

PREPARATION AND CHARACTERIZATION OF WOOD-BASED ADHESIVE FROM OIL OF PYROLYSED LIGNOCELLULOSES WASTE

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Abstract

In this study, wood-based adhesive were prepared using pyrolytic oil obtained from lignocellulosic waste with urea-formaldehyde (UF) resin. The obtained pyrolytic oil-urea formaldehyde (PyOUF) blends were characterized by the physical (pH, viscosity, solid content) and chemical properties (reactivity-gelation time, stiasny value and Fourier transform infrared-FTIR spectroscopy analysis). The results showed that pH, viscosity, solid content, and gelation time ranged from 3.77 to 3.53, 318.00 to 384.33 mPa.s, 47.69 to 53.22%, and 58 to 203s. The stiasny value was recorded as 65% to the mass of Pyrolytic oil. FTIR characterization of PyOUF confirmed that the phenolic compounds of pyrolytic oil were successfully introduced into UF resin. The characterization showed that the wood-based adhesive could be relevant in pressed wood product such as wood-based panel products with reduction in off-gases level of formaldehyde emission.

Key words: Pyrolysis, pyrolytic oil, lignocelluloses waste, wood-based adhesives.

INTRODUCTION

Urea formaldehyde resins are widely used in the manufacturing of wood composites and their usage is always combined with release of formaldehyde during and after the manufacturing of the products. Formaldehyde is suspicious to be hazardous to the health (IARC 2004), this call for a serious attention to measure the level of the formaldehyde emissions of wood-based panel products.

In recent time, research has shown that efforts have been made to develop an effective new ways to reduce formaldehyde emissions from petroleum-based adhesives. The replacement of petroleum-based adhesives by bio-based adhesives has been subject of several studies (Klasnja and Kopitovic 1992; Trosa and Pizzi 2001; Pizzi 2006; Kong et al. 2011; Wang et al. 2015; Feng et al. 2016). Some of the studied natural products were tannins, lignin, soy protein, vegetable oil, starch, bark among others.

The most used adhesives with urea-formaldehyde was modified with different oils in the manufacture of wood-based panel products such as particleboard, plywood, oriented strandboard among others has indicated that the new adhesive with reduced emissions (Li et al. 2014) demonstrates satisfactory physical and mechanical characteristics (Amen-Chen et al. 2002, Gagnon et al. 2004, Li et al. 2014).

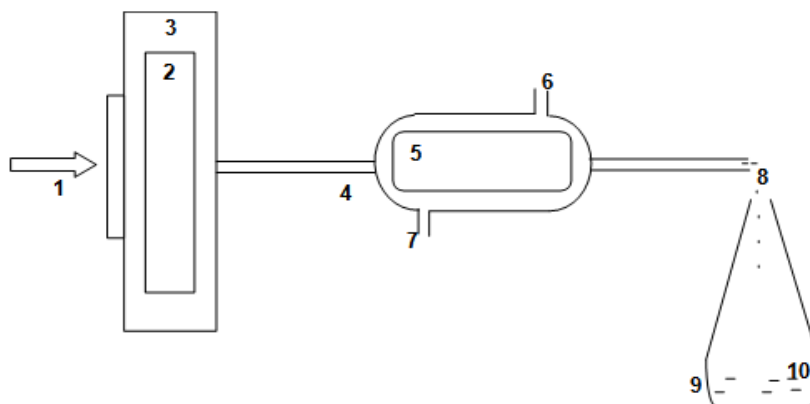
Pyrolysis is one of the suitable thermochemical conversion processes for obtaining pyrolytic oils from lignocellulosic waste. Pyrolytic oils is a dark-brown organic liquid and also it includes a lot of the organic compounds like phenols, alcohols, ketones, esters, aldehydes, oxygenated hydrocarbons (Czernik and Bridgwater 2004, Goyal et al. 2008, Fuwape et al. 2011). This product can be readily stored, transported, and also used as chemical feedstock for the production of various industrialized chemicals (Adegoke and Ayodele 2014).

This study became necessary because, there has been no research up to date on the wood-based adhesive made from lignocellulosic waste (sawdust). Hence, the aim of this research work was based on modification of UF resin with Pyrolytic oil (PyO) to form PyOUF resin with the view of analyzing PyO compatibility with UF resins.

