

MATERIAL PROPERTIES OF EPOXY-REINFORCED BIOCOMPOSITES WITH LIGNIN FROM EMPTY FRUIT BUNCH AS CURING AGENT

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Lignin was obtained from black liquor samples from soda-AQ pulping of oil palm empty fruit bunch (EFB) fiber. Oil palm EFB reinforced epoxy composite samples with varying lignin content of 15, 20, 25, and 30% as curing agent were prepared. The chemical structures of lignin were characterized by FT-IR, and CHN analysis. FT-IR and CHN analysis confirmed structural changes of epoxy resin after use of EFB-lignin as curing agent in epoxy resin. Thermal analysis of composites was carried out by thermogravimetric analysis (TGA). The TGA graphs showed that crosslinking of epoxy and lignin as curing agent may induce relatively high-chain rigidity in the polymer and may result in an enhanced thermal stability of the EFB/lignin-epoxy composite systems. The mechanical properties (tensile, flexural, and impact behavior) and physical properties (water absorption) of the composite samples were evaluated. Mechanical properties of epoxy composites cured with 25% lignin were found to be higher than that of the composite prepared from a commercial curing agent. Scanning electron micrographs showing tensile fracture of the composites showed evidence of good fiber–matrix interaction, induced by the curing agent.

Keywords: Empty fruit bunches (EFB); Lignin; EFB reinforced epoxy composite

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INTRODUCTION

Wood is one of the principal sources of cellulosic fiber and is used as the raw material for the production of pulp and paper. However, increasing concerns over future fiber supplies and potential increases in wood costs have caused the pulp and paper industry to search for alternative fiber sources such as non-wood fiber plants. Within the category of non-wood fibers, oil palm (*Elaeis guineensis*) is one that shows great potential as a papermaking raw material, particularly for Malaysia, because it is an important commercial plant in Malaysia. Oil palm empty fruit bunch (EFB), a lignocellulosic waste generated during the palm oil extraction process, is a good source of cellulose, lignin, and hemicelluloses, which can be used in many industrial processes. Well over 15 million tons of EFB waste residues generated annually are unutilized. These wastes are mostly burned off, creating considerable pollution and economical problems in the country (Abdul Khalil et al. 2007; Alriols et al. 2008).

Black liquor is a thick, dark liquid that is a byproduct of the process that transforms wood into pulp, which is then dried to make paper. The pulp and paper

industry generates 500 billion pounds of black liquor annually. One of the main ingredients in black liquor is lignin, which is the material in trees that binds wood fibers together and makes them rigid, and which must be removed from wood fibers to create paper. The process of producing cellulosic pulp from wood and non-wood fiber requires delignification with sodium hydroxide under pressure, which liberates the cellulosic fiber and produces a large quantity of black liquor (Sun and Tomkinson 2001). In pulp and paper mills, a large volume of the spent liquor from the pulp could be recycled in order to recover lignin rather than having it discarded as waste. Precipitation of lignin from the black liquor has been reported by a number of researchers using mineral acids (Sun and Tomkinson 2001; Sun et al. 1999; Hattalli et al. 2002; Sun et al. 2000).

Lignin and its derivatives have the right chemistry to be used in making coatings and composites because they have small particle size, are hydrophobic, and have the ability to form stable mixtures (Park et al. 2008). The most important future application of lignin may be as a natural plastic in the field of general polymer application, especially as adhesives for wood composites (Haars et al. 1989). The utilization of polymeric lignin in solid material systems has been reported to be constrained by adverse effects on mechanical properties, (resin) viscosity, cure rate, and other important material characteristics (Kringstad 1980). On the other hand, studies by Simionescu et al. (1983) showed that significant lignin loads could be incorporated into the epoxy resin whilst still maintaining good electrical (volume and surface resistivity, dielectric constant, loss in dielectric tangent angle, and dielectric rigidity) and mechanical properties, and high impact toughness compared to the lignin-free phenol epoxy resins.

Most curing agents for epoxy resin can be classified into three groups, namely, tertiary amines, polyfunctional amines, and acid. These curing agents are toxic and are capable of causing severe irritation, serious rash, or an asthmatic response in sensitized persons. Therefore, this study was carried out to develop an environmental friendly curing agent from bio-resources materials. Lignin obtained from soda-anthraquinone black liquor of oil palm EFB fibers was used as the curing agent in epoxy resin matrix for this study. The effect of varying the lignin content in the epoxy resin on mechanical properties of EFB reinforced epoxy composite was studied, and the results were compared with those resulting from traditional commercial amine.

EXPERIMENTAL

Materials

The oil palm empty fruit bunch (EFB) fibers used in this research were supplied by Ecofibre Sdn Bhd, Johor. The EFB fibers were soaked in water for 24 hours to remove dirt before the pulping process. The epoxy 331 used in this study is diglycidyl ether of biphenol A (DGEBA), with an epoxide equivalent weight of 182 to 192. The reference curing agent was clear epoxy hardener 8161 [isophorone diamine (IPD)] with an amine value of 260 to 284 (mg KOH gm⁻¹). Both the epoxy resin and commercial curing agent were obtained from ZARM Scientific and Supplies. Figures 1 and 2 show the structures of epoxy resin and hardener, respectively.

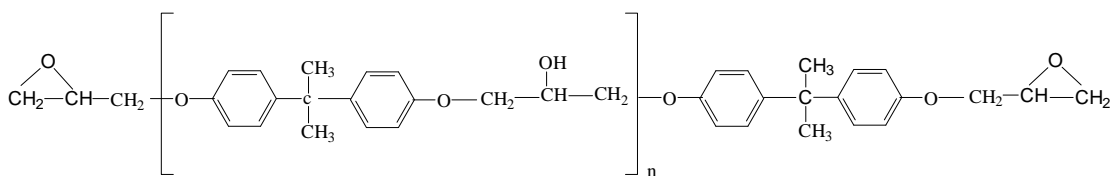


Fig.1. Diglycidyl ether of bisphenol A

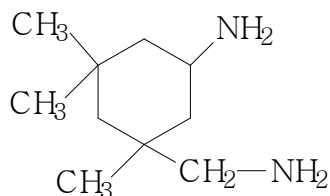


Fig. 2. Epoxy hardener 8161 [isophorone diamine (IPD)]

Methods

Soda pulping

Soda anthraquinone pulping of the pre-treated oil palm EFB fibers was performed using 25% (w/v) NaOH and 0.1% (w/v) anthraquinone (AQ) solution in a solid:liquid ratio of 1:10. The pulping process was optimized and carried out in a 20 L stainless steel rotary digester unit at 160 °C for 3 hours.

