Synthesis and Thermal Stability of Glyoxalated Alkali Lignin-Polyvinylpyrrolidone Resins

Aikfei Ang,[a,]* Zaidon Ashaari,[a] Edi S. Bakar,[a] and Ibrahim Nor Azowa[b]

Natural, renewable, and non-toxic lignin-based resin was synthesized through copolymerization with monomeric N-vinyl-2-pyrrolidone (VP) in the presence of benzoyl peroxide (BPO) as the free radical initiator. Glyoxalated lignin was used as the feedstock. The mechanism of copolymerization between the glyoxalated alkali lignin and VP monomer was determined through Fourier-transform infrared spectroscopy (FT-IR). The optimum amount of VP monomer used and the reflux time required in the synthesis process were determined through thermogravimetric analysis (TGA). In the presence of BPO, copolymerization between glyoxalated alkali lignin and VP monomer was accomplished *via* the formation of ether linkages in a condensation reaction at pH 7.0. More ether linkages were formed with higher amounts of VP monomer and longer reflux times. The addition of VP monomer into glyoxalated alkali lignin increased its thermal stability. FT-IR and TGA indicated that 0.012 moles of VP monomer and an 8-h reflux time were optimum conditions for the synthesis of glyoxalated alkali lignin-polyvinylpyrrolidone resins.

Keywords: Bio-resin; Lignin; Polyvinylpyrrolidone; Copolymer

Contact information: a: Department of Forest Production, Faculty of Forestry, Universiti Putra Malaysia, 43400 Serdang, Selangor D.E., Malaysia; b: Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor D.E., Malaysia;
** Corresponding author: afang1129@gmail.com*

INTRODUCTION

Bio-resins first gained attention during the oil crisis of the early 1970's, and the new consumer demand for bio-resins is driven by environmental issues, with growing public opinion that petroleum-based products are harmful to the environment (Jones 2007). Thus, environmental and economic factors have increased the demand for wood resins made from renewable raw materials.

Bio-resins have been synthesized from naturally renewable raw materials, such as lignin. Lignin is polyphenolic and contains an unsubstituted carbon at either the C_3 or C_5 position on the aromatic ring. It also contains free phenolic and aliphatic hydroxyl groups that can form a quinone methide intermediate, which reacts with an aldehyde, tannin, phenol, or isocyanate group with heating under alkaline conditions (Ballerini *et al.* 2005; El Mansouri 2007a; Abdelwahab and Nassar 2011; Mansouri *et al.* 2011). Due to these chemical characteristics, lignin is a good starting material for wood adhesives (Cetin and Ozmen 2002; Cavdar *et al.* 2008). A study has been conducted to investigate the potential of using kraft lignin substituted phenol formaldehyde (PF) resin to produce experimental aspen oriented strand board (OSB) panel (Cavdar *et al.* 2008). The authors reported that the properties of aspen OSB panel bonded with kraft lignin substituted PF resin (50% of phenol was substituted by kraft lignin) including bending strength, internal bonding strength, thickness swelling, and water absorption, met the minimum requirements specified in the related standards, and they were comparable to those commercially manufactured OSB panels. Sulfur-free organosolv lignin was also found to be capable of substituting for the phenol in phenol formaldehyde resin for production of particleboard (Cetin and Ozmen 2002). It is found that 30% substitution of phenol with organosolv lignin was the appropriate proportion for the replacement of phenol in commercial type PF resin, as the physical strength and dimensional stability properties of the particleboard bonded are comparable to the commercial type PF resin bonded particleboard.

To be effectively used in value-added applications such as the synthesis of resins, lignins usually require modifications to enhance their chemical reactivity, for example, glyoxalation (El Mansouri *et al.* 2011). Glyoxalation of lignin introduces hydroxymethyl units (CH_2OH) that enhance reactivity (Hu *et al.* 2011).

Glyoxalated lignin has been incorporated into PF resin, tannin, and polymethylene polyphenyl isocyanate (pMDI) to use as an adhesive in wood composites (El Mansouri *et al.* 2007b; Navarrete *et al.* 2012). Particleboard containing 10% of adhesive was fabricated with two formulations, which consisted of 55/20/25 glyoxalated calcium lignosulfonate/pMDI/PF proportions and 60/40 glyoxalated calcium lignosulfonate/pMDI proportions (El Mansouri *et al.* 2007a). It was found that IB strengths of the particleboard bonded with these adhesives met the minimum requirement as stipulated in EN 312 1995. Navarrete *et al.* (2012) reported that particleboards adhered with mixtures of kraft and wheat straw glyoxalated lignin with mimosa tannin and hexamine as a hardener. These particleboards were classified as interior panel P2 in according with the standard EN 312 1995 based on their highest IB strength. Particleboards prepared with these natural resins were tested for their free-formaldehyde through the flask method according to EN 717-3 1996. The results showed that the free-formaldehyde emission from the panels were at least 87% and 75% lower than the commercial UF and MUF resins. The panels were classified as E0.