MATERIAL AND METHODS

Pyrolysis experiment

Lignocelluloses waste (sawdust) was obtained from *Triplochiton scleroxylon* and put inside the pyrolytic chamber and then subjected to a predetermined temperature of 500°C. The gases that evolved were distilled in the condenser to form pyrolytic oil which was retained in a conical flask. The oil retained was condensed at 4°C using a reflux system. The above method used for pyrolysis of sawdust follows previous work from Adegoke *et al.* 2014.



(1) Feedstock, (2) Pyrolytic chamber, (3) Furnace, (4) Chamber rod, (5) Condenser (6) Cold water inlet (7) Cold water outlet (8) Emitted gas (9) Conical flask (10) Pyrolytic oil and tar

Fig. 1.

Schematic diagram of pyrolyser experimental set-up (Adegoke *et al.* 2014).

Preparation Wood-Based Adhesive

The blending was carried out with different ratio of PyO to UF resin: 1:1, 1:2, 1:3, 2:1, and 3:1 under reflux system on hot plate magnetic stirrer. This process was made at ambient temperature.

Characterization of physical properties of PyOUF by pH, viscosity and solids content

The pH was determined with the use of a pH meter with a calibrated electrode using buffer solutions of pH 7. Meanwhile, the viscosity of the PyOUF was determined using Ostward viscometer and this followed the standard by ASTM D-445-12 (ASTM 2017), while determination of solids content was performed by weighing 1g of the PyOUF, then drying in an oven at 103±2°C until constant weight.

$$SC = \frac{IW - FW}{IW} \times 100 [\%] \quad (1)$$

where:

SC = solid content

IW = initial weight of PyOUF

FW = final weight of PyOUF

Evaluation of Reactivity

Stiasny Value

Ten (10ml) of a 37% formaldehyde solution (formalin) and 5ml of a 38% hydrochloric acid was added to 50ml PyO and final solution was heated for 30 minutes at boiling temperature, then, the solution was filtrated through filter by suction and the solid residue was washed and dried at 105°C and weighed. The reactivity was calculated by the formula below:

$$S(\%) = \frac{A}{B} \times 100[\%] \quad (2)$$

where:

S = reactivity (stiasny-number)

A = dry weight of the solid (g)

B = dry weight of the PyO

Gelation Time

In order to measure the reactivity of wood-based adhesive consisting of ratio of PyO and UF, PyO and UF was placed in a test tube and heated in boiling water bath at 100°C under continuous mixing. A stop watch was set on motion immediately and the mixture was stirred until even the gluing (Teodoro and Lelis 2005).

Fourier Transform Infrared Analysis of PyOUF

FTIR of PyOUF was performed on a Perkin Elmer Spectrum One FTIR spectrophotometer. PyOUF was ground and mixed with 150mg of KBr and then pressed into pellets and quantified. All spectra were normalized to the height of the aromatic skeletal vibrations peak at 1432cm⁻¹.

RESULTS AND DISCUSSION

Production of (PyOUF)

PyOUF contained the blending of pyrolytic oil and urea formaldehyde in different proportion. It was clearly noticed during the production of wood-based adhesives, the colour changes with an increase or decrease in pyrolytic oil (Fig. 1). All of the PyOUF resins had a dark to brown colour with the odour of the pyrolytic oil. The different in colours observed in this study for PyOUF may have been due to the presence of micro-carbon in the liquid and the chemical composition as opined by Bridgwater, 1999. Although, Pyrolytic oil is typically a dark brown free flowing liquid, depending on the initial feedstock and mode of fast pyrolysis.

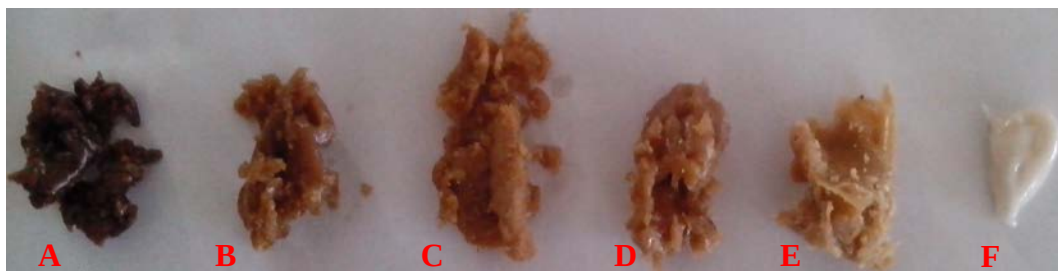


Fig. 2.
Prepared PyOUF. (A, B, C, D, and E for 1:1, 1:2, 1:3, 2:1, 3:1 and UF).

