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Curing kinetics and mechanical properties of bio-based epoxy composites comprising lignin-based epoxy resins

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ABSTRACT

Lignin-based epoxy resins derived from de-polymerized Kraft/organosolv lignins were blended with a conventional bisphenol A (BPA)-based epoxy resin at various percentages to prepare bio-based epoxy systems as polymer matrices for manufacturing of fiber-reinforced plastics (FRPs) and coatings. The curing process of epoxy composites was studied using DSC and the activation energy was calculated by isoconversional methods. Epoxy composites comprising a low percentage (25 wt%) of lignin-based epoxy resin can be cured faster than the pure BPA-based epoxy resin used in particular at the early stage of curing. However, blending a large amount (>50 wt%) of lignin-based epoxy resin with the BPA-based epoxy resin retarded the curing process particularly at the late stage of curing. Tensile and flexural strengths of the prepared FRPs using bio-based epoxy composites were found to be superior or comparable to those of the FRP with the pure BPA-based epoxy resin when the lignin-based epoxy resin blending ratio is less than 50–75 wt%. Furthermore, the bio-based epoxy films comprising up to 50 wt% of DOL-based epoxy resin were exhibited high adhesion strength on a metal substrate.

1. Introduction

In recent decades, synthesis of bio-based chemicals and materials using bio-renewable resources has drawn increasing attention in academia and industry due to the concerns over the environment impacts and the depleting reserves of fossil fuels (currently the dominant sources for chemicals and materials) [1,2].

Epoxy resin is one of the most widely used thermosetting polymers because of its superior properties, e.g., great chemical resistance, good thermal stability and high adhesion strength to various substrates. These properties provide diverse applications of epoxy resins in coatings, adhesives to other engineering applications [3,4]. The ultimate properties of epoxy resins are determined mainly by their chemical composition and their curing conditions [5,6]. Therefore, it is of great significance to investigate on the curing process of epoxy resins for better control of their final properties.

Synthesis of bio-based epoxy resins were reported in several literature studies. Also, several review papers have been published on the potential of production of bio-based epoxy resins [7,8]. However, limited attention has been paid on

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simultaneous characterization of the curing kinetics of the resins and mechanical properties of fiber reinforced plastics (FRPs) and coatings using lignin-based epoxy matrices. Bio-resources including vegetable oil [9,10], tannins [11], vanillin [12,13], rosin [14], bark [15], liquefied biomass [16,17] and lignin [18,19] have been used for the synthesis of bio-based epoxy resins. Kim and Sharma [10] reported a novel process for epoxidation of several plants oils without using solvent, and demonstrating that the epoxidized linseed oil have excellent modulus and impact resistance. Liu et al. [14] developed a 100% rosin-based epoxy resin possessing a high glass transition temperature of around 164 °C. Kuo et al. [15] synthesized a bark-based epoxy resin exhibiting higher tensile strength and stiffness in comparison with other bio-based epoxy resins. Lignin was also demonstrated to be a promising bio-substitute for bisphenol A (BPA) in synthesis of bio-based epoxy resins with mechanical and thermal properties comparable to the conventional BPA-based epoxy resins [17,20]. However, only a small portion of the research focused on curing process and kinetics of lignin-based epoxy resins in order to provide products with excellent performance. Sun et al. [5,6] studied the curing kinetics of lignin-based epoxy resins with three various curing agents including methylhexa-hydrophthalic anhydride, maleic anhydride and 2-methyl-4-methylimidazole using a DSC. The kinetics parameters were evaluated based on Kissinger method and autocatalytic model. Hirose et al. [3] determined the activation energy by Ozawa method for curing of bio-based epoxy resins synthesized with polyester chains derived from biomass components including saccharides, lignin and glycerol. In some studies, lignin was blended with epoxy resin and the curing kinetics of the mixture were studied. For example, Kong et al. [4] blended a conventional epoxy resin with a hydrolyzed lignin at 5% blending ratio, and investigated the curing kinetics and the bonding properties of the resins as adhesives. The results revealed that the introduction of a small amount of lignin promoted the curing process of the epoxy resin and improved the shear strength. Yin et al. [21] studied the mechanical properties and curing of an epoxy resin mixed with enzymatic hydrolysis corn straw lignin. It was suggested that the hydroxyl and carboxyl groups of lignin could react with the epoxy groups, and the polyphenol structure of lignin could catalyze the curing reactions.

As described in our previous published works [22,23], a novel method has been developed for the synthesis of bio-based epoxy resins with reduced side reactions, employing de-polymerized Kraft lignin (DKL) and de-polymerized organosolv lignin (DOL) under alkaline condition in the presence of a phase transfer catalyst, tetrabutylammonium bromide (TBAB). Lignin-based epoxy resins derived from de-polymerized Kraft/organosolv lignins were blended with a conventional bisphenol A (BPA)-based epoxy resin at various percentages (25–100 wt%) to prepare bio-based epoxy systems. The thermal stability of the prepared bio-based epoxy systems were investigated by a TGA-FTIR [24]. The limiting oxygen index (LOI) of all lignin-based epoxy composites are higher than that of the conventional epoxy resin indicating that the lignin-based epoxy systems are more effective fire retardants than the conventional epoxy resin. The percentage of lignin-based epoxy resin in the bio-based epoxy systems had a significant effect on the activation energy of the thermal decomposition process. With increasing the amount of the lignin-based epoxy resins, the activation energy reduces at the early stage of the process but drastically increases at the final stage of the decomposition. In the present work, the curing mechanism and kinetics for the epoxy systems were studied based on differential scanning calorimetry (DSC) measurements. In addition, the epoxy systems were applied as polymer matrices for manufacturing of fiber-reinforced plastics (FRPs) and coatings. The mechanical properties of these FRPs were examined with a universal testing machine (UTM) and by dynamic mechanical analysis (DMA). The adhesion strength of coatings was tested by using a pull-off tester.