Vinylpyrrolidone polymers have been extensively used in the pharmaceutical, cosmetic, and food industries (Haaf *et al.* 1985). Uncrosslinked polyvinylpyrrolidone (PVP) polymer is used in the medical and pharmaceutical fields and has been found to be non-toxic and non-thrombogenic. It has been incorporated into a melamine-formaldehyde copolymer resin, where the –C=N– melamine units reacted with formaldehyde (Singh and Kumar 2009). The resulting methylol group from the melamine-formaldehyde adduct forms an ether bond *via* the carbonyl group in PVP. This resin has excellent adhesive strength on wooden strips and micellar behavior in aqueous solution. Preparation of polyvinylpyrrolidone/lignin blends has been reported by Silva *et al.* (2005). The authors reported that the incorporation of sugarcane bagasse lignin (SCBL) in PVP (up to 15%), causes the thermal stability of PVP to decrease, but increased the photostability of PVP.

This study examined the polymerization mechanism of glyoxalated alkali lignin-polyvinylpyrrolidone (GL-PVP) resins through FT-IR spectroscopy and optimized the ratio of N-vinyl-2-pyrrolidone monomer to glyoxalated alkali lignin for the synthesis of thermally stable lignin-based resins.

EXPERIMENTAL

Materials

The chemicals used in this study included a glyoxalated alkali lignin (GL) solution with optimal proportions of glyoxal and sodium hydroxide (NaOH) (Ang *et al.* 2015). The source of alkali lignin is from softwood. The GL solution was further neutralized to pH 7.0 through titration with hydrochloric acid (HCl). The N-vinyl-2-pyrrolidone (VP) monomer solution was stabilized with a solution of NaOH and HCl (37%) purchased from Fisher Scientific (M) Sdn. Bhd (Shah Alam, Malaysia). The VP monomer solution was further neutralized to pH 7.0 through titration with HCl to remove NaOH. Benzoyl peroxide (BPO, with 25% H_2O) generated free radicals for VP polymerization and was supplied by Merck Sdn. Bhd (Petaling Jaya, Malaysia).

Methods

Radical polymerization of polyvinylpyrrolidone (PVP) homopolymer

Neutralized VP monomer solution was polymerized *via* radical polymerization using BPO as free radical generator. Neutralized VP monomer (1.35 g) was added to a 50 mL flat bottom flask, and then 2% BPO (per g VP) was added to the neutralized VP monomer. Afterward, the mixture was stirred vigorously to obtain a homogeneous solution. The homogeneous solution was then put in an oven at 80 °C for 72 h for the radical polymerization of VP monomer to taking place. Once the polymerization had been completed, the mixture was cooled at ambient temperature. The obtained PVP homopolymer was stored in a desiccator.

Synthesis of glyoxalated alkali lignin-polyvinylpyrrolidone (GL-PVP) resins

Neutralized GL solution (2.0 g) was added to a 50 mL flat bottom flask. The solid content for the neutralized GL was 37 ± 2%. Different amounts of neutralized VP monomer were and 2% BPO (per g VP) were added to the neutralized GL (Table 1), and the mixture was stirred vigorously to obtain a homogeneous solution. The flask was equipped with a condenser, thermometer, and magnetic stir bar and then transferred to a 75 ± 2 °C water bath for reflux for 240, 360, or 480 min. Afterward, the mixture was cooled at ambient temperature, and the pH was measured with a digital pH meter. The final pH of the mixture was 6.0 to 7.0. The mixture was pre-cured at 105 °C for 24 h, followed by full curing at 180 °C for 1 h in an oven. The fully cured samples were stored in a desiccator.

Table 1. Parameters used in the Synthesis of GL-PVP Resins

Sample	Temperature (°C)	Time (min)	Neutralized GL (g)	Neutralized VP (mole)	BPO (g)
R1	75	240	2.0	0.0049	0.0108
R2	75	240	2.0	0.012	0.027
R3	75	360	2.0	0.0049	0.0108
R4	75	360	2.0	0.012	0.027
R5	75	480	2.0	0.0049	0.0108
R6	75	480	2.0	0.012	0.027

Determination of solid content in GL-PVP resins

To determine the solids content of the GL-PVP resins, approximately 2 g of the GL-PVP resin was heated in oven at 120 °C for 3 h. The solids content for all the GL-PVP resins was approximately 36 ± 2%. The percentage of solid content was calculated as follows,

$$\text{Solid content (\%)} = W_0 / W_1 \text{ X } 100 \qquad (1)$$

where the W_0 is the weight of dried resin and W_1 is the weight of resin sample. The samples used in this test were stored in a desiccator for further analysis.