Isolation and purification of lignin from black liquor

Lignin was obtained from EFB black liquor using the method described by Park et al. (2008) and Bhat et al. (2009) with few modifications necessary to isolate and purify lignin from black liquor. For lignin precipitation, the black liquor after pulping was acidified with 20 % sulfuric acid (H₂SO₄) to pH 2.0. The black liquor was then heated in a steam bath at 100°C for 1 hour. After 1 hour of heating, the samples were filtered (Whatman #42) using a Bushnel funnel. Slurry of lignin cake was formed upon the filter paper and dried in an oven at 105°C. The sample was then subjected to cyclohexane/ethanol (1:1, v/v) extraction in a soxhlet apparatus for 6 hours to remove waxes, lipids, tannins, and low molecular weight lignin (Park et al. 2008). The lignin obtained then was washed with hot water (70 °C) and dried at room temperature.

Structure and thermal analysis

FT-IR spectra were measured in a Nicolet Avatar Model 360 instrument using a KBr pellet and a spectral range from 4000 to 400 cm⁻¹. Carbon-Hydrogen-Nitrogen (CHN) elemental analysis was carried out by using Perkin Elmer 2400 Series II. The samples were characterized for their thermal stability using a thermogravimetric analyzer (TGA), model 2050, (TA Instruments, New Castle, DE). All specimens were scanned from 30 °C to 800 °C at the rate of 20 °C/min in a nitrogen environment.

Composite preparation

The epoxy resin and the lignin as hardener were mixed based on the weight ratio epoxy resin to lignin (lignin content of 15, 20, 25 and 30%). Figure 3 shows the curing mechanism of the epoxy resin with the lignin serving as a hardener. The epoxy resin-lignin mixture (lignin content of 15, 20, 25 and 30%) was spread evenly on the EFB mat placed in a mould with dimensions of 120 mm x 120 mm x 30 mm. The composite was allowed to set for one hour. Thereafter, the composite was compression-moulded at 3 MPa and 80 °C for 24 hours. The molded sheet was further post-cured at 80 °C for 24 hours in an oven. The composite derived was used for mechanical analysis. For the purpose of comparison, a reference composite was prepared using the aforementioned isophorone diamine (without lignin).

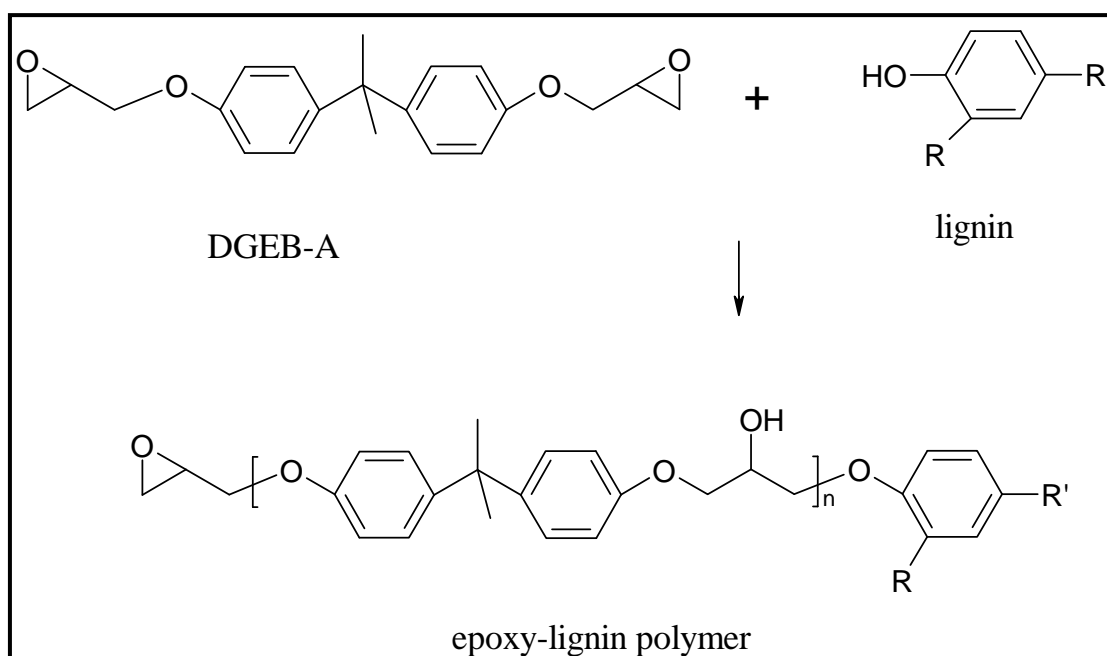


Fig.3. Idealized network formation during curing reaction of epoxy-lignin system (where R represents $-\text{OCH}_3$; and R' represents $-\text{CH}=\text{CH}-\text{CHO}$, etc.)

Mechanical tests

Tensile tests were performed by using an Instron Universal Testing Machine Model 5582 at a crosshead speed of 3 mm/min and gauge length of 60 mm. The tensile test was carried out by using rectangular strips of 120 mm x 15mm x 3 mm. The test was evaluated according to ASTM D638-03. A flexural test was performed according to ASTM D790 by using the same machine. Rectangular strips of 120 mm x 20 mm x 3 mm were used and carefully sanded to remove small cracks. A crosshead speed of 3 mm/min was used. Izod impact test was conducted according to ASTM D256 by using Impact Pendulum Tester (Zwick) Model CS-1370; composites sample dimensions were 65 mm x 15 mm x 3 mm. The samples were rigidly mounted on a horizontal position and were struck by using a pendulum with a force of 5 Joule at the centre of the samples.

Physical test

Water absorption tests were carried out according to ASTM D570 at ambient temperature ($25 \pm 3^\circ\text{C}$). The water absorption was determined by weighing the samples daily up to 2 weeks. The samples were weighed and immersed in water. They were removed at a specified time daily and gently blotted with tissue paper to remove the excess water on the surface, and then the weight was recorded. The water absorption was calculated according to Equation 1,

$$\text{Water Absorption (\%)} = \frac{(M_2 - M_1)}{M_1} \times 100 \quad (1)$$

where M_2 is the mass of the sample after immersion (in grams), and M_1 is the mass of the same sample before immersion (in grams).

RESULTS AND DISCUSSION

Structural Characterization of Lignin

Fourier transform infrared (FT-IR) spectroscopy absorption spectra of lignin isolated from the black liquor by-product of EFB soda-AQ pulping and epoxy resin were compared with EFB-epoxy composite cured with the lignin isolated (Fig. 4).