2. Experimental

2.1. Materials

As detailed in our previous published works [22,23], two kinds of lignin-based epoxy resins were synthesized from de-polymerized Kraft lignin (DKL, softwood) and de-polymerized organosolv lignin (DOL, hardwood), denoted as DKL-epoxy resin and DOL-epoxy resin, respectively. In a typical run for the synthesis of depolymerized lignin (DL)-based epoxy resin, 4 g of DL dissolved in 12 g epichlorohydrin (ECH) (at an epichlorohydrin/DL molar ratio of 6) and mixed with tetrabutylammonium bromide (TBAB, 0.2 wt% of DL) and 12 mL of distilled water. Then the mixture was loaded into a 200 mL three-neck reactor and heated up to 80 °C and kept at this temperature for 1 h under stirring. Then, the system was cooled to 60 °C and sodium hydroxide solution was added into the reactor and maintained at the reaction temperature. Finally, the system was cooled down to the room temperature and the organic phase was separated. The non-reacted epichlorohydrin was removed using a rotary evaporator at 100 °C under a reduced pressure. The yields of epoxidation for DOL and DKL were 99% and 97%, respectively.

Araldite® GZ 540 X 90, supplied from Huntsman, as a conventional bisphenol A (BPA)-based epoxy resin (DGEBA) was used in this study to prepare epoxy composites comprising the BPA-based epoxy resin and 25–100 wt% of the above lignin-based epoxy resin. The epoxy equivalent weight (EEW), EC and the solid content of this liquid BPA-based epoxy resin are approx. 295 g/eq, 14.6 wt% and 90 wt% (containing 10 wt% of xylene solvent), respectively. Prior to the kinetic study, the BPA-based epoxy resin was completely dried in a vacuum oven to remove the xylene solvent. 4,4′-Diaminodiphenylmethane (DDM) obtained from Sigma Aldrich was used as a curing agent for the epoxy resins. BGF fiberglass cloth (E-Glass, Plain weave fiber glass with 0.015 in. thickness) was purchased from Freeman, Ohio.

2.2. Sample preparation for kinetic study

To prepare epoxy samples for kinetic study, the desire amount of lignin-based epoxy resin and the conventional BPA-based epoxy resin (DGEBA) were added into a vial and heated in an oil bath at 80 °C. When the resin mixture was melted and its viscosity decreased, a stoichiometric amount of curing agent, i.e. 4,4′-diaminodiphenylmethane (DDM), was added into the vial and mixed for approximately 1 min at 80 °C to ensure that the curing agent was dispersed sufficiently. Finally, the sample was immediately quenched in an ice bath to avoid any further reactions before DSC measurements. The sample names and specifications are shown in Table 1.

2.3. Preparation of fiber-reinforced plastics (FRPs) using bio-based epoxy resins

Fiber-reinforced plastics (FRPs) were prepared using epoxy resins as polymer matrices and fiberglass mat, according to ASTM D638-10. The desire amount of lignin-based epoxy resin, the conventional BPA-based epoxy resin and DDM as the curing agent were mixed based on specifications listed in Table 1. The fiberglass mat was cut into a rectangular shape with dimensions of 200 mm × 150 mm. The epoxy resin blend (containing varying percentage of lignin-based epoxy resin) was dissolved in a small amount of acetone and applied uniformly with a brush on the pre-cut fiberglass mat placed in a release bag. This step was repeated 10 times to reach an approximate thickness of 3 mm (containing 10 layers of the fiberglass mat). Then, the bio-based epoxy composites left for 3 h before curing. Afterward, the bio-based epoxy composites were placed in a hot press and cured at respective curing conditions as determined by using DSC, in terms of the peak curing temperature (T_p) and the end-set curing temperature (T_{end}). Generally, each composite sample was pressed on a hot-press under 2000 psi at its T_p for 1 h and then at its T_{end} for 45 min. The obtained composites were all post-cured at T_{end} for 3 h in a pre-heated oven.

2.4. Characterization

Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer) was used to analyze the chemical structure of the synthesized lignin-based epoxy resins by scanning from 500 to 4000 cm^{-1}. The epoxy content (EC, weight percent epoxide) of lignin-based epoxy resins was measured with a potentiometric titrator (Titroline 7000 Titrator) based on ASTM D1652-11 standard. The average molecular masses of DKL-epoxy and DOL-epoxy resins as well as the reference DGEBA were measured by using a GPC instrument (Waters Breeze 1525 binary lamp, UV detector set at 270 nm, Waters Styragel HR1 column at 40 °C). The samples were dissolved in THF and the molecular masses were obtained using a method based on the molecular mass calibration curve as determined from the linear polystyrene standards.

2.5. DSC measurements

The DSC measurements were performed on a Mettler Toledo DSC 1 to investigate the curing behavior of the bio-based epoxy resins (containing various percentages of lignin-based epoxy resin). The DSC measurements were carried out under a constant flow of nitrogen of 50 ml/min. For each DSC run, small quantities of the epoxy resin blend and the curing agent (7–8 mg in total) were sealed in an aluminum DSC pan. The DSC measurements were conducted at various heating rates of 4, 6, 8, 10 °C/min over a temperature range of 25–300 °C. The samples cured at 10 °C/min were cooled to the room temperature and then re-heated to 300 °C at 10 °C/min to measure the glass transition temperature (T_g) of the cured epoxy systems.

In the DSC measurements, it is assumed that the extent of consumption of the reactive groups is proportional to the amount of heat evolved. The degree of conversion or extent of the curing reaction (α) and the reaction rate as a function of time can be calculated from the DSC data by the following equations [25]:

$$\alpha = H_t/H_T \tag{1}$$

Table 1
Sample names and their specifications.

Sample name	DGEBA (g)	DOL-epoxy resin (g)	DKL-epoxy resin (g)	DDM[a] (g)
DGEBA-DDM	100	0	0	16.8
25% DOL-DDM	75	25	0	14.9
50% DOL-DDM	50	50	0	13
75% DOL-DDM	25	75	0	11.1
100%DOL-DDM	0	100	0	9.2
25% DKL-DDM	75	0	25	14.2
50% DKL-DDM	50	0	50	11.7
75% DKL-DDM	25	0	75	9.1
100%DKL-DDM	0	0	100	6.5

[a] Based on the stoichiometric ratio of amine group in the curing agent to the epoxy group in the resin.