Fourier-transform infrared spectroscopy (FT-IR)

An FT-IR spectrophotometer (Spectrum 100 series, Perkin-Elmer, Massachusetts, USA) was used to determine the functional groups in pure samples of the GL-PVP resins and PVP polymer. Spectra were collected at ambient temperature from 400 to 4000 cm^{-1} and a resolution of 4 cm^{-1}. The absorption bands were assigned as suggested by Tejado *et al.* (2007), Laot (1997), and Schultz and Glasser (1986).

Thermogravimetry analysis (TGA)

Approximately 8 to 10 mg of GL-PVP resin powder was weighed in an aluminum pan and placed in the TGA/SDTA 851e instrument (Mettler-Toledo, Columbus, USA). Samples were heated from room temperature to approximately 700 °C at a rate of 5 °C/min and a nitrogen atmosphere. The curve of weight loss *vs*. temperature was constructed (TG), and the derivative of this curve (DTG) indicated the temperatures at which the maximum rate of weight loss occurred.

RESULTS AND DISCUSSION

Quantitative FT-IR Spectra

The lignin content can be determined by univariate analysis with FT-IR spectroscopy. In a univariate analysis, the intensity of one lignin band is used to calculate the lignin concentration. This is possible because the observed IR band intensity is usually a linear function of the lignin concentration. The absorption intensities for each band were normalized based on the vibration of the aromatic ring appearing at 1600 cm^{-1}. The quantitative analysis was described previously by Malutan *et al.* (2008), El Mansouri *et al.* (2011), and Mancera *et al.* (2011). The band assignments for FT-IR spectra and the relative absorbance bands for each functional group for glyoxalated lignin (GL) and the glyoxalated alkali lignin-polyvinylpyrrolidone (GL-PVP) resins are shown in Table 2.

Compared with the GL sample, there were new absorbance bands in the GL-PVP spectra at 1416 cm^{-1}, 1280 cm^{-1}, and 1125 cm^{-1} (Figs. 2, 3, and 4). The band at 1416 cm^{-1} corresponded to C-H deformation of cyclic C-H_2 (vinyl group) in PVP. Absorbance at 1280 cm^{-1} corresponded to the stretching of C-N (aromatic amines) groups in PVP. The band at 1125 cm^{-1} was assigned to in-plane deformation vibration of aromatic C-H in guaiacyl units.

The absorbance band at 1663 cm^{-1} (C=O group) in the PVP spectrum (Fig. 1) disappeared in all GL-PVP resin spectra (Figs. 2 and 3). In addition, the relative absorbance of phenolic OH and aliphatic OH groups at 3420 cm^{-1} to 3405 cm^{-1} in all GL-PVP resins was decreased compared to GL. Thus, polymerization occurred between the C=O group of the VP monomer and an aliphatic OH group in lignin. The ether linkage reaction between these groups was apparent as an increase in relative absorbance of aliphatic ether (C-O-C) at 1030 cm^{-1} and emergence of a new absorbance band at 1180 cm^{-1} which was assigned as an ether group (Table 2; Figs. 2, 3, and 4).

The absorbance of the phenolic OH band at 1365 cm^{-1} was increased relative to GL for all GL-PVP resins. This result was attributed to reformation of the phenolic OH group from sodium phenolate ions during the titration process, where the sodium phenolate ion was present in the base condition. The average relative absorbance band of CH_3 and CH_2

and methoxyl-OCH_3 groups decreased in all GL-PVP resins as a result of acid hydrolysis during titration. The band at 913 cm^{-1} corresponded to OH bending of carboxylic acid. This band became more intense in all GL-PVP resins compared with GL due to the partial hydrolysis of VP aromatic amides group by the strong acid, HCl during the titration process through nucleophilic acyl substitution reaction.

The relative absorbance of aliphatic ether groups for R1, R2, R3, R4, R5, and R6 were 0.49, 0.49, 0.48, 0.49, 0.47, and 0.52, respectively. When the reflux time was the same, these values remained unchanged, and there was no difference in the intensity of aliphatic ether linkages formed in GL-PVP resins regardless of the amount of VP monomer used. Thus, using more VP monomer did not increase the formation of aliphatic ether linkages or the formation of high molecular weight GL-PVP resins. However, the formation of aliphatic ether linkages was influenced by the time required for the reflux process, especially when 0.0121 moles of VP was used. When 0.0121 moles of VP was used (samples R2, R4, and R6), the relative absorbance of the aliphatic ether group was increased from 0.49 to 0.52. Thus, a longer reflux time favours the formation of high molecular weight GL-PVP resin. The absorbance band of the ether group (1180 cm^{-1}) shifted to a higher wavenumber as the time for reflux process increased regardless of the amount of VP monomer used (Figs. 2 and 3). The wavenumber of the absorbance band for ether group in sample R6 was 1183 cm^{-1}, whereas in sample R1, it was 1160 cm^{-1}.