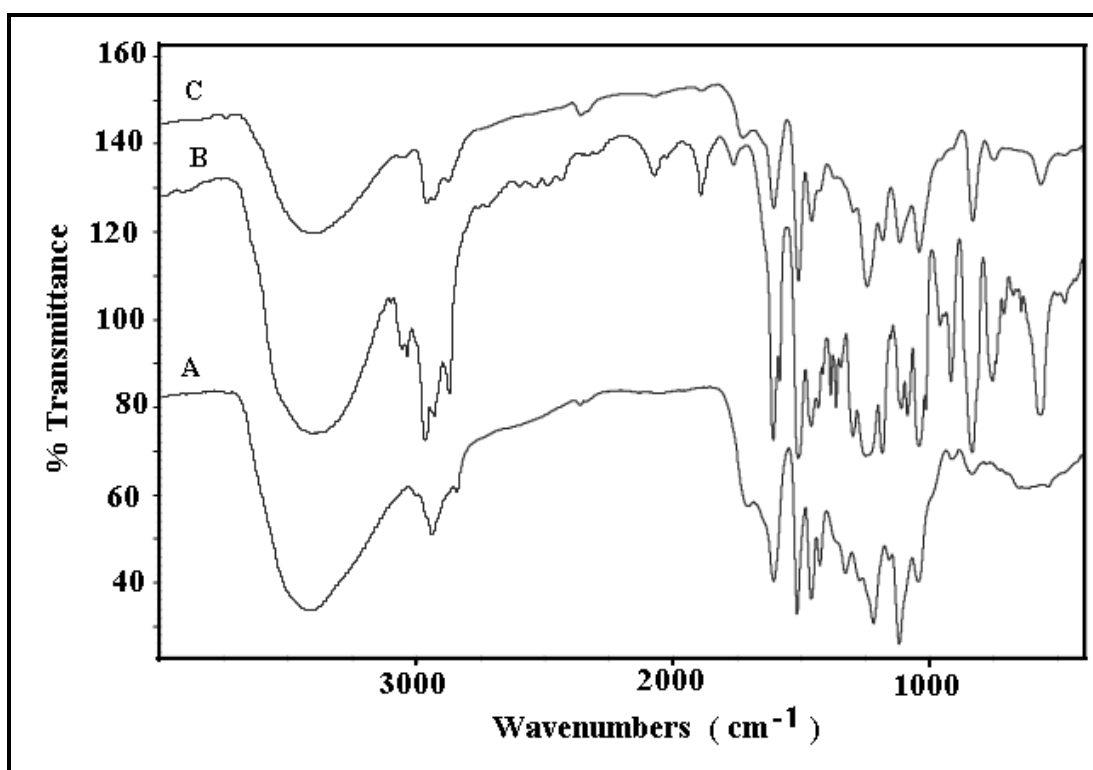


Fig. 4. Comparison FTIR spectra of (a) soda AQ lignin, (b) epoxy resin, and (c) lignin + epoxy

A broad absorption band at 3400 cm^{-1} was assigned to aromatic and aliphatic OH groups. The bands at 2917 cm^{-1} , 2920 cm^{-1} and 1460 cm^{-1} were assigned to C-H stretching vibration of CH_2 and CH_3 groups respectively. The FTIR spectra of all lignin samples showed some characteristic bands at 1600, 1515, and 1425 cm^{-1} , which correspond to aromatic ring vibrations of the phenyl propane skeleton. The clear peaks at about 2935, 2840, and 1460 cm^{-1} are attributed to CH stretching of methyl (CH_2) or methylene groups (CH_3). On the other hand, epoxy resins (Fig. 4B) are characterized by the stretching vibration of the C-O of the epoxy at 915 cm^{-1} . The assignments of other notable absorption characteristics of the epoxy polymer are as follows: the absorptions at 1607, 1581, and 1509 cm^{-1} are due to the phenyl group; 1248 cm^{-1} to the aromatic ether; and, 1106 and 1036 cm^{-1} to the deformation of the aromatic CH. The use of EFB-lignin as curing agent in epoxy resin, as shown in reaction (Fig. 3), was evidenced in Fig. 4C. The characteristic stretching vibration of the epoxy was observed at 915 cm^{-1} (C-O), and this band completely disappeared upon curing. The band positions and corresponding assignments are given in Table 1.

Table 1. Summary of IR Bands Associated with Different Types of Bonds

Maximum band position (cm^{-1})	Band group
3400-3200	O-H stretching vibration
2962-2840	C-H in methylene group
~ 1600 ~ 1500-1430	Aromatic ring
1610-1509	Phenyl group
1485-1445	C-H (bending vibrations from aromatic ring)
~ 1248	Aromatic ether
1106-1036	Deformation of the aromatic CH
~ 915	CO-C (vibration of the epoxide moieties)

CHN analysis was carried out to determine the percentage weights of carbon, hydrogen, and nitrogen. The results for CHN elemental analysis of lignin are summarized in Table 2 and compared with those of Mohamad Ibrahim *et al.* (2006), corresponding to lignin soda-AQ. The result for CHN elemental analysis of extracted lignin was summarized as follows: carbon (59.53%), hydrogen (6.07%), nitrogen (0.37%), and oxygen (34.03%). According to Mohamad Ibrahim *et al.* (2006), results of CHN analysis were almost the same as for soda lignin.

Table 2. CHN of Extracted EFB Lignin

Element	Experimental (%)	Reference* (%)
Carbon	59.53	53.77
Hydrogen	6.07	5.25
Nitrogen	0.37	0.66
Oxygen	34.03	40.32

* Mohamad Ibrahim *et al.* (2006)

Thermal Analysis for Lignin and Composites

The results, which are presented in Fig. 5, show the TGA curves and derivative thermograms (DTG) for EFB soda-AQ lignin. It has been reported that initial losses of weight during thermal analysis are due to water, carbon monoxide, carbon dioxide, and other pyrolysis products (Alriols et al. 2008; Sun et al. 2001). As shown in Fig. 5, the thermogravimetric curve that exhibited 10% weight loss degradation (T_{10}) appeared at about 270 °C. It is apparent that the maximum weight loss of lignin fractions occurred between 300 and 450 °C. When the temperature rose to 420 °C, the weight loss accounted for 50% of the initial mass. The non-volatile residue at 800 °C was large, amounting to 33% of the lignin material, which reflected a high degree of branching and substantial condensation of the lignin preparations (Sun and Tomkinson 2001). Degradation of lignin in the temperature region involved fragmentation of inter-unit linkages, releasing monomeric phenols into the vapour phase. Decomposition or condensation of aromatic ring was most likely to take place between 400 and 600 °C (Sun and Tomkinson 2001). Lignin is full of aromatic rings with various branches and it show a wide variety of chemical bonds in lignin, which led to the degradation of lignin occurring in a wide temperature range (100 to 800 °C), but at a very low mass loss rate (Yang et al. 2007). The major decomposition peak temperature of EFB-based lignin was observed at 393 °C. However, the observed minor peak at 308 °C ($T_{1 \text{ max}}$) could be attributed to the low molecular weight polyphenolic compounds with high carboxylic acid content (Mousavioun and Doherty 2010). The EFB-based lignin was soluble in tetrahydrofuran and dimethyl sulfide, while it was sparingly soluble in chloroform and ethanol.