$$d\alpha/dt = (1/\mathrm{H_T}) \times (dH/dt) \tag{2}$$

where α denotes the degree of conversion, H_t is the enthalpy of the reaction within time t, H_T is the total enthalpy of the reaction for a fully cured sample, $d\alpha/dt$ is the rate of reaction and dH/dt is the heat flow rate. The enthalpy of reaction up to time t can be calculated by integration of the heat flow over the time t of the exothermic peak from DSC. In this study, two model-free methods were used to analyze the dynamic DSC data. The first method is Kissinger method, which determines the overall activation energy. The following equation can be expressed based on the Kissinger method [26]:

$$\ln(\beta_i/T_{p,i}^2) = \mathrm{Const.} - (E/(RT_{p,i})) \tag{3}$$

where β is the heating rate, T_p is the peak curing temperature, the subscript i is ordinal number of DSC runs performed at different heating rates. The overall activation energy can be obtained from the slope while plotting $\ln(\beta_i/T_{p,i}{}^2)$ vs. $1/T_p$. The second method is a differential isoconversional method originally presented by Friedman, which enable calculation of activation energy of the curing reaction at any particular extent of conversion (α) by the following equation [27]:

$$\ln[(d\alpha/dt)_{\alpha,i}] = \ln[\beta_i d\alpha/dT] = \ln[A_\alpha f(\alpha)] - E_\alpha/(RT_{\alpha,i}) \tag{4}$$

Hence, the slop of the plot of $\ln[\beta d\alpha/dT]$ vs. $1/T$ at constant degree of conversion (α) for a set of heating rates (β) gives the activation energy at the specific value of α.

2.6. Mechanical properties tests

Tensile tests of the prepared FRPs using bio-based epoxy resins were performed on a Universal Testing Machine Model Instron 8800 with a load cell of 250 kN at a crosshead speed of 5 mm/min and the gage length of 50 mm in accordance to ASTM D638-10. A 50 mm extensometer was used to accurately measure the strain to obtain modulus. The FRP panels were cut into dumbbell-shaped specimens, based on ASTM D638-10. For the flexural tests, the FRP specimens were cut into rectangular samples of dimensions of 3.2 mm × 12.7 mm × 127 mm in accordance to ASTM D790-10. The measurements were conducted on another set of Universal Testing Machine (Admet 7000) in three-point bending mode at 25 °C with a strain rate of 1.5 mm/min and span length of 48 mm. Five measurements were conducted for each sample and the mean value was reported. In 3-point bending experiments, the flexural modulus (E, GPa) and flexural strength (σ, MPa) are defined by Eqs. (5) and (6), respectively:

$$E = (L^3F)/(4wh^3d) \tag{5}$$

$$\sigma = (3FL)/(2wh^2) \tag{6}$$

where L is the length of the support span (mm), F is the load (force) at the fracture point (N), w and h are the width (mm) and thickness (mm) of beam, respectively, and d is the deflection due to the force applied at the middle of the beam.

The epoxy systems (containing various percentages of lignin-based epoxy resin without fiberglass) were also characterized by dynamic mechanical analysis (DMA, Q800, TA Instruments). In the DMA measurements, the shear moduli were measured in oscillating bending at a frequency of 1 Hz and strain amplitude of 1% of the length of the sample heated from 30 °C to 150 °C at 5 °C/min. Sample dimensions for the DMA tests were 60 mm × 10 mm × 2 mm. The average molar mass between crosslinks can be determined from DMA data by using Eq. (7) [28],

$$M_c = (\rho qRT)/G_e \tag{7}$$

where M_c is the number average molar mass between crosslinks, q is the front factor (usually equal to 1 [29]), ρ is the density at temperature T (K), G_e is the equilibrium modulus in the rubbery region at temperature T, and R is the universal gas constant.

The adhesion strength of the bio-based epoxy films containing various percentages of DOL-epoxy resin (dry thickness 50 µm) on stainless steel substrate was evaluated with a Posi Test AT-A automatic adhesion Pull-off tester (DeFelsko) by measuring the greatest tensile pull-off force needed to detach a 10 mm diameter aluminum dolly adhered to the epoxy film by means of epoxy adhesive (Loctite 907 Hysol, curing process: 25 °C for 3 days).

3. Results and discussion

3.1. Characteristics of lignin-based epoxy resins

The chemical structure and the average molecular masses of the de-polymerized Kraft lignin-based epoxy resin (DKL-epoxy resin), the depolymerized organosolv lignin-based epoxy resin (DOL-epoxy resin), compared with the reference DGEBA, were analyzed using FTIR and GPC, respectively. FTIR spectra are shown in Fig. 1. The FTIR spectra of lignin-based epoxy resins were normalized based on C═C aromatic bonds at 1600 cm^{-1} which are expected to remain constant in all samples in order to provide a better comparison of their chemical structure. The vibration of the epoxy group in the spectra of DKL-epoxy and DOL-epoxy resins at 915 cm^{-1} which confirms the grafting of epoxy groups to DKL and DOL, respectively,

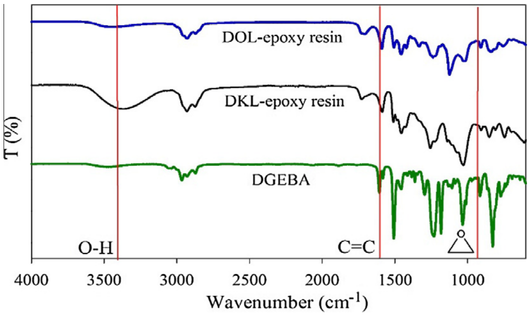

Fig. 1. FTIR spectra of DOL-epoxy resin and DKL-epoxy resin, compared with the reference DGEBA.

through the epoxidation reaction. The strong absorption band between 3200 and 3550 cm^{-1} is associated with O—H stretching vibration of phenolic and aliphatic hydroxyl groups, and the absorbance at 1600 cm^{-1} is related to the C=C aromatic bands. Moreover, the intensity of hydroxyl groups is lower in DOL and DOL-epoxy resin in comparison with DKL and DKL-epoxy resin.

Average molecular masses, polydispersity index (PDI), and epoxy content of DKL-epoxy, DOL-epoxy resins, compared with the reference DGEBA, are presented in Table 2. The synthesized DKL-epoxy resin is in black powder form with the average molecular mass (M_w) of 2800 g/mol and its PDI is 3.5. While, the prepared DOL-epoxy resin is a viscous liquid whose M_w and PDI are 1400 g/mol and 2.8, respectively. In addition, the epoxy contents of the synthesized epoxy resins are 5.6 wt% and 8.0 wt% for DKL-epoxy and DOL-epoxy resins, respectively, as measured by potentiometric titrator. A higher epoxy content for DOL-epoxy resin than that of DKL-epoxy resin suggests that DOL has better reactivity for the epoxidation reaction than DKL due to its lower molecular mass.