Table 2. Functional Groups in FT-IR Spectra of GL and GL-PVP Resins

Band (cm^{-1})	Functional Group	Relative Absorbance							
		Sample	GL	R1	R2	R3	R4	R5	R6
3420 to 3405	Phenolic OH and aliphatic OH		0.52	0.28	0.28	0.29	0.27	0.30	0.24
1365	Phenolic OH		0.52	0.67	0.61	0.74	0.61	0.66	0.59
		Mean Value	0.52	0.48	0.45	0.52	0.44	0.48	0.42
2960 to 2925	CH_3 and CH_2		0.31	0.21	0.19	0.15	0.18	0.22	0.15
1460			0.57	0.36	0.34	0.37	0.31	0.37	0.34
		Mean Value	0.44	0.29	0.27	0.26	0.25	0.30	0.25
1220	Ether, C-O(Ar)		0.39	0.37	0.34	0.36	0.31	0.39	0.34
1125	Guaiacyl, Ar C-H		0.39	0.39	0.36	0.40	0.33	0.41	0.36
1030	Ether, C-O(C)		0.47	0.59	0.61	0.60	0.57	0.61	0.64
1180			0.39	0.39	0.36	0.35	0.41	0.33	0.39
		Mean Value	0.43	0.49	0.49	0.48	0.49	0.47	0.52
2850 to 2840	Methoxyl-OCH_3		0.25	0.15	0.13	0.15	0.13	0.16	0.11
1600	C-C vibration, aromatic ring		1.00	1.00	1.00	1.00	1.00	1.00	1.00