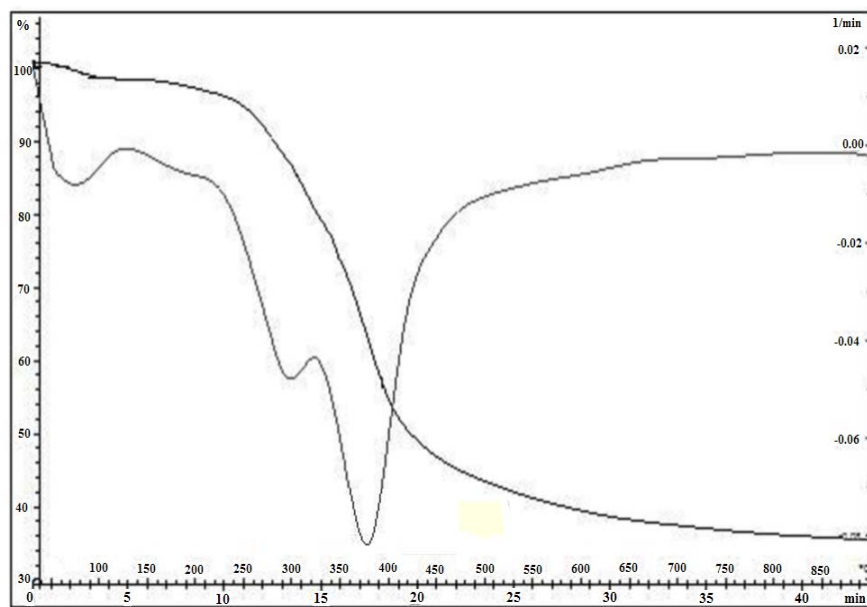


Fig. 5. TGA and DTG curves of EFB soda-AQ lignin under N_2 atmosphere at 20 °C/min

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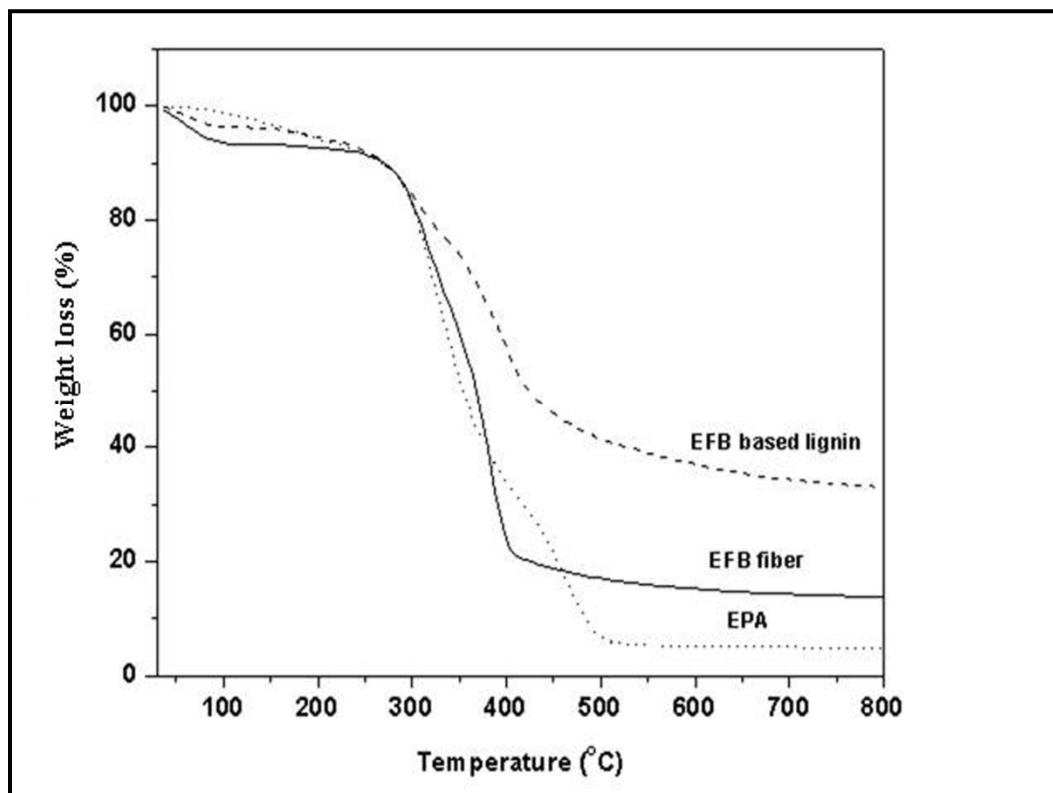


Fig.6. TGA curves of EFB fiber, EFB based lignin and epoxy- amine cured polymer (EPA) under N_2 atmosphere at $20\text{ }^\circ\text{C}/\text{min}$

Thermal degradation of EFB fiber and EFB-based lignin gave an initial weight loss below $100\text{ }^\circ\text{C}$ due to loss of moisture. The weight loss observed with epoxy polymer at this region might be due to the low molecular weight compounds. The EFB fiber, EFB-based lignin, and epoxy polymer started to decompose at $253\text{ }^\circ\text{C}$. A distinct weight loss appeared between 260 and $412\text{ }^\circ\text{C}$ on the EFB fiber (Fig. 7). However, EFB-based lignin underwent slow decomposition over a wide temperature ranges from 250 to $650\text{ }^\circ\text{C}$. The values of the thermal behaviour of these materials are compared in Table 3 using the onset decomposition temperature (T_{on}) and temperatures at which various weight losses of the samples were achieved. Also, at $420\text{ }^\circ\text{C}$, over 80% of the weight loss for EFB fiber compared with only 50% of the EFB based lignin. The result revealed that lignin from EFB is more thermally stable than EFB fiber.