3.2. Dynamic DSC data analysis

The curing behaviors of the conventional BPA-based epoxy resin (DGEBA) and the bio-based epoxy systems comprising DGEBA and various percentages of lignin-based epoxy resin were investigated by dynamic DSC using DDM as the curing agent at four heating rates (i.e. 4, 6, 8 and 10 °C/min). The dynamic DSC thermographs of DGEBA, the bio-based epoxy systems comprising DGEBA and various percentages of DOL-epoxy resin, and the bio-based epoxy systems comprising DGEBA and various percentages of DKL-epoxy resin, are shown in Figs. 2–4, respectively. Tables 3 and 4 summarize some key curing properties such as the onset curing temperature (T_{onset}), the peak curing temperature (T_p) and the end-set curing temperature (T_{end}) for DGEBA and the bio-based epoxy systems comprising DGEBA and various percentages of lignin-based epoxy

Table 2
Average molecular masses, polydispersity index, and epoxy content of DKL-epoxy and DOL-epoxy resins, compared with the reference DGEBA.

Sample	M_n (g/mol)	M_w (g/mol)	PDI	Epoxy content (wt%)
DKL-epoxy resin	790	2800	3.5	5.6
DOL-epoxy resin	500	1400	2.8	8.0
DGEBA	550	822	1.5	14.6

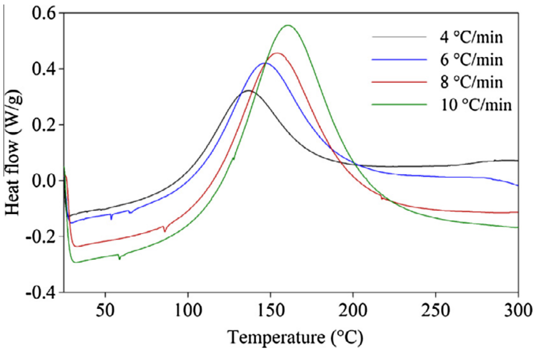

Fig. 2. DSC curves of the conventional BPA-based epoxy resin (DGEBA) at different heating rates.

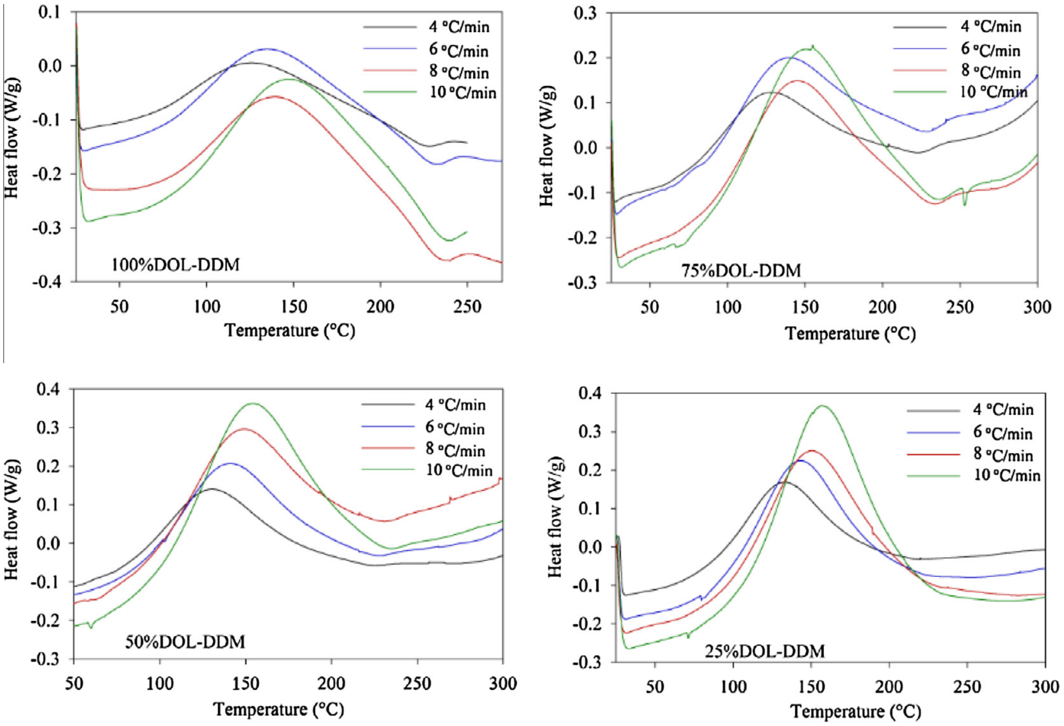

Fig. 3. DSC curves of epoxy systems comprising DGEBA and various percentages of DOL-epoxy resin at different heating rates.