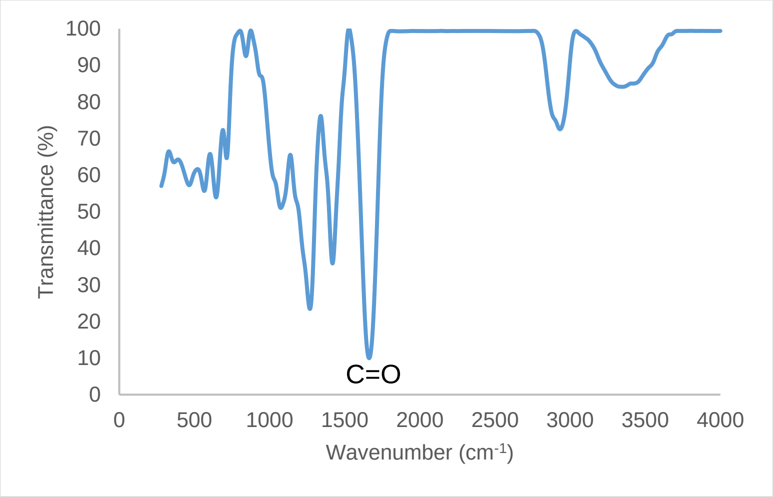

Fig. 1. FT-IR spectrum of PVP

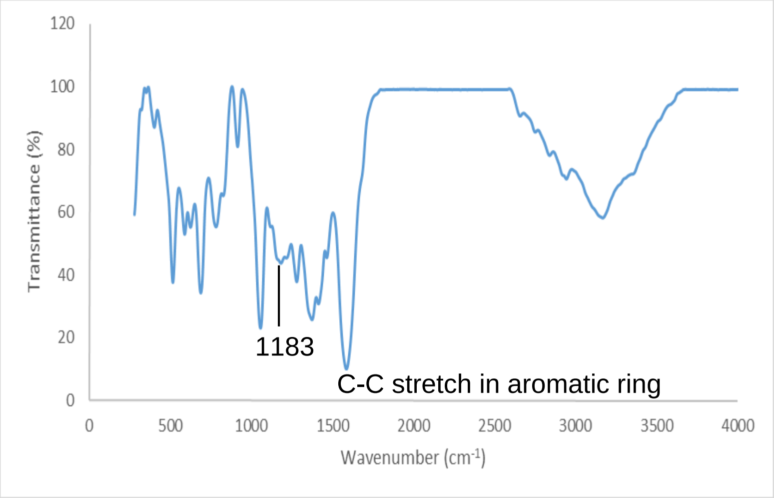

Fig. 2. FT-IR spectrum of sample R6

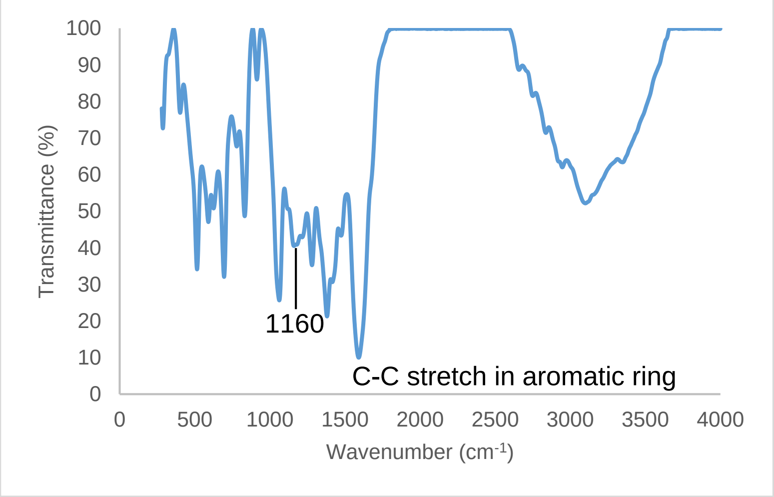

Fig. 3. FT-IR spectrum of sample R1

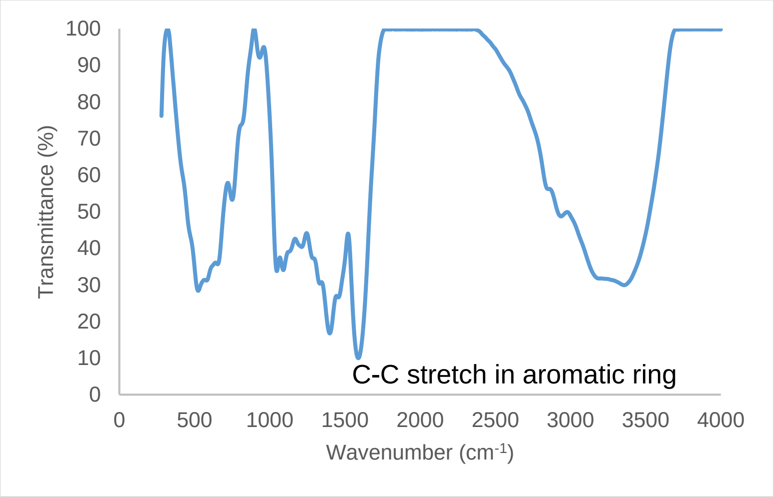

Fig. 4. FT-IR spectrum of GL

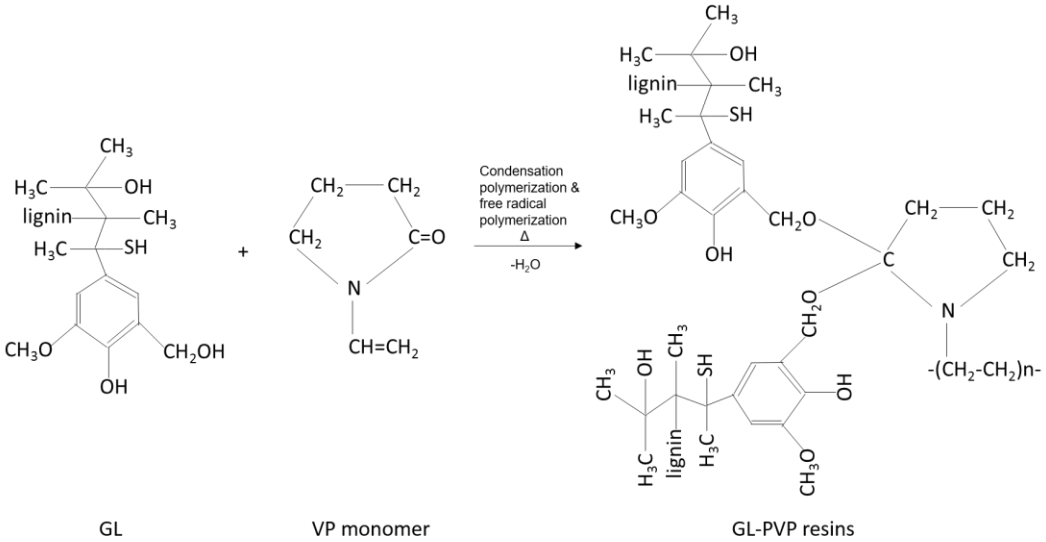

Fig. 5. Condensation polymerization between GL and VP monomer, which took place at the C_5 position of aromatic ring of GL

