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PHYSICAL CHARACTERIZATION AND BONDING PERFORMANCE OF PHENOL-FORMALDEHYDE/WASTE TYRE PYROLYTIC OIL BLEND ADHESIVE

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Abstract:

Several million tons of waste tyres are generated every year all over the world. Many researches have been conducted on the use of recycled tyre products in the industrial area including chemical feedstock. In this study, the bonding performance of commercial phenol-formaldehyde (PF) adhesive containing different amounts of waste tyre pyrolytic oil (10-40 wt%) was investigated. The chemical structure of the waste tyre pyrolytic oil was analysed using Fourier transform infrared spectroscopy (FT-IR). The effect of the substitution level of the tyres pyrolytic oil on the physical characteristics of the PF adhesive was determined. In addition, the shear strength of single lap-joint wood samples bonded with the blended PF adhesives was determined for indoor and outdoor conditions. It was found that the solid content of the blended PF adhesives decreased with increasing amount of the pyrolytic oil. The bonding performance of the wood samples bonded with the PF adhesives containing up to 20 wt% pyrolytic oil were about the same as that of commercial PF adhesive. Finally, pyrolytic oil could be partially blended with commercial PF adhesive.

Key words*: tyre pyrolytic oil; phenol-formaldehyde; bonding performance; wood; chemical analysis.*

INTRODUCTION

Many chemicals including adhesives, lubricants, pharmaceuticals, solvents and plastics are made from petroleum. Continued depletion of petroleum and increasing environmental concerns on the use of petroleum have an important impact on the chemical industries. Therefore, researchers have a keen interest in alternative feedstocks such as renewable or recyclable to petroleum (Singh et al. 2003; Clarens et al. 2010).

Phenol formaldehyde resin (PF) is a kind of synthetic polymers produced by the reaction of phenol with formaldehyde. PF resin is commonly used as molding powders, laminates, adhesives, and coating resins. PF adhesives are also used in wood composites such as oriented strandboards, laminated veneer lumber, plywood, particleboards etc. (Ge and Jin 1996; Pizzi 1993; Schmidt 2005; Matsunaga and Nambu 1981; Zhang et al. 2007; Hauptt and Sellers 1994).

Every year, several million tons of waste tyres are produced all over the world. Their waste tends to resist biodegradation, thus the issue of waste tyres pollution has turned into a major economic and environmental pollution threat for modern society. Pyrolysis is thermal decomposition occurring in the absence of oxygen to liquid (oil), gaseous and solid (char) fractions. Chemically, tyre pyrolytic oil, derived from pyrolysis processes, consists mainly of benzene, toluene, xylene and limonene. The pyrolytic oil acquired from pyrolysis of waste tyres can be used to produce chemicals or used to obtain fuel (Mazloom et al. 2009; Gao et al. 2009; Williams 2013; Ariyadejwanich et al. 2003; Bridgwater 2004; Chen et al. 2008; Umeki et al. 2016; Gonzales et al. 2001; Nkosi and Muzenda 2014).

In the literature, there are plenty of studies on pyrolysis of waste tyres oil to investigate the effect of the experimental conditions on products yield and composition (Roy et al. 1999; Gonzalez et al. 2001; Helleur et al. 2001; Li et al. 2004; Laresgoiti et al. 2004; Kyari et al. 2005; Murillo et al. 2006; Islam et al. 2008; Lopez et al. 2009; Miranda et al. 2013), but there is still need for research on the usage of pyrolytic oil in the chemical industry. In this study, the commercial PF adhesive was partially substituted with pyrolytic oil. The effects of the substitution level in the PF adhesive on the physical properties of the adhesive were investigated. Additionally, the bonding performance of the blended adhesives was evaluated using shear strength tests.

MATERIALS AND METHODS

Pyrolytic Oil

Unmodified commercial tyre pyrolytic oil was obtained from EN-TEK company in Bilecik, Turkey. The main characteristics of the tyre pyrolytic oil are listed in Table 1.

Table 1

The main characteristics of the tyre pyrolytic oil

Characteristics	Value of characteristic	Elemental analysis	Value of elemental analysis (%)
Density (g/cm^3) at 20 °C	0.9768	C	83.75
Dynamic viscosity (cPs) at 25 °C	350	H	8.47
pH at 25 ºC	4.60	N	0.33
-	-	S	1.43
-	-	O^a	6.02

a: calculated from the difference.