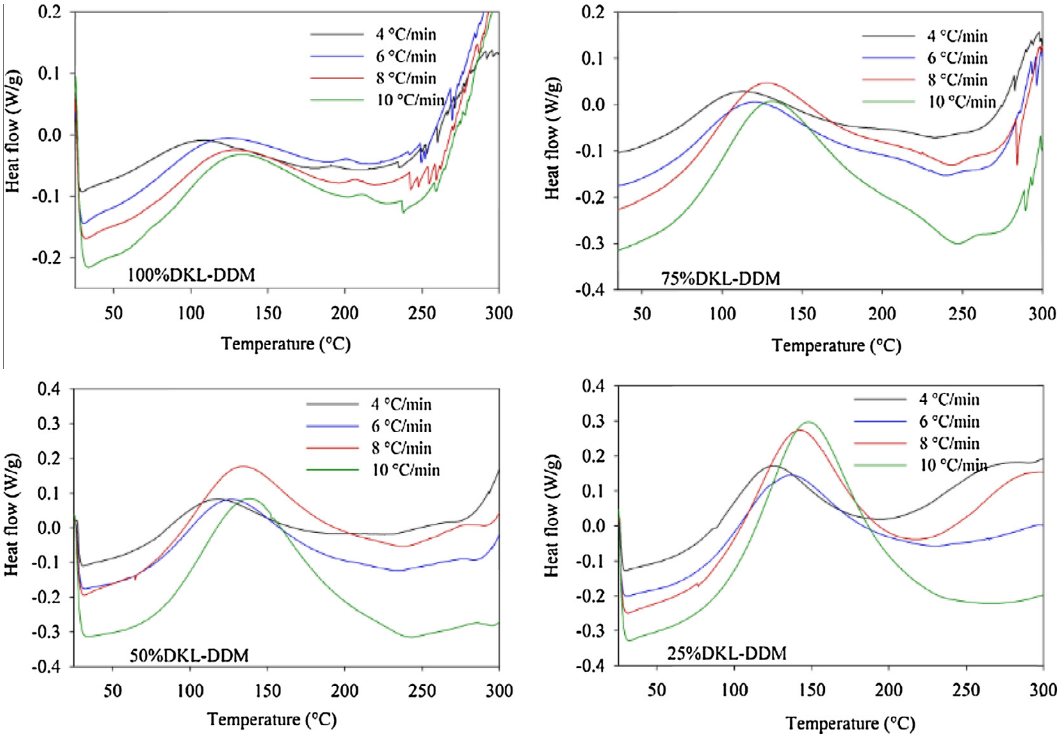

Fig. 4. DSC curves of epoxy systems comprising DGEBA and various percentages of DKL-epoxy resin at different heating rates.

Table 3
Curing characteristics of the conventional BPA-based epoxy resin (DGEBA).

Sample name	Heating rate (°C/min)	ΔH_{total} (J/g)	T_{onset} (°C)	T_p (°C)	T_{end} (°C)
DGEBA-DDM	4	288.7	51.6	135.7	215.3
	6	279.9	61.5	146.0	231.1
	8	288.2	67.	153.7	249.7
	10	289.9	76.8	160.2	260.4

Table 4
Curing characteristics of the epoxy systems comprising DGEBA and various percentages of lignin-based epoxy resins.

Heating rate (°C/min)	ΔH_{Total} (J/g)	T_{onset} (°C)	T_p (°C)	T_{end} (°C)	Heating rate (°C/min)	ΔH_{Total} (J/g)	T_{onset} (°C)	T_p (°C)	T_{end} (°C)
25% DOL-DDM					*50% DOL-DDM*				
4	243.2	54.8	132.0	221.7	4	212.2	54.6	129.3	202.3
6	239.8	61.8	142.1	236.8	6	208.7	59.0	139.5	226.9
8	234.8	64.3	150.2	261.3	8	198.1	64.4	146.7	232.1
10	236.7	74.9	155.7	271.6	10	203.8	69.0	151.1	235.2
75% DOL-DDM					*100%DOL-DDM*				
4	189.7	61.8	127.4	203.0	4	182.8	45.0	128.0	222.1
6	190.4	66.6	137.5	227.5	6	177.9	49.5	136.5	228.7
8	185.1	68.0-	144.1	233.5	8	176.8	51.8	143.1	233.4
10	186.9	72.9	149.9	237.7	10	180.1	54.4	150.0	240.0
25% DKL-DDM					*50% DKL-DDM*				
4	198.7	44.1	123.3	196.4	4	178.1	40.8	117.2	221.7
6	200.3	51.1	135.0	220.8	6	180.8	46.6	125.7	233.0
8	197.0	58.8	142.0	222.3	8	179.2	51.6	132.7	237.7
10	199.6	65.9	147.8	236.1	10	178.0	58.1	138.5	242.7
75% DKL-DDM					*100%DKL-DDM*				
4	151.3	31.3	111.7	233.0	4	86.4	29.9	104.5	207.2
6	151.8	35.5	120.7	239.0	6	82.2	33.3	117.4	216.3
8	158.7	40.0	125.7	244.5	8	81.6	35.0	123.3	222.2
10	155.3	42.5	131.0	247.3	10	84.3	38.8	127.5	229.2

resin. The T_{onset}, T_p and T_{end} of each resin sample during its curing process are consistently higher with increasing the heating rate. This behavior can be attributed to this fact that at a higher heating rate the resin sample has less time at a specific temperature which retards the curing process [30]. However, the total heat of curing reactions remains constant for a specific resin sample, irrespective of the heating rates. The DGEBA has the highest value of the curing reaction heat (enthalpy) of around 289 J/g, followed by 180–236 J/g for the bio-based epoxy systems comprising DGEBA and various percentages of DOL-epoxy resin, and the bio-based epoxy systems comprising DGEBA and various percentages of DKL-epoxy resin has the lowest value of enthalpy (around 84–199 J/g). This behavior on the curing heat effects is believed to be attributed to the different epoxy contents (EC) of the epoxy resins tested. For instance, the DKL-epoxy resin has the lowest amount of EC (=5.6 wt%), compared with EC = 8.0 wt% for the DOL-epoxy resin, while the DGEBA has the highest value of EC (=14.6 wt%). With decreasing the overall epoxy content of an epoxy system, the total heat of reaction would decrease due to a smaller number of the reactive sites for the curing reactions. In addition, from Figs. 3 and 4 and Table 4, the addition of a lignin-based epoxy resin (in particular the DKL-epoxy resin) to DGEBA decreases its onset, peak and end-set curing temperatures likely because the presence of hydroxyl groups on the lignin-based epoxy resins could enhance the curing process via the etherification and homopolymerization reactions [31,32].

3.3. Curing kinetic analysis

Elucidation of curing kinetics and mechanism can be helpful for seeking effective means to minimize the internal stress and produce a high performance finished product of thermosetting polymers [33,34]. In this work, the curing kinetics of lignin-based epoxy systems were evaluated by Kissinger method to obtain the overall activation energy, and the isoconversional Friedman method to determine the activation energy as a function of conversion (i.e., extent of the curing process). In Kissinger method, as explained previously in Eq. (3) the overall activation energy was calculated from the slope of the curve of $\ln(\beta_i/T_{p,i}^2)$ versus $1/T_p$ for the bio-based epoxy systems comprising DGEBA and various percentages of lignin-based epoxy resins, as displayed in Fig. 5. Table 5 presents the overall activation energies for curing of these two types of lignin-based epoxy systems with DDM. As presented in this table, the overall activation energies of all resin systems are in a narrow range of 42–56 kJ/mol which is close to the reported value for the conventional petroleum-based epoxy systems cured with amine [34–36]. In general, the overall activation energy of bio-based epoxy systems containing DOL-epoxy resin is higher than that