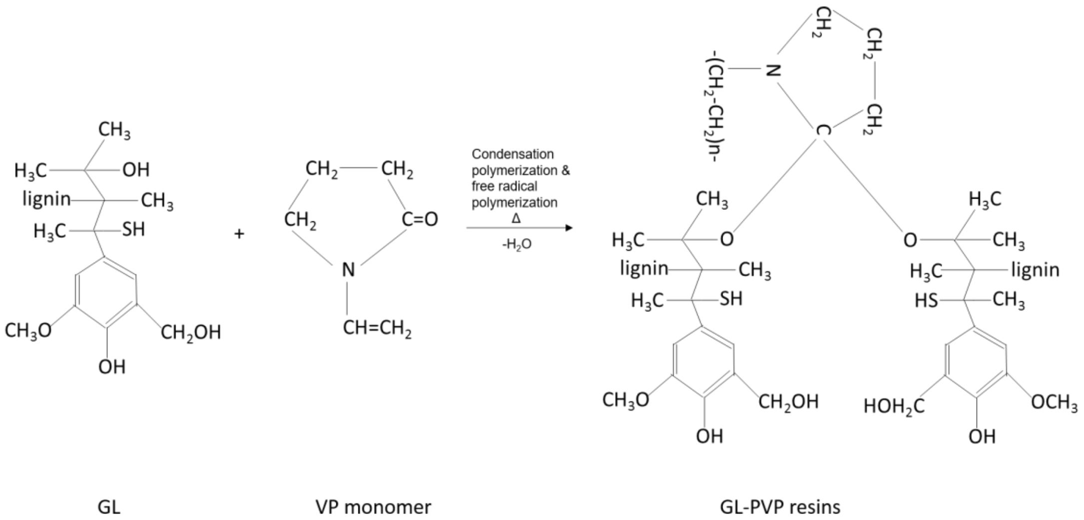

Fig. 6. Condensation polymerization between GL and VP monomer, which took place at the aliphatic hydroxyl group of GL

The wavenumber of an absorbance band for a functional group in polymers with bulkier structure will tend to shift to higher wavenumber compared to polymers with less bulky structure. The higher wavenumber of absorbance for the ether group in sample R6 revealed that the polymer structure in sample R6 was bulkier compared to the polymer in sample R1. The proposed oligomer structure of GL-PVP resins is shown in Figs. 5 and 6.

Thermal Stability of GL-PVP Resins

Thermogravimetric (TG) curves reveal mass loss associated with the temperature of thermal degradation, while the first derivative of that curve (DTG) shows the corresponding rate of mass loss. The peak of this curve (DTG_{max}) is the thermal decomposition temperature and is used to compare the thermal stability of different materials.

The DTG_{max} and mass loss of GL and GL-PVP resins are summarized in Table 3. The TG curves of the PVP homopolymer and R6 samples are shown in Figs. 7 and 8, and the DTG curves of PVP homopolymer and R6 are shown in Figs. 9 and 10. The data revealed that the PVP homopolymer polymerized via free radical polymerization using benzoyl peroxide at 80 °C for 72 h was highly thermally stable, where the PVP homopolymer only degrades at around 432 °C.

While in the case of GL-PVP copolymer resin, three events took place during the TG test, as three DTG_{max} peaks were recorded. Glyoxalated lignin underwent polymerization through a condensation reaction (Ang *et al.* 2015), which corresponded to the highest DTG_{max} peak as shown in Fig. 10. The TGA results suggested that new lignin-PVP copolymers were generated after the GL-PVP resins had undergone the solids-content test.

Table 3. TGA Data for GL and GL-PVP Samples

Run	Peak 1		Peak 2		Peak 3	
	DTG_{max} (°C)	Mass Loss (%)	DTG_{max} (°C)	Mass Loss (%)	DTG_{max} (°C)	Mass Loss (%)
GL	106.66	3.38	266.43	15.25	353.33	7.41
R1	123.87	0.84	280.12	32.07	334.32	5.32
R2	112.51	1.44	262.08	31.75	344.80	5.47
R3	59.10	7.54	268.30	33.92	334.89	5.10
R4	99.70	0.94	282.51	31.09	335.09	5.39
R5	100.41	1.27	268.43	31.53	330.76	5.64
R6	120.83	0.90	283.49	31.09	339.00	5.47

The first DTG_{max} peak in all samples was between 59.10 °C and 123.87 °C. This peak corresponded to the mass loss (0.84% to 7.54 %) resulting from the evaporation of moisture and volatiles. The second DTG_{max} peak in all GL-PVP samples was attributed to the newly generated polymers. The recorded temperatures for this peak ranged from 262.08 °C to 283.49 °C, and the mass loss rate was between 15.25% and 33.92%. The recorded temperatures of this peak for all GL-PVP samples were generally higher than in the GL sample. Thus, the addition of VP monomer to GL produced thermally stable lignin-based resin; a higher degree of copolymerization between GL and VP monomer was accomplished to promote the generation of high molecular weight GL-PVP copolymers.