Also, the minor degradation peak of the EFB fiber (denoted as T_{1max}), which appeared at $317\text{ }^\circ\text{C}$, corresponds to hemicelluloses decomposition, while the major temperature peak at $379\text{ }^\circ\text{C}$ represents the degradation of cellulose (Antal Jr. and Varhegyi 1995; Bakare et al. 2010). The major decomposition peak temperature of EFB based lignin (Fig. 7) was observed at $393\text{ }^\circ\text{C}$. The observed minor peak at $308\text{ }^\circ\text{C}$ (T_{1max})

could be attributed to the low molecular weight polyphenolic compounds with high carboxylic acid content (Mousavioun and Doherty 2010).

Table 3. Thermal Properties of EFB/Lignin Epoxy Composites

Composite Samples	Degradation temperatures (°C)			DTG peak temperatures (°C)		
	T_{on}	$T_{10\%}$	$T_{50\%}$	T_{1max}	T_{2max}	T_{3max}
EFB fiber	253	271	364	317	379	-
Epoxy+Amin (EPA)	152	266	389	328	384	-
EP-L15 (Epoxy+15% lignin)	239	266	346	272	301	384
EP-L20 (Epoxy+20% lignin)	257	284	364	295	331	397
EP-L25 (Epoxy+25% lignin)	266	284	363	301	341	394
EP-L30 (Epoxy+15% lignin)	248	275	354	295	331	386

T_{on} denotes the on-set decomposition temperature, while $T_{10\%}$ and $T_{50\%}$ represent the temperatures at which 10 and 50 % weight loss were attained. (- means no peak)

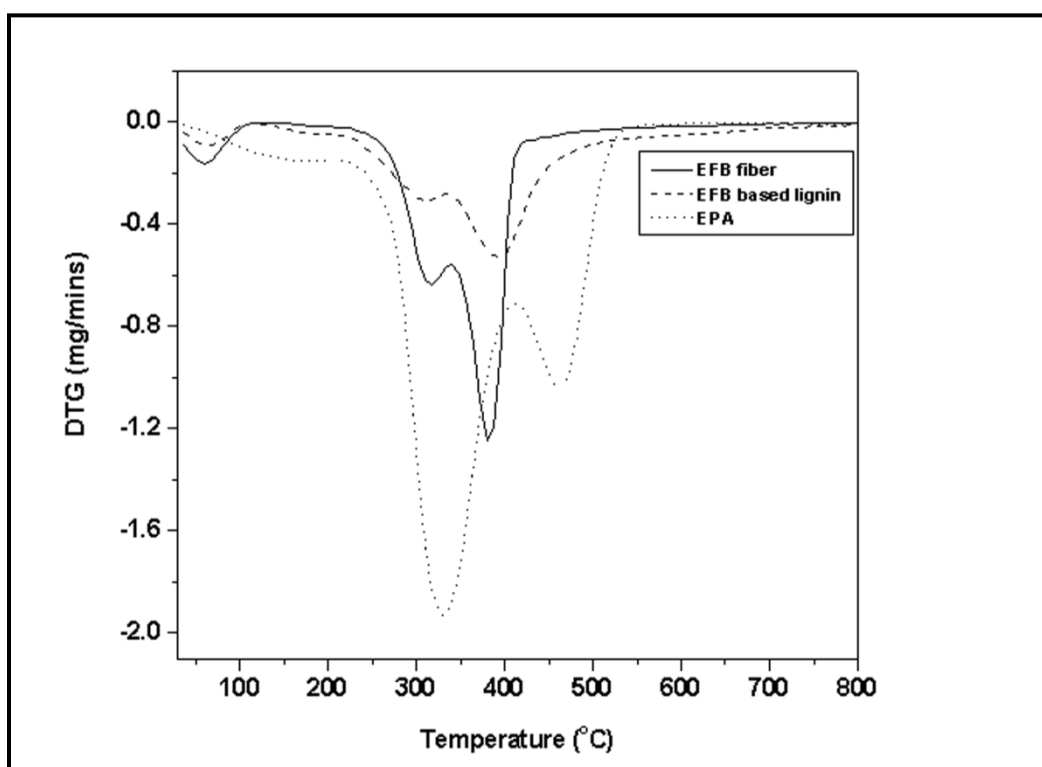


Fig. 7. DTG curves of EFB fiber, EFB based lignin and epoxy-amine cured polymer (EPA) under N_2 atmosphere at 20 °C/min

These results are consistent with previously published studies on lignocellulosic fibers and the derived lignin (Gronli et al. 2002; Gómez et al. 2007). The epoxy polymer showed a weight loss at the temperature interval between 268 °C and 375 °C followed by a more slow stage weight loss, with a broad degradation temperatures ranging between 375 °C and 510 °C, leaving about 5% char when heated under nitrogen. According to Grassie et al. (1986), the primary degradation (1st) occurs at the N–C and O–CH₂ bonds

of the cross-linked resin network. This degradation is followed by complex secondary reaction and formation of volatile products which arose from random chain scission and intermolecular transfer involving tertiary hydrogen abstractions from the polymer (Grassie et al. 1986).

In this research we also studied the influence of lignin on thermal properties of the composites. TGA is the most widely used technique to characterize thermal decomposition of materials because of its simplicity and the useful information afforded from a single TGA thermogram. Figures 8 and 9 show the TGA curves and derivative thermograms (DTG) for EFB fiber used as reinforcement, EFB based lignin, and unreinforced epoxy polymer (Table 3). The onset degradation temperature for Epoxy-15% lignin to Epoxy-30% lignin-based composites shifted to a higher temperature well over 250 °C. This compared to the onset degradation temperature of epoxy-amine composite that was around 150 °C, indicating the higher thermal stabilities of the soda-AQ lignin based composites. In addition, all the soda-AQ lignin based composites gave three distinct decomposition peaks (Fig. 8), which are related to the decomposition of the different components of the composites (EFB, epoxy, or lignin-epoxy matrix). For Epoxy-15% lignin, the first ($T_{1 \text{ max}}$) and the second decomposition peaks ($T_{2 \text{ max}}$) at 272 °C and 301 °C, respectively, are attributed to the thermal decomposition of the fiber constituents, which are mainly cellulose and hemicellulose (Mishra et al. 2004; Seo et al. 2007). On the other hand, the third degradation peak ($T_{3 \text{ max}}$) at 384 °C may be due to the decomposition of epoxy moiety (Khalil et al. 2010).