Characterization of PyOUF

pH

The pH of a solution is a measure of the molar concentration of hydrogen ions in the solution and such is the measurement acidity or basicity of the solution. The initial pH value of PyO before being introduced into UF was 2.99. Similarly, final pH with respect to blending proportion (PyOUF) had a close pH which range from 3.38 to 3.77 which is acidic. This can be explained by large amounts of oxygenated compounds present in the pyrolytic as it was been introduced into the UF (Goyal *et al.* 2008; Fuwape *et al.* 2011).

Viscosity

The value for viscosity is presented in the Table 1 with 1:3 having the highest value of 384.33 mPa.s, followed by 1:2 (365.00 mPa.s) and the lowest was recorded for UF with the 322.00 mPa.s. The low result of viscosity may be due to non-introduction of PyO. All of the PyOUF resins exhibited higher viscosities which was determined at room temperature (23°C) than that UF resin and the viscosity values of the PyOUF resins increased with increasing amounts of pyrolytic oil (Table 1).

This phenomenon may be explained by the highly complex compounds in pyrolytic oil, such as aldehydes, phenolic compounds, long-chain ketones, and esters (Goyal *et al.* 2008; Fuwape *et al.* 2011), which may participate in methylation or condensation reactions with urea and formaldehyde to form large complicated molecules, which increased the viscosity of the final products (Cheng *et al.* 2011).

Solid Content

The result of the solid content of PyOUF and UF was revealed in Table 1. The highest and lowest solid content of PyOUF was recorded at (1:3) and (2:1) with 53.22 and 47.69% respectively. It was clearly noticed that as the PyO was increase, there was an increase in the solid content.

Table 1

<i>Physical properties of PyOUF</i>			
PyOUF	pH	Viscosity (mPa.s)	Solid content (%)
1:1	3.38(0.05)	352.00(12.12)	51.45(0.17)
1:2	3.39(0.39)	365.00(5.00)	52.58(0.45)
1:3	3.43(0.14)	384.33(4.04)	53.22(0.54)
2:1	3.53(0.20)	318.00(9.85)	47.69(0.62)
3:1	3.77(0.18)	330.33(5.50)	48.37(0.38)
UF	3.50(0.16)	322.00(2.00)	49.75(0.64)

Mean; standard deviation in parenthesis.

Evaluation of reactivity

Stiasny value

One of the tests commonly used for evaluating the reactivity of complex phenolic mixtures is the Stiasny test, frequently used for tannins (Yazaki and Hillis 1980). For pyrolysis oil, this test means the higher the Stiasny value is, the more reactive is the oil. Due to the complexity of the oil, it was necessary to tests and evaluates its reactivity to formaldehyde and assess its potential as phenol replacement in wood adhesive synthesis. Stiasny test was recorded at 65% which indicate that PyO can easily react with UF.

Gel time

The preliminary testing of mixtures of PyO with UF resin consisted of measuring the time required for the formation of gel like cross linked polymer, at 100°C. The gel time is the initial criterion for assessing the usefulness of such an adhesive in the particle board production. Fig. 2 shows the gel time of PyOUF and it was observed that variations in such behavior increases with increase in UF but there noticed a draw back when PyO increases. The shortest gel time was noticed in 3:1 while the highest was at 1:3 (Fig. 2). The low or short gel time of the PyOUF shows the high reactivity of the PyO relative to that

of formaldehyde which promotes faster curing and reduces the adhesive's shelf life. This can be attributed to the highly complex compounds in pyrolytic oil, such as aldehydes, phenolic compounds, long-chain ketones, and esters (Goyal *et al.* 2008, Fuwape *et al.* 2011).