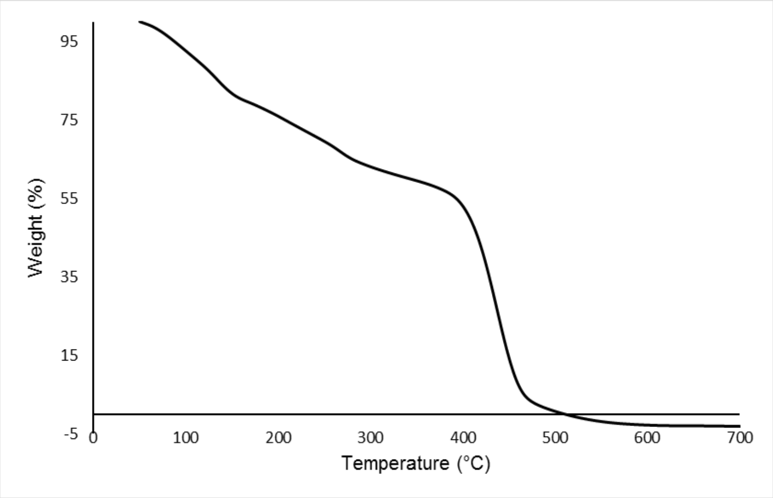

Fig. 7. TGA curve of the PVP homopolymer sample

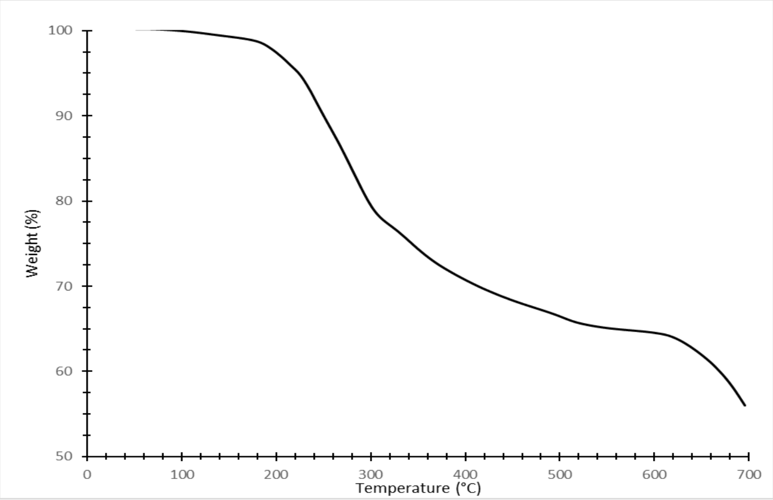

Fig. 8. TGA curve of the R6 sample

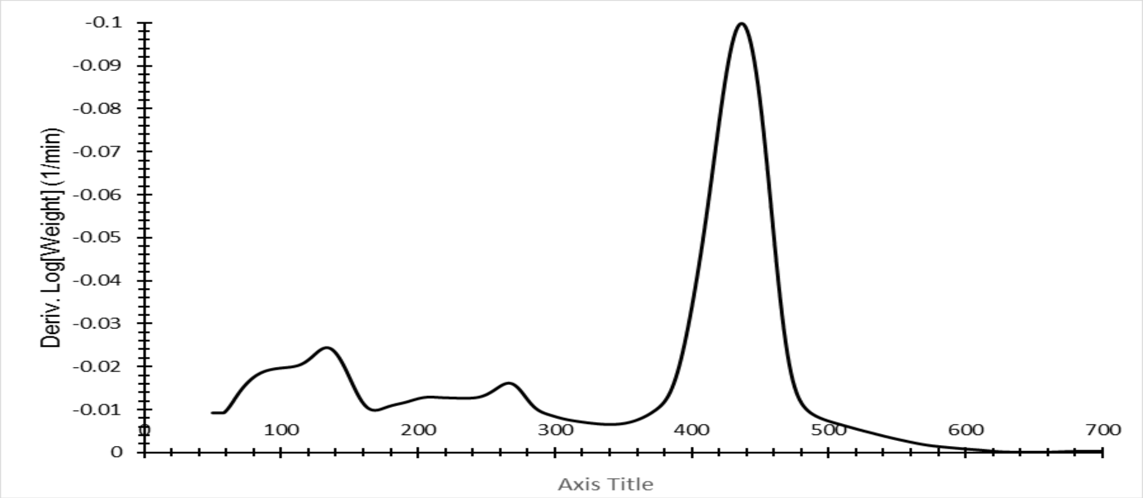

Fig. 9. DTG curve of the PVP homopolymer sample

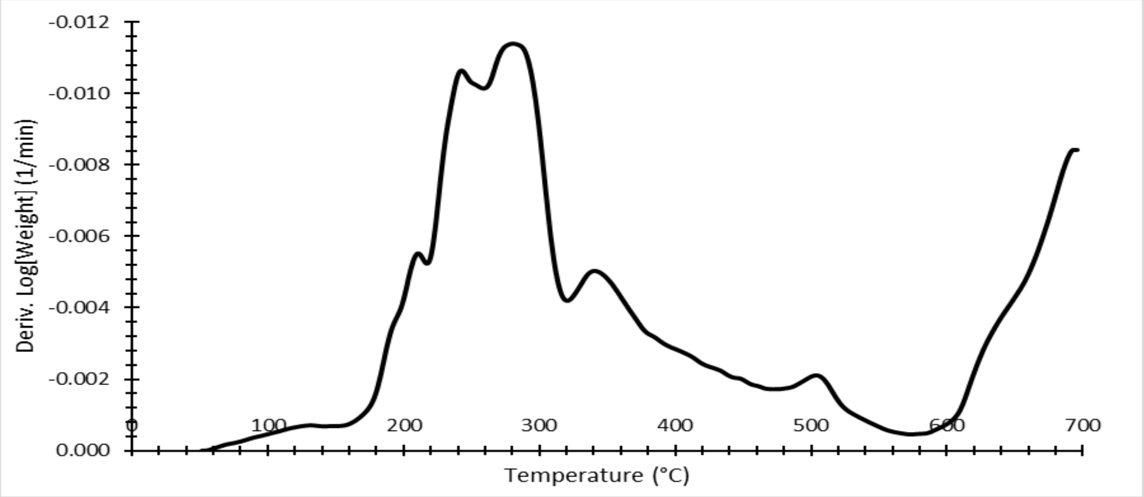

Fig. 10. DTG curve of the R6 sample

The third DTG$_{max}$ peak was found in all GL and GL-PVP samples. This peak corresponded to the mass loss of the samples as a result of the decomposition of the remaining lignin polymers, which were not involved in the formation of GL-PVP copolymers. The recorded temperatures for this peak ranged from 330.76 °C to 353.33 °C, and the mass losses ranged from 5.10% to 7.41%.

According to Ang *et al.* (2015), the temperatures for the third DTG$_{max}$ peak in the methanol fractionated alkali lignin without glyoxalation (ML) sample was 313.0 °C, while the mass loss for this peak was 29.94%. The temperatures of the third DTG$_{max}$ peak for all GL-PVP samples were higher than that of ML but slightly lower than that of GL. Hence, all GL-PVP samples were partially repolymerized during the condensation reaction in the solids content test; as a result, more thermally stable lignin polymers were generated (Sun *et al.* 2000).

However, the slightly inferior thermal stability of the repolymerized lignin molecules in all the GL-PVP samples compared to those in the GL sample. As the repolymerization reaction of lignin molecules was similar to the curing reaction of phenolic resin (Wang *et al.* 2009), synthesis of GL-PVP resin in neutral medium might cause the degree of repolymerization of lignin molecules become lower.