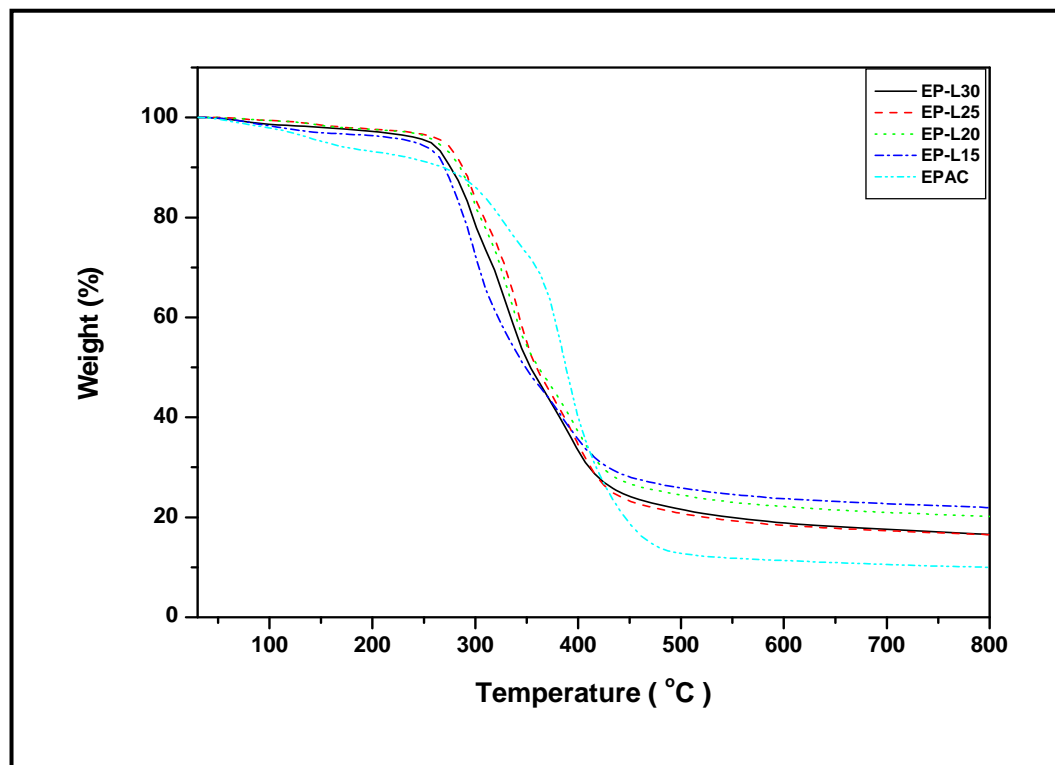


Fig. 8. TGA curves for epoxy + amine (EPAC), epoxy + 15% lignin, epoxy + 20% lignin, epoxy + 25% lignin, and epoxy + 30% lignin

The significant thermal behavior of the composites was determined from the onset decomposition temperature (T_{on}) which is taken as the temperature at which 5% degradation occurred, the temperatures at which 10 and 50% weight loss of various composite conversions were attained ($T_{10\%}$ and $T_{50\%}$, respectively), and the residual weight at 800 °C, denoted as the char. The onset decomposition temperatures and the temperature at which 10% degradation occurred for epoxy-lignin composites were higher than the amine-cured epoxy composite. At 50% weight loss, the decomposition temperature occurred at 389 °C for amine-cured epoxy composite and between 345 to 363 °C for lignin-epoxy composite samples. Also, the thermal degradation behavior of the lignin-epoxy composite was largely influenced by the lignin contents. All the composites had rapid degradation within a narrow temperature range between 260 and 425 °C. The lignin-based composites recorded 63 to 66 % weight loss compared with amine-cured epoxy composites which recorded well over 70% weight loss within a similar temperature range of 286 to 475 °C. However, it was observed that EPAC gave better heat resistance than lignin-epoxy composites at temperatures between 300 °C and 410 °C. Further heating to 800 °C led to an average residual weight of 10 to 21% for all the composites.

It was observed that epoxy-amine composites had better heat resistance than lignin-epoxy composites at temperatures between 300 °C and 410 °C. Further heating to 800 °C led to an average residual weight of 10 to 21% for all the composites. It has been reported that cross-linking of polymer chains can increase the thermal stability of epoxy resin (Seo et al. 2007). Therefore, the use of lignin as a curing agent may induce relatively high-chain rigidity in the polymer moiety due to an increase in the degree of crosslinking. This phenomenon may result in an enhanced thermal stability of the EFB/lignin-epoxy composite systems.

Furthermore, increase in lignin content beyond an optimum extent may not necessarily improve the degree of crosslinking; instead, it may possibly act as a filler. This may restrict further improvement in the thermal stability of the cured polymers matrix as observed in Epoxy-30% lignin composites. It was also observed that Epoxy-15% lignin and Epoxy-20% lignin had significant higher residual weight. This result indicated that the introduction of the lignin skeleton into the epoxy matrix improved the inherent thermal stability of the composites. Similar results were obtained by DTG analysis (Fig. 9). From Fig. 9, the peak decomposition temperatures for the composites can be seen in the derivative weight loss curve. These temperatures were designated as $T_{1\ max}$, $T_{2\ max}$, and $T_{3\ max}$, respectively, and are summarized in Table 3. For EP-L15, the first ($T_{1\ max}$) and the second decomposition peaks ($T_{2\ max}$) at 272 °C and 301 °C respectively are attributed to the thermal decomposition of the fiber constituents, which are mainly cellulose and hemicellulose (Mishra et al. 2004; Seo et al. 2007). On the other hand, the third degradation peak ($T_{3\ max}$) at 384 °C may be due to the decomposition of the epoxy moiety (Abdul Khalil et al. 2010).

The decomposition temperature peaks for the EFB-lignin based epoxy composites increased with increase in lignin contents to an optimum lignin content of 25%. From the viewpoint of practical use of lignin epoxy materials, the lignin contents in the composites should not be more than 25%. The good mechanical and thermal properties of the 25% lignin based epoxy composites must have been due to good fiber-matrix interaction

induced by the curing agent. High lignin content in these composites gives resistance to biodegradation and thermal degradation (Ndazi et al. 2006).