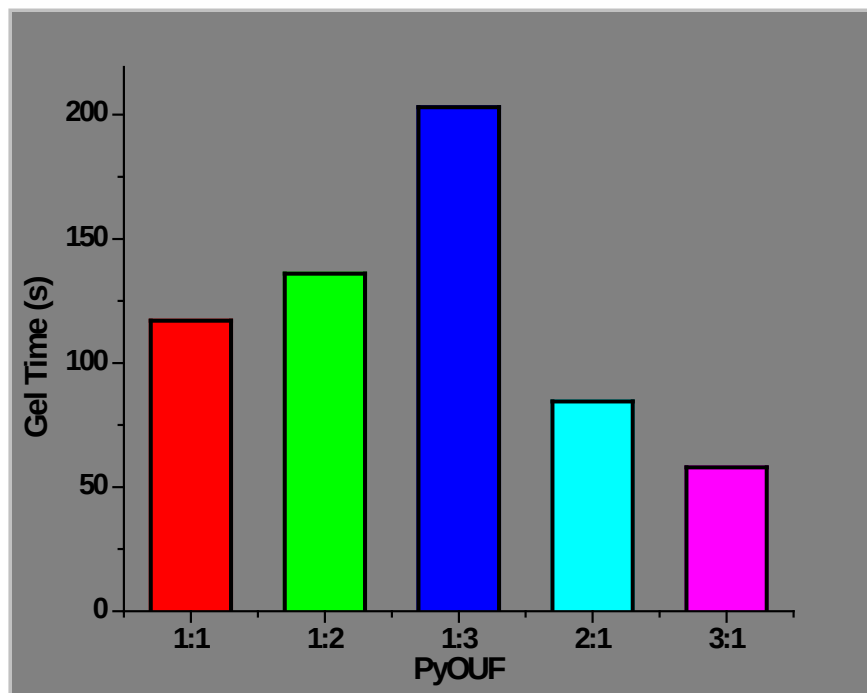


Fig. 3.
Gel times of mixtures of PyO with UF at different ratio.

FTIR Analysis

FTIR spectroscopy was used to confirm the modification of UF resin and examine the effect of pyrolytic oil on the structure of UF wood adhesive (Figs. 2-3). The spectra of the conventional and modified resins (PyOUF) were almost identical in some peak area. As shown in Fig. 3, the absorption peak at 3345cm^{-1} was assigned to the OH stretching modes, PyOUF resins showed sharper characteristic absorption peaks in this region. The sharpness of these bands indicated a reduction in the extent of hydrogen bonding interaction, which was expected because the structure was more cross-linked (Samarzija-Jovanovic *et al.* 2010). The band between $455\text{--}461\text{cm}^{-1}$ and $1174\text{--}1180\text{cm}^{-1}$ shows the Naphthalenes and Ethers for only modified oil respectively while UF show no present of phenol and alcohol as in the of $3747\text{--}3764$ and $3405\text{--}3415\text{cm}^{-1}$ peak. Compared with the pure UF resin, each PyOUF resins showed the characteristic C=C peaks of benzene ring at 1643cm^{-1} and 1652cm^{-1} , confirming that the phenolic compound of pyrolytic oil were successfully introduced into UF resin.

Table 2

Band position (cm⁻¹), peak assignment and structural polymer present in PyOUF determined by FT-IR analysis

s/n	Position (cm ⁻¹)						Peak assignment	Polymer structure
	1:1	1:2	1:3	2:1	3:1	UF		
1	3753.50	3753.50	3747.59	3764.70	3747.89	-	OH stretching from cellulose	Phenol and Alcohols
2	3423.00	3405.00	3415.00	3409.00	3410.00	-	OH stretching from cellulose	Phenol and Alcohols
3	-	-	-	-	-	3359.00		
4	2935.57	2969.18	2963.58	2969.18	2969.18	2963.58	C-H	Methyl and methylene groups
5	-	-	-	-	-	2464.98		
6	2364.14	2356.54	2364.14	2364.14	2364.14	2358.54	P-H stretch, sharp peak	Phosphines
7	1643.66	1646.00	1647.53	1648.09	1647.61	1652.00	Aromatic skeletal vibration (C=C)	Olefinic compounds
8	1555.24	1555.24	1549.65	1552.44	1549.65	1546.85	-CO-NH-	Secondary Amides
9	1376.22	1361.81	1381.81	1379.02	1379.02	1379.02	C-H deformation	Cellulose, hemicellulose
10	1252.42	1252.84	1253.22	1253.87	1253.00	1252.14	C-O of guaiacyl ring	Aromatic methoxy group
11	1174.62	1177.62	1180.41	1177.62	1180.41	-	O-H	alcohol (primary and secondary and aliphatic ethers)
11	1020.51	1022.83	1021.26	1018.21	1016.74	1013.00	C-O deformation	Primary Alcohols
13	839.16	-	-	833.56	839.16	841.95	CH out-of-plane deformation	1,2,4-trisubst benzenes
14	766.43	769.23	766.43	766.43	766.43	766.43	C-Cl stretch	alkyl chlorides
15	545.45	537.06	539.86	556.64	556.64	615.00	=CH ₂ twisting	Vinyl compounds
16	458.74	461.85	461.53	461.53	455.94	-	Out-of-plane ring bending	Naphthalenes

