of addition-cure-type and condensation-addition-type phenolic resins. *European Polymer Journal*, 41: 903-912. <https://doi.org/10.1016/j.eurpolymj.2004.11.036>.
38. Wang, W.; Zhao, Z.; Gao, Z.; Guo, M., 2011: Whey protein-based water resistant and environmentally safe adhesives for plywood. *BioResources*, 6 (3): 3339-3351.
39. Yaman, S., 2004: Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Conversion and Management*, 45 (5): 651-671. [https://doi.org/10.1016/S0196-8904\(03\)00177-8](https://doi.org/10.1016/S0196-8904(03)00177-8).
40. Yanik, J.; Kommayer, C.; Sağlam, M.; Yüksel, M., 2007: Fast pyrolysis of agricultural wastes Characterization of pyrolysis products. *Fuel Processing Technology*, 88: 942-947. <https://doi.org/10.1016/j.fuproc.2007.05.002>.
41. Yi, J.; Zhang, J.; Yao, S.; Chang, J.; Li, B., 2012: Preparation of bio-oil-phenol-formaldehyde resins from biomass pyrolysis oil. *Applied Mechanics and Materials*, 174-177: 1429-1432. <https://doi.org/10.4028/www.scientific.net/AMM.174-177.1429>.
42. Zhao, Y.; Yan, N.; Feng, M., 2010: Characterization of phenol-formaldehyde resins derived from liquefied lodgepole pine barks. *International Journal of Adhesion & Adhesives*, 30: 689-695. <https://doi.org/10.1016/j.ijadhadh.2010.07.007>.
43. Zhao, Y.; Yan, N.; Feng, M., 2013: Thermal degradation characteristics of phenol-formaldehyde resins derived from beetle infested pine barks. *Thermochimica Acta*, 555: 46-52. <https://doi.org/10.1016/j.tca.2012.12.002>.
44. ***EN 205, 2003: Adhesives-Wood adhesives for non-structural applications – Determination of tensile shear strength of lap-joints. European Committee for Standardization, Brussels.
45. ***EN 12765, 2002: Classification of thermosetting wood adhesives for non-structural applications. European Committee for Standardization, Brussels.

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