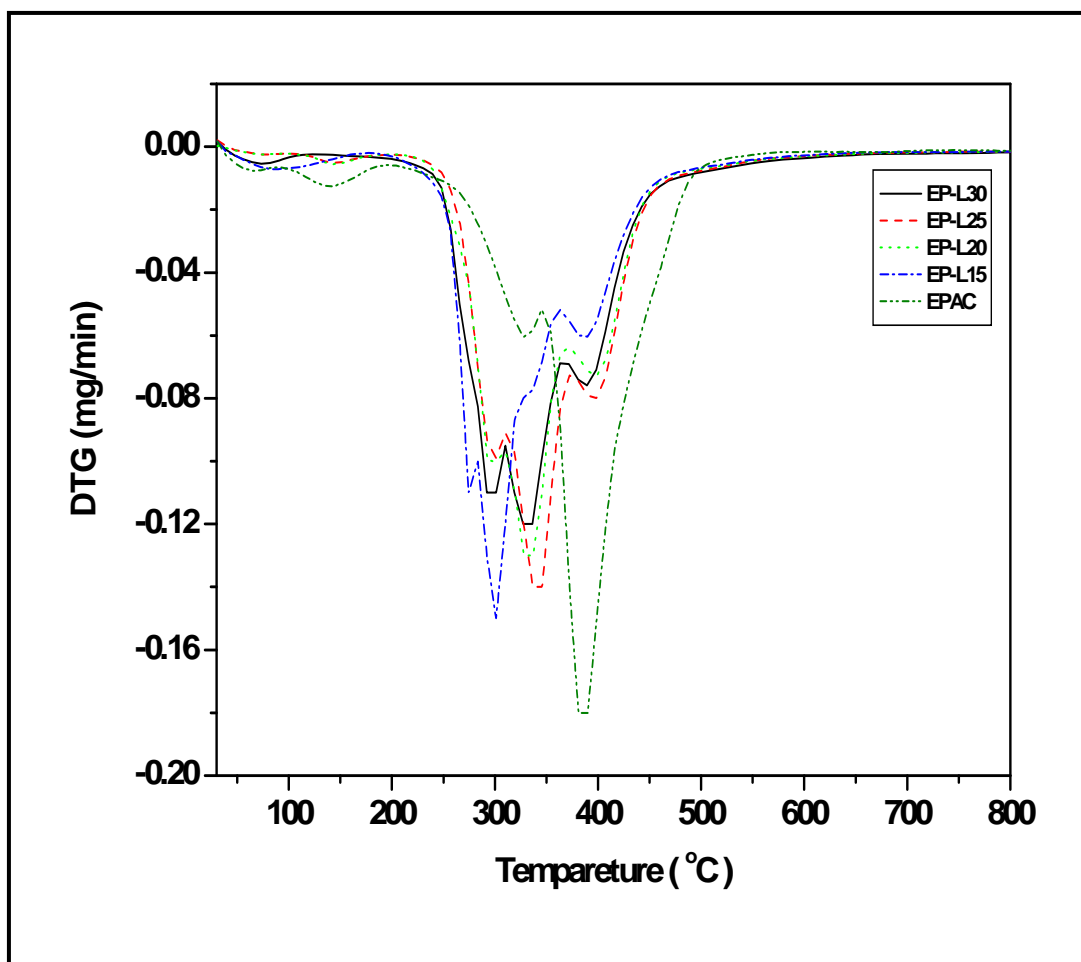


Fig. 9. DTG curves for composites (a) epoxy + amine (b) epoxy + 15% lignin (c) epoxy + 20% lignin (d) epoxy + 25% lignin (e) epoxy + 30% lignin

Mechanical Properties of Composites

The effects of lignin on the mechanical properties of composites obtained were studied and the results are summarized in Table 4. From the data of the tensile strength of the EFB/epoxy-lignin composite, it may be observed that the epoxy-25% lignin showed the highest tensile strength, which is 13.60 MPa, compared to the other ratios. This phenomenon is due to the structure of the hydroxyl group in lignin being crosslinked with epoxy and increasing flexibility of the main structures of epoxy. The presence of epoxy matrix adhered on the surface of the fibers indicates better adhesion resulted in fiber fracture.

It was shown that the tensile strength of reinforced composite significantly decreased when a higher ratio was used. EFB fiber is a lignocellulosic fiber with a high cellulose content (49.6%) but low lignin content (21.2%). Thus, EFB fiber is highly

hydrophilic due to its polarity caused by the free hydroxyl groups from the cellulose and lignin structures. This may lead to poor bonding quality between fiber and the matrix. When the content of epoxy resin is much higher than lignin, there are not enough hydroxyl groups to react with the epoxy ring to perform the crosslink. The weak interfacial adhesion between the oil palm empty fruit bunch fibers leads to the pullout of fiber from matrix as shown in Figs. 10 and 11. This may result in low mechanical properties of composites at higher ratios of lignin epoxy.

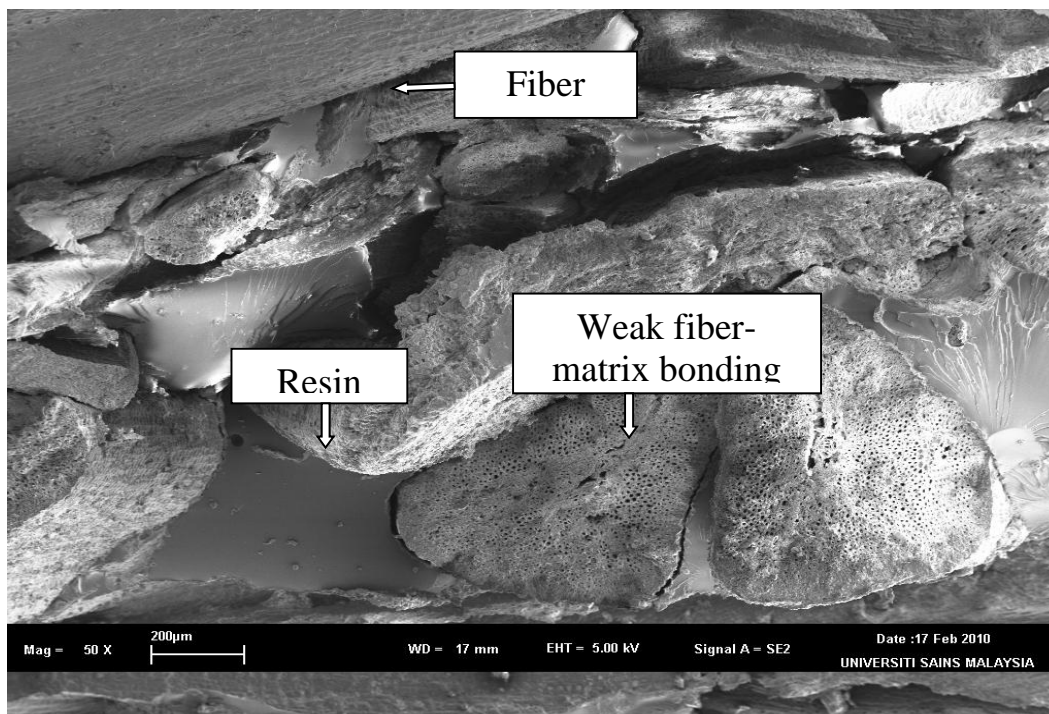


Fig. 10. Scanning electron micrographs of the tensile-fractured surface of the oil palm EFB fiber-reinforced composite (magnification 50 X)