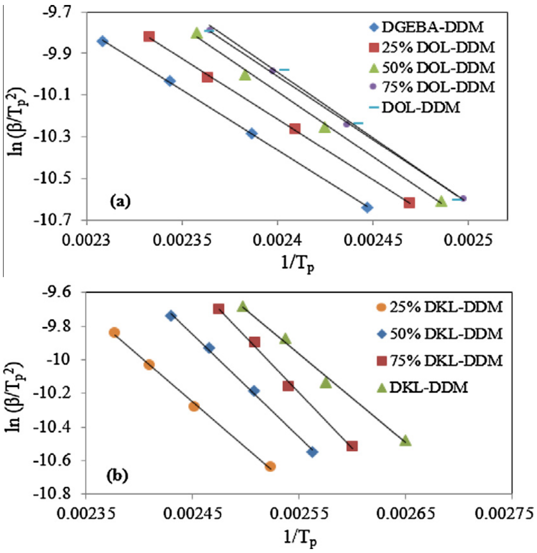

Fig. 5. Plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for the bio-based epoxy systems comprising DGEBA and various percentages of DOL-epoxy resin (a) and DKL-epoxy resin (b), respectively.

Table 5
Overall curing activation energies for all epoxy systems determined by Kissinger method.

Sample name	Activation energy (kJ/mol)
DGEBA-DDM	48.4
25% DOL-DDM	48.3
50% DOL-DDM	51.9
75% DOL-DDM	50.8
100%DOL-DDM	52.4
25% DKL-DDM	45.1
50% DKL-DDM	50.8
75% DKL-DDM	55.5
100%DKL-DDM	42.4

of the bio-based epoxy system containing DKL-epoxy resin at the same percentage of blending. The overall activation energies of the DGEBA-DDM and the 25%DOL-DDM are almost the same (~48 kJ/mol). However, the activation energy of 25%DKL-DDM and 100% DKL-DDM is 45 kJ/mol and 42 kJ/mol, respectively, which are lower than that of the DGEBA-DDM. The rest samples all have a higher activation energy in comparison with the DGEBA-DDM. These results indicate that blending DGEBA with a lignin-based epoxy resin at a low blending ratio (25 wt%) could promote the curing process likely via the presence of free hydroxyl groups on the structure of lignin-based epoxy resins. The hydroxyl content of DKL-epoxy resin is higher than that of DOL-epoxy resin, which account for a greater curing enhancement effect for the 25% DKL-DDM (Table 5). Similar results were reported by Kong et al. [4] on the catalytic effects of lignin on the curing process of epoxy resin, likely because the presence of hydroxyl groups on the lignin-based epoxy resins could promote the curing process [31,32] as discussed previously in Figs. 3 and 4. However, further increasing the percentage of lignin-based epoxy resin in the bio-based epoxy systems to above 25 wt%, do not decrease the overall activation energies as predicted but generally increase overall activation energies (Table 5). This is probably due to the fact that the viscosity of a resin system increases with increasing the amount of lignin-based epoxy resin, which compromises the promoting effects of the hydroxyl groups and retards the curing process. As an interesting finding, the curing of the 75% DKL-DDM system gives the highest activation energy (55 kJ/mol), much higher than that of the 100% DKL-DDM system, suggesting some interaction occurring between the BPA-based epoxy and lignin-based epoxy resins while curing the bio-based epoxy systems if containing a high amount (i.e., 75 wt%) of lignin-based epoxy resin. For the bio-based epoxy systems containing DOL-epoxy resin, an increase in the percentage (0–100 wt%) of DOL-epoxy resin in the systems consistently increases the overall activation energy in curing of the bio-based epoxy systems, suggesting that the negative effect of viscosity increase might dominate over the positive effect of the hydroxyl groups on the overall activation energy of the curing process.

In addition, the Friedman method was used to determine the actual activation energy during the curing process in the conversion range of 0.05–0.95. Fig. 6(a) and (b) exhibit the variation of activation energy during the curing process for the bio-based epoxy systems comprising various percentages of DOL-epoxy resin or DKL-epoxy resin, respectively. It is

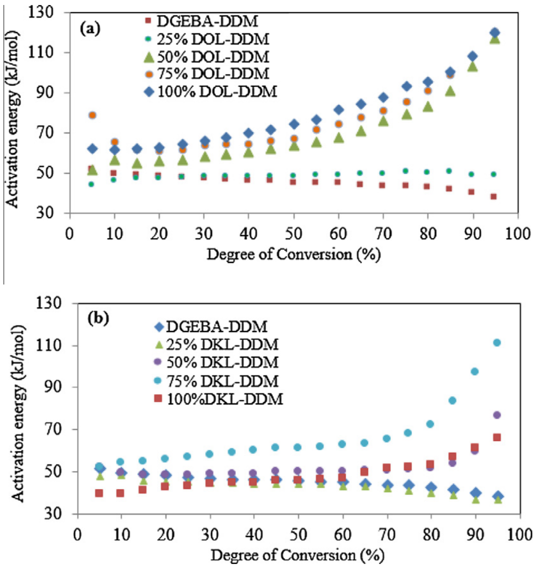

Fig. 6. Variation of activation energy vs. degree of conversion for the bio-based epoxy systems comprising DGEBA and various percentages of DOL-epoxy resin (a), and DKL-epoxy resin (b), respectively, (Friedman method).

obvious that the amount of lignin-based epoxy resin in the bio-based epoxy systems has a significant effect on actual activation energy of epoxy systems suggesting changes in the curing reaction mechanism. It can be found that, in the curing of DGEBA-DDM and 25%DOL–DDM system as well as 25% DKL-DDM system follows the similar trend: all activation energies are <50 kJ/mol and generally decrease with increasing the extent of curing (conversion), suggesting that (1) the autocatalytic curing mechanism may be present in these epoxy systems [36,37], and (2) curing of bio-based epoxy composites comprising BPA-based epoxy and a low amount (25 wt%) of lignin-based epoxy resin is dominant by the curing behavior of the BPA-based epoxy resin. Although the hydroxyl groups in lignin-based epoxy resin could promote the curing process via the etherification and homopolymerization reactions [31,32], as discussed previously, the curing of bio-based epoxy systems comprising a higher amount (>25 wt%) of either DOL-epoxy resin or DKL-epoxy resin results in not only a much higher activation energy than that of DGEBA-DDM but also a climbing trend of the activation energy vs. the degree of conversion during the whole curing process (except for the 100%DKL-DDM system which exhibits lower curing activation energies than those of the DGEBA-DDM and any other bio-based epoxy systems at the initial curing stage $\alpha < \sim 0.4$). These results suggest that the negative effect of viscosity increase (causing reduced mobility of the curing agent in the resin system [38,39]) might dominate over the positive effect of the hydroxyl groups on the actual activation energy in curing of the bio-based epoxy systems containing a higher amount (>25 wt%) of lignin-based epoxy resin.