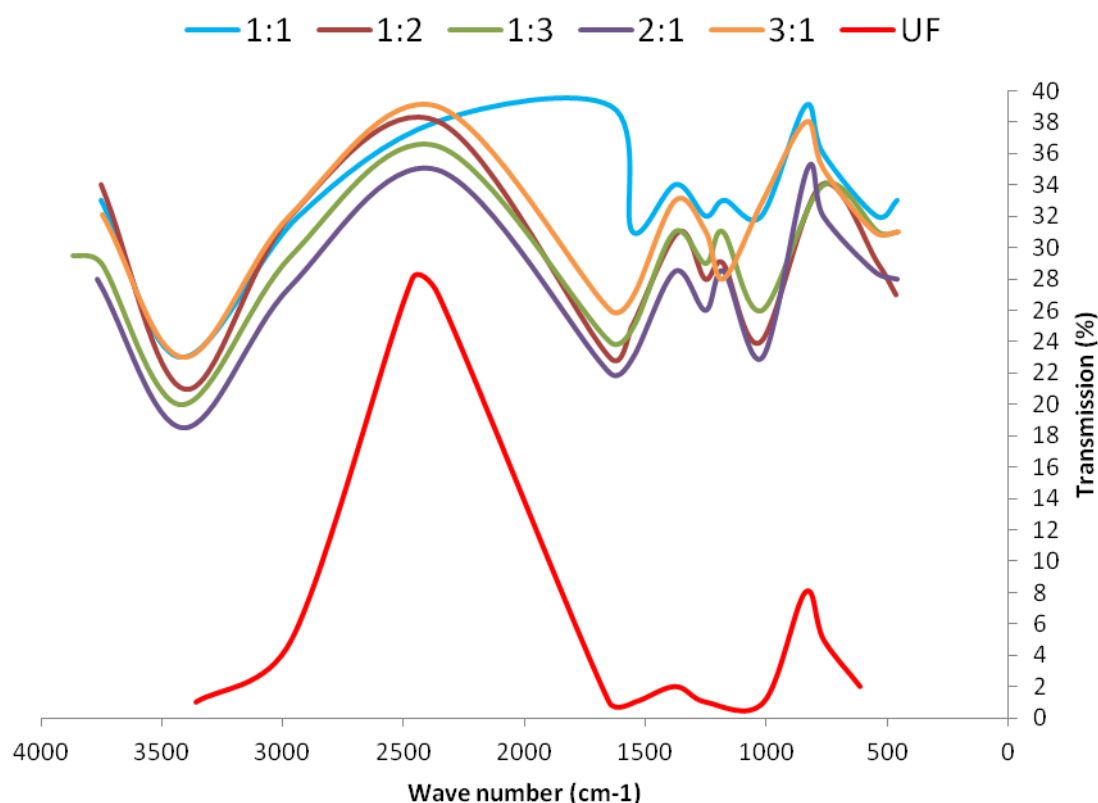


Fig. 4.
FTIR Spectra of PyOUF.

CONCLUSION

The study has shown various blending proportion of PyO and UF to make PyOUF adhesive called wood-based adhesive. The pH, viscosity, solid content results show the characteristics of PyOUF. It is also evidence from the study that PyO can easily react with UF having indicated by the presence of phenolic compound through FTIR conducted. Moreover, the study therefore has made it possible that PyO could be used to replace the phenolic compound in UF and much relevant in pressed wood with off-gases level of formaldehyde reduction. Also, the study further suggested that similar performances of new adhesives could be achieved in the near future when compare with petroleum-based adhesives.

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