PF adhesive

The commercial PF adhesive with the solids content of 47.1% was tested in this study as reference adhesive. The PF adhesive was provided by the POLİSAN chemical company in Izmit, Turkey. The density (20ºC), pH (25ºC), and viscosity (20ºC) of the PF adhesive were 1.201g/cm^3, 11, and 385cPs, respectively.

Wood planks

Beech wood planks (*Fagus orientalis Lipsky*) were purchased by a commercial timber company in Karabuk, Turkey. The lamellas with dimensions of 10mmx20mmx150mm were prepared from the planks. The lamellas were planed to ensure the flat surface before bonding. Subsequently, the lamellas were conditioned in a climate room at 20ºC and 65%.

FT-IR spectra

FT-IR spectra of the tyre pyrolytic oil was carried out in an Alpha FT-IR instrument by direct transmittance using KBr pellet technique. Each spectrum was recorded in 10 scans, in the range from 4000 to 400cm^{-1} with a resolution of 4cm^{-1}.

Preparation of the adhesives

The pyrolytic oil was filtered through a filter paper with the mesh size of 75µm. An experimental study was carried out to test the performance of various commercial PF – pyrolytic oil mixtures; the content of pyrolytic oil is 0, 10, 20, 30, and 40% by weight. The PF/pyrolytic oil mixture was stirred by a magnetic stirrer to make it uniform. The mixture was left at room temperature for 30min.

Physical properties of the PF/pyrolytic oil adhesives

The pH values were measured with a pH meter (TES-1380) at 25ºC. The dynamic viscosity of the adhesives was measured with a rotational viscometer (Brookfield digital viscometer, model: Dv-IPrime) according to ASTM D1084-08 (2008). The solids content evaluation was according to ASTM D 3529 (2003). Gel time was evaluated by filling 5 g of adhesive into a test-glass and heating the glass in an oil bath at 100°C. Gel time was defined as the period from the submersion of the test-glass into the oil bath to the beginning of the hardening of the adhesive. The elapsed time until the point when no further stirring was possible was defined as the gel time for the sample.

Evaluation of bonding strength

Beech wood samples were prepared to investigate the bonding performance of the PF adhesive blended with the pyrolytic oil. Planed wood samples with dimensions of 5mm×50mm×500mm were bonded together with the PF adhesive having different amounts of pyrolytic oil. The adhesive mixture was applied by using a brush at the rate of about 180g/m^2 on the single bonding surface of the sample as recommended by the manufacturer. The temperature, press pressure and duration were applied as 130°C and 1.6MPa for 10min, 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 Fig. 1 (EN 205 2003).

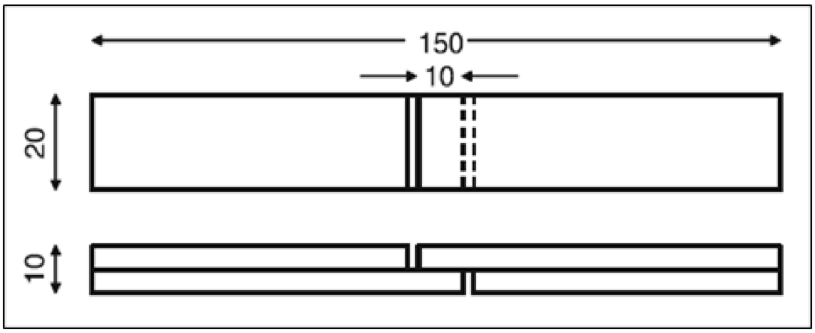

Fig. 1.
Shear strength test sample (size given in mm).

Samples from each group were divided into three groups as pre-treatment-1, pre-treatment-2 and pre-treatment-3. Table 2 summarizes the proposed scale for evaluating the quality of bonds according to EN 12765 (2002) standard. The first group of samples (the dry samples) was tested in the dry state after conditioning for 7 days in 65±5% relative humidity and 20±5°C standard climate (pre-treatment 1); the second group of samples was soaked in cold water (20°C) for 24h (pre-treatment 2); the third group of samples was boiled for 3h, then cooled in water (20°C) for 2h (pre-treatment 3). The measurement of shear strength was carried out in a Zwick/Roel Z50 universal testing machine, according to EN 205 (2003) and EN 12765 (2002).