3.4. Glass transition temperature (T_g)

The glass transition temperature (T_g) of the cured epoxy systems was measured by DSC based on the inflexion point of the stepwise transition. Fig. 7 shows the T_g of the cured bio-based epoxy systems comprising DGEBA and various percentages of

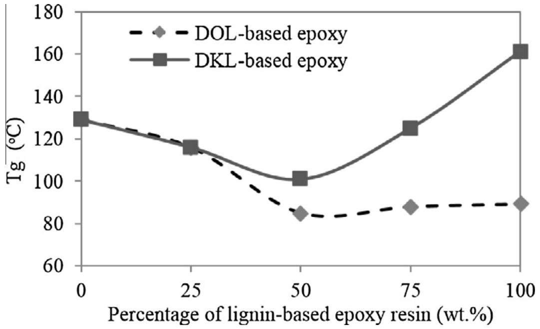

Fig. 7. Glass transition temperature (T_g) of the cured bio-based epoxy systems comprising DGEBA and various percentages of DOL-epoxy or DKL-epoxy resins.

DOL-epoxy resin or DKL-epoxy resin. The results demonstrate that the amount of lignin-based epoxy resin in the bio-based epoxy systems has a significant effect on T_g. T_g of an epoxy system comprising the DKL-epoxy resin is higher than that with the DOL-epoxy resin, which might be attributed to the greater hydroxyl content in the DKL-epoxy resin than that in the DOL-epoxy resin. The hydroxyl group in lignin-based epoxy resin could promote the curing process via the etherification and homopolymerization reactions [31,32], as discussed previously, leading to a higher cross-linking density of the cured resin samples, hence an increased T_g. The Fig. 7 also clearly shows that for both epoxy systems containing DOL-epoxy resin and DKL-epoxy resin, a common trend can be observed: T_g decreases with increasing the amount of lignin-based epoxy resin in the epoxy systems up to 50 wt%, which could be explained by the lower epoxy content of lignin-based epoxy resins in contrast with the DGEBA, leading to a lower cross-link density in the bio-based epoxy systems. Afterwards with further increasing the amount (>50 wt%) of lignin-based epoxy resins in the epoxy systems, the T_g increases slightly for the DOL-epoxy resin containing systems, but drastically for the DKL-epoxy resin containing systems, which could be attributed to the greater hydroxyl content in the DKL-epoxy resin that could promote the curing process via the etherification and homopolymerization reactions [31,32], leading to a higher cross-linking density of the cured resin samples.

3.5. Mechanical properties

The tensile and flexural properties of the fiber-reinforced plastics (FRPs) using bio-based epoxy systems comprising various amounts of lignin-based epoxy resins (0–100 wt%) as matrices are illustrated in Figs. 8 and 9, respectively. As shown, the tensile (flexural) strength of the FRP with DGEBA-DDM, 100%DKL-DDM and 100%DOL-DDM were measured as 214 MPa (260 MPa), 141 MPa (180 MPa) and 154 MPa (100 MPa), respectively. Thus, both the tensile and flexural strengths of the FRP with a pure lignin-based epoxy resin are much lower than those of the FRP with the conventional BPA-based epoxy, however the modulus of elasticity or the flexural modulus of the FRPs with pure lignin-based epoxy resins are all comparable to those of the FRP with the conventional BPA-based epoxy. The FRPs prepared with bio-based epoxy systems comprising up to 50–75 wt% of lignin-based epoxy resins as matrices have better or comparable tensile and flexural strengths when compared with the FRP with DGEBA-DDM. For modulus of elasticity and flexural modulus, the FRPs prepared with all bio-based epoxy systems comprising up to 100 wt% of lignin-based epoxy resins have better or comparable properties than the FRP with 100 wt% BPA-based epoxy resin. These promising results showed that the lignin-based epoxy resin has great potential

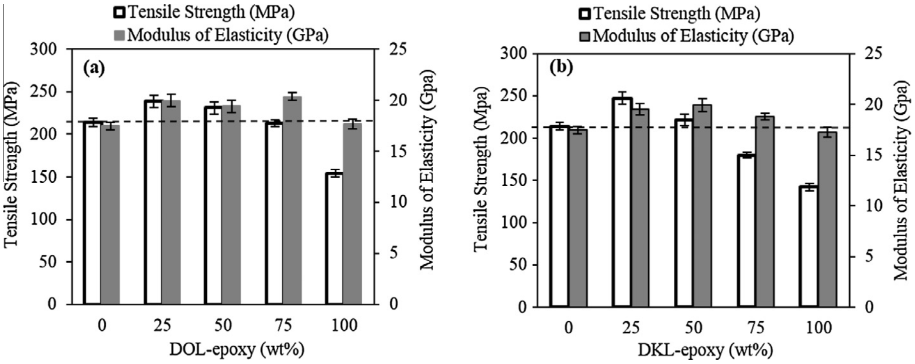

Fig. 8. Tensile strength and elastic modulus of the FRPs prepared with epoxy systems comprising DGEBA and various percentages of DOL-epoxy resin (a) and DKL-epoxy resin (b), respectively.