As discussed above, the highest DTG$_{max}$ peak was attributed to the copolymerization of the GL and VP monomer *via* C-O-C linkages to form GL-PVP copolymers *via* the condensation reaction during the solids content test. Because the highest temperature of the highest DTG$_{max}$ peak (283.49 °C) and a mass loss of 31.09% was found in the R6 sample, a higher degree of copolymerization *via* C-O-C linkages was accomplished in this sample. The weight of the VP monomer used for this sample was 0.012 moles.

The data revealed that the thermal stability of GL-PVP resins was inferior to that of the PVP homopolymer. This finding is in good agreement with data as reported by Silva *et al.* (2005), which also reported that the incorporation of sugarcane bagasse lignin in PVP imparted negative effect on the thermal stability of PVP. However, the thermal stability of GL-PVP resins was superior to that of GL alone, as reported by Ang *et al.* (2015).

CONCLUSIONS

1. FT-IR spectroscopy confirmed that the copolymerization of GL and VP monomer was accomplished *via* formation of C-O-C linkages in a condensation reaction.
2. The thermal stability of GL was enhanced with the additional of VP monomer due to the grafting of GL-PVP copolymer.
3. Based on FT-IR and TGA results, high thermally stable GL-PVP copolymer resin was produced with 0.012 moles of VP monomer in a reaction at pH 7.0 and reflux at 75 °C for 8 h.

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