Table 2

Proposed scale to evaluate the quality of adhesive lines on the basis of their strength and durability

Test number	**Test conditions**	**Scale Strength (N/mm^2)**			
		C1	**C2**	**C3**	**C4**
Pre-treatment 1	7 days in standard conditions	≥10	≥10	≥10	≥10
Pre-treatment 2	7 days in standard conditions 24 h in cold water at (20±5) °C	-	≥7	≥7	≥7
Pre-treatment 3	7 days in standard conditions 3 h in boiled water 2 h in cold water at (20±5) °C	-	-	-	≥4

RESULT AND DISCUSSION

Chemical analysis of the tyre pyrolytic oil

The FT-IR spectrum of the tyre pyrolytic oil is displayed in Fig. 2. The FT-IR spectrum was recorded in the transmission mode between 4000 and 400 cm^{-1} for the sample. The aliphatic C–H stretching vibrations at 3000–2800cm^{-1} and C–H deformation vibrations at 1360–1480cm^{-1} indicate the presence of alkanes. The absorbance peaks between 1775 and 1680cm^{-1} represent the C=O stretching vibration can indicate the presence of aromatic compounds. The peaks at 1604cm^{-1} and 813cm^{-1} represent C=C stretching vibrations and are indicative of alkenes. The FT-IR analysis of the oil obtained from waste tyres consists mostly of aliphatic and aromatic compounds such as alkanes, alkenes, ketones and aldehydes. Results were in accordance with the previous studies reported in the literature (Gonzalez et al. 2001; Banar et al. 2012; Kyari et al. 2005; Islam et al. 2004; Fernandez et al. 2012).

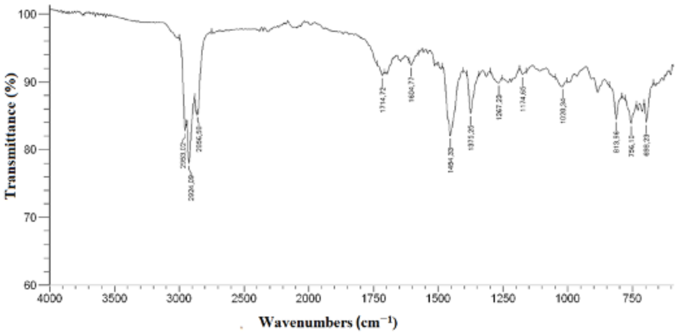

Fig. 2.
FT-IR spectrum of the tyre pyrolytic oil.

Physical properties of the PF/pyrolytic oil adhesives

The physical properties of the PF/pyrolytic oil and commercial PF adhesives are presented in Table 3. The pH values of the blended PF adhesives were lower than that of commercial PF adhesive, and significantly decreased with the pyrolytic oil addition rising. The pyrolytic oil caused lower pH values of the blended PF adhesives (e.g. 10.46 and 10.58). The viscosities of the blended PF adhesives were lower than that of reference PF adhesive, and slowly decreased with the pyrolytic addition rising. The blended PF adhesives had the shortest gel time when compared to the commercial PF adhesive. The solid content of the blended PF adhesives decreased with increasing amount of the pyrolytic oil. The lowest solid content with a value of 43.75wt% was determined for the mixture of commercial PF adhesive (60wt%) and pyrolytic oil (40wt%), while the highest solid content with a value of 50.46wt% was measured for the commercial PF adhesive. This result could be due to the fact that commercial PF adhesive contained a significant amount of urea (Zhao et al. 2010).

Table 3

Physical properties of the adhesives

Type of adhesive	pH (20 °C)	Viscosity (25 °C, cPs)	Solids content (%)	Gel time at 100 °C (s)
Com. PF	11.00 (0.014)	385 (0.47)	50.46 (0.23)	171 (0.14)
PF/pyrolytic oil (90/10)	10.83 (0.023)	359 (0.24)	48.72 (0.22)	166 (0.17)
PF/pyrolytic oil (80/20)	10.76 (0.016)	347 (0.43)	45.61 (0.12)	152 (0.11)
PF/pyrolytic oil (70/30)	10.58 (0.012)	325 (0.51)	44.12 (0.08)	136 (0.25)
PF/pyrolytic oil (60/40)	10.46 (0.020)	314 (0.22)	43.75 (0.15)	134 (0.05)

The values in the parentheses are standard deviations.