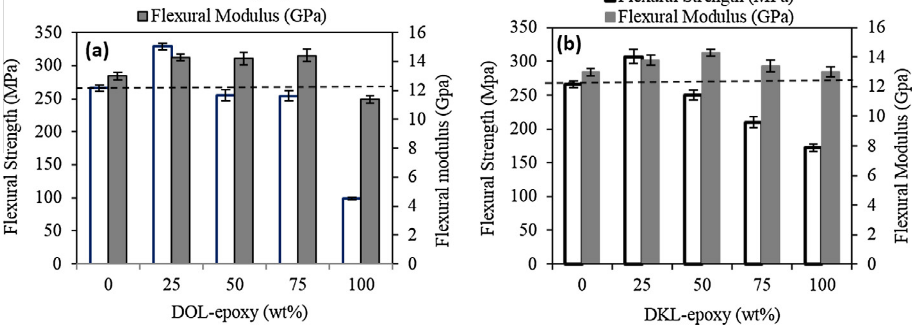

Fig. 9. Flexural strength and flexural modulus of FRPs prepared with epoxy systems comprising DGEBA and various percentages of DOL-epoxy resin (a) and DKL-epoxy resin (b), respectively.

to be used as a substitute for petroleum-based epoxy resins in the manufacture of FRPs for structure and automobile applications that demand weight savings, precision engineering and finite tolerances.

The mechanical properties of typical bulk bio-based epoxy systems (fully cured by DDM) were investigated further by DMA, the DMA profiles are displayed in Fig. 10, where the storage modulus (E') and $\tan\delta$ are plotted versus temperature. In addition, T_g and the average molar mass between crosslinks (M_c) were obtained and are summarized in Table 6. The T_g was determined by the peak temperature of $\tan\delta$ and the average molar mass between crosslinks were calculated from Eq. (7). Also, the T_g of these three samples were determined from DSC measurement, and are presented in Table 6. The storage moduli of the two bio-based epoxy systems are both higher than that of the conventional BPA-based epoxy resin (DGEBA) at a low temperature (<50 °C). The T_g of BGEBA, 50%DOL-DDM and 50%DKL-DDM based on DMA (DSC) measurement are 117 °C (129 °C), 83 °C (85 °C) and 100 °C (101 °C), respectively. These results indicated that the obtained T_g's from both DSC and DMA are in a very good agreement. Also, the calculated M_c values for these resins are in a narrow range of 46–58 g/mol, suggesting similar cross-link densities, in a good agreement with their similar tensile and flexural properties.

3.6. Pull-off adhesion tests

The adhesion strength between the cured epoxy films containing DGEBA and various percentages of DOL-epoxy resin (0–100 wt%) and a stainless steel substrate was measured on a pull-off adhesion tester. As reported in Table 7, the adhesive strength improves when the content of DOL-epoxy increases up to 50 wt%. Afterward, the adhesion strength reduces with further increasing the percentage of DOL-epoxy resin in the formulated coating. 50%DOL-DDM film has the highest value of adhesion strength 7.7 MPa, followed by 25%DOL-DDM (6.3 MPa) and DGEBA-DDM films (6.1 MPa). The DOL-epoxy films are found to present interesting adhesive strength on metal for application in the field of high-performance coatings.

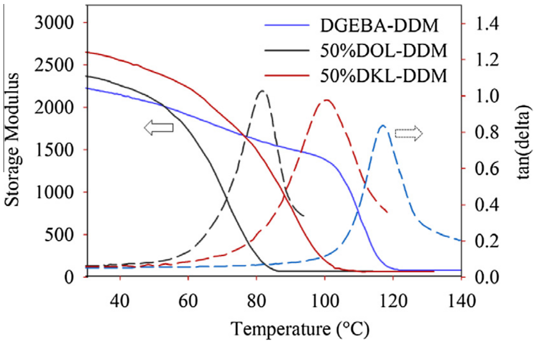

Fig. 10. DMA results for the cured DGEBA-DDM and bio-based epoxy systems comprising DGEBA and 50 wt% of DOL-epoxy or DKL-epoxy resins.

Table 6
Glass transition temperature and crosslink density of the cured DGEBA-DDM and bio-based epoxy systems comprising DGEBA and 50 wt% of DOL-epoxy or DKL-epoxy resins.

Sample	T_g (°C)		M_c (g/mol)
	DSC	DMA	
DGEBA	129	117	47.2
50%DOL-DDM	85	83	46.1
50%DKL-DDM	101	100	57.9

Table 7
Adhesion strength of bio-based epoxy films with different contents of DOL-epoxy resin.

Sample name	Pull-off adhesion strength (MPa)
DGEBA-DDM	6.1 ± 0.2
25%DOL-DDM	6.3 ± 0.1
50%DOL-DDM	7.7 ± 0.3
75%DOL-DDM	4.7 ± 0.1
100%DOL-DDM	3.9 ± 0.4

4. Conclusions

In this study, lignin-based epoxy resins, prepared from de-polymerized Kraft lignin (DKL) and de-polymerized organosolv lignin (DOL), were mixed with the conventional BPA-based epoxy resin at different percentages (0–100 wt%) to produce bio-based epoxy systems. DSC analysis was used to investigate the curing kinetics of lignin-based epoxy systems, and it was shown that the BPA-based epoxy has the highest value of the curing reaction heat (enthalpy) of around 289 J/g, followed by DOL-based epoxy systems (180–236 J/g) and the DKL-based epoxy systems (84–199 J/g). This difference in the curing reaction enthalpy may be attributed to the different epoxy contents (EC) in the epoxy resins tested. Blending a lignin-based epoxy with conventional BPA-based epoxy at a low blending ratio (25 wt%) could promote the curing process likely via the presence of free hydroxyl groups on the structure of lignin-based epoxy resins. However, further increasing the percentage of lignin-based epoxy in the epoxy system to above 25 wt% generally increases overall activation energies probably due to the fact that the viscosity of an epoxy system increases with increasing the amount of lignin-based epoxy resin, which compromises the promoting effects of the hydroxyl groups and hence retards the curing process. The mechanical performance of the fiber-reinforced plastics (FRPs) were characterized by a UTM machine. The FRPs prepared with bio-based epoxy resins comprising up to 50–75 wt% of lignin-based epoxy resins as matrices have better or comparable tensile and flexural strengths compared with the FRP with 100% BPA-based epoxy resin. For modulus of elasticity and flexural modulus, the FRPs prepared with all bio-based epoxy resins comprising up to 100 wt% of lignin-based epoxy resins have better or comparable properties than the FRP with 100% BPA-based epoxy resin. In addition, the lignin-based epoxy films comprising up to 50 wt% of DOL-based epoxy resin are shown promising adhesion properties on metal substrate. This study demonstrates that the lignin-based epoxy resin has great potential to be used as a substitute for petroleum-based epoxy resins in the manufacture of FRPs and coatings.

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