Bond performance of the PF/pyrolytic oil adhesives

The results of the tensile shear strength of the single lap-joint samples bonded with different portions of the PF adhesive and pyrolytic oil are given in Table 4. The commercial PF adhesive exhibited the highest tensile shear strength values under all pre-treatment conditions. However, the tensile shear strength of the samples insignificantly decreased with increasing pyrolytic oil content up to 20wt% for all treatments.

The highest bond performance with a value of 13.87N/mm^2 was found for the commercial PF adhesive, followed by PF/pyrolytic-oil (90/10) adhesive (12.65N/mm^2), PF/pyrolytic-oil (80/20) adhesive (11.77N/mm^2), PF/pyrolytic-oil (70/30) adhesive (10.82N/mm^2), and PF/pyrolytic-oil (60/40) adhesive (9.58N/mm^2) under dry conditions. The values of the samples bonded with the PF adhesive containing 10wt%, 20wt% and 30wt% pyrolytic oil meet the requirements for durability class C1 (EN12765 2002). The standard requires the tensile shear strength values to be at least 10N/mm^2 after conditioning of the samples for seven days in a standard climate. Additionally, the values of the PF adhesive containing 40wt% pyrolytic oil (9.58N/mm^2) are slightly lower than the requirement for class C1. The strength values of the samples significantly decreased with increasing pyrolytic oil content above 30wt% under all three conditions.

The strength values decreased drastically after pre-treatment-2 and pre-treatment-3, as expected. It was found that all adhesives excluding the PF adhesive containing 40wt% pyrolytic oil meet the minimum requirement for durability class C2 (7N/mm^2) after submersion in water for 24h (EN12765 2002). For the pre-treatment-3 (treatment in boiling water for 3 h and then submersion in room temperature water for 2h), all the blended PF adhesives meet the requirements for durability class C3 (4N/mm^2) EN12765 (2002).

The test results revealed that strength values of the samples bonded with the PF adhesives containing up to 20wt% pyrolytic oil were about the same as that of commercial PF adhesive. Further increment in the pyrolytic oil content (above 20wt%) considerably decreased the bonding performance of the PF adhesive. These findings were similar to the incidences reported in previous studies (Nakos et al. 2001; Cheng et al. 2012; Huang et al. 2012; Özbay and Ayrilmis 2015). Aslan et al. (2010), blended bio-oil, obtained from pyrolysis of wood sawdust, with commercial PF adhesive. They reported that bond quality of the PF adhesive containing 20wt% bio-oil was better than that of the commercial PF adhesive under dry conditions. The PF adhesive containing 20wt% bio-oil met the requirements for durability classes of 1–3 specified in EN 12765 (2002).

Table 4

The tensile shear strength values of single lap-joint samples

Type of adhesive mixture	Phenol-formaldehyde adhesive (wt%)	Pyrolytic oil (wt%)	The tensile shear strength (N/mm^2) /std. deviation		
			Dry condition (Pre-treatment-1)	24-h submersion in normal water (Pre-treatment-2)	3-h boiling and then 2-h submersion in normal water (Pre-treatment-3)
Com. PF	100	0	13.87±0.88	9.13±0.98	6.83±1.20
PF/pyrolitic oil (90/10)	90	10	12.65±1.1	8.73±1.41	6.36±1.28
PF/pyrolitic oil (80/20)	80	20	11.77±0.83	7.80±0.84	6.06±0.91
PF/pyrolitic oil (70/30)	70	30	10.82±1.04	7.73±0.68	5.19±1.21
PF/pyrolitic oil (60/40)	60	40	9.58±0.97	5.21±1.23	4.11±1.30

CONCLUSIONS

In this study, the commercial PF adhesive was partially blended with pyrolytic oil, obtained from waste tyres. The effects of the substitution level in the PF adhesive on the physical properties of PF adhesives were examined. Afterwards, the bonding performance of the blended adhesives was evaluated by using shear strength tests. The pyrolytic oil caused lower pH values of the blended PF adhesives. The blended PF adhesives had the shortest gel time when compared to the commercial PF adhesive. The solid content of the blended PF adhesives decreased with increasing amount of the pyrolytic oil. The viscosities of the blended PF adhesives were lower than that of commercial PF adhesive. The bonding performances of the samples bonded with the PF adhesives containing up to 20wt% pyrolytic oil were about the same as that of commercial PF adhesive. Further increment in the pyrolytic oil content (above 20wt%) considerably decreased the bonding performance of the PF adhesive. Finally, pyrolytic oil could be partially blended with commercial PF adhesives.

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