As shown in Table 4 the values of flexural strength of epoxy-lignin composites increased and showed a steady behavior until 25%, with increasing lignin content. It indicates that increase in amounts of epoxy resin causes reduction in molecular interaction with lignin, thereby enhancing the rigidity (Mishra et al. 2007). It is observed that the flexural strength of the EFB/epoxy-lignin composite behaves similarly to tensile properties, in that the flexural behavior increases until 25% of lignin content. In flexural loading, the composite samples are subjected to compression, tension, and shear stresses. In a three-point flexure test, failure occurs due to bending and shearing. The increased flexural strength of the EFB/epoxy-lignin composite with 25% lignin content could be mainly due to the increased resistance to shearing of the composites as a result of the inclusion and the rigidity of lignin. This is because phenolic components in lignin are responsible for the stiffness and initiation of cracks in the composite. The values of the impact strength presented in Table 4 gave a similar observation. Impact strength is defined as the ability of the material to resist fracture under stress applied at high speed.

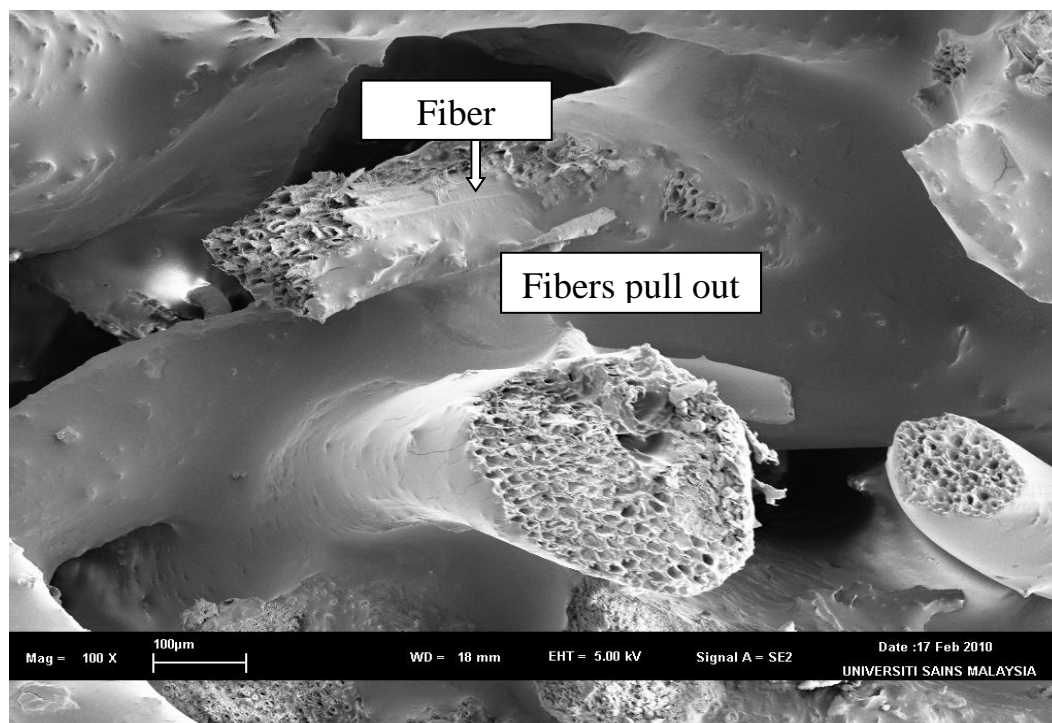


Fig.11. Scanning electron micrographs of the tensile-fractured surface of the oil palm EFB/epoxy-lignin composite (magnification 50 X)

Table 4. Mechanical Properties of Composites

Samples	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Impact Strength (KJ/m ²)
Epoxy + Amine	20.85 (0.88)	1.37 (0.05)	59.55 (1.81)	2.75 (0.10)	18.54 (0.90)
Epoxy + 15% lignin	8.56 (0.38)	0.18 (0.04)	19.29(1.50)	0.28(0.14)	4.41(0.41)
Epoxy + 20% lignin	10.36(0.64)	0.38(0.06)	36.00(3.20)	0.92(0.12)	7.21(1.12)
Epoxy + 25% lignin	13.60(0.91)	0.45(0.06)	74.09(3.08)	3.02(0.13)	12.77(1.10)
Epoxy + 30% lignin	9.95(1.22)	0.62(0.07)	49.32(3.50)	2.85(0.12)	6.94(0.91)

The value in bracket represents the standard deviation

The impact properties of a composite material is directly related to its overall toughness, which is highly influenced by the interfacial bond strength, the matrix, and fiber properties. In EFB/epoxy-lignin composites, impact strength was found to have increased with an increase in the lignin content as hardener of up to 25%. The fibers play a very important role in the impact resistance of the composite, as they interact with the crack formation in the matrix and act as a stress transferring medium (Abdul Khalil et al. 2008). In this study, the impact strength increases because of the flexibility of the interface molecular chains between the fiber and resin. The use of soda-AQ lignin improved the flexibility at the EFB fibers/matrix interface, thereby delaying the onset of the crack formation in the matrix.

Physical Properties of Composites

The water absorption behavior of epoxy lignin-based composites is shown in Fig. 12. The figure indicates that the addition of lignin reduced the water absorption of the composite. The highest value of water absorption was observed in the case of epoxy +15% lignin, and the lowest with epoxy + 25% lignin. This is due to having sufficient crosslinking established between the matrix and lignin, which is hydrophobic and will prevent accessibility to water. The high water absorption behavior of the oil palm fiber reinforced composite was also due to the highly hydrophilic nature of the oil palm fibers. The hydrophilic nature of the oil palm fibers was caused by the presence of polar groups such as hydroxyl, acetal, and ether linkages in the cellulose structure of the fibers. The free hydroxyl groups from the cellulose and lignin structure of the oil palm fiber were able to interact with the water molecules by forming a hydrogen bond (Abdul Khalil et al. 2008). The high water absorption leads to changes in the dimensional properties of the samples. As a result, a crack may be formed in the matrix due to the swelling of the fibers. This may contribute to the penetration of more water into the composites during prolonged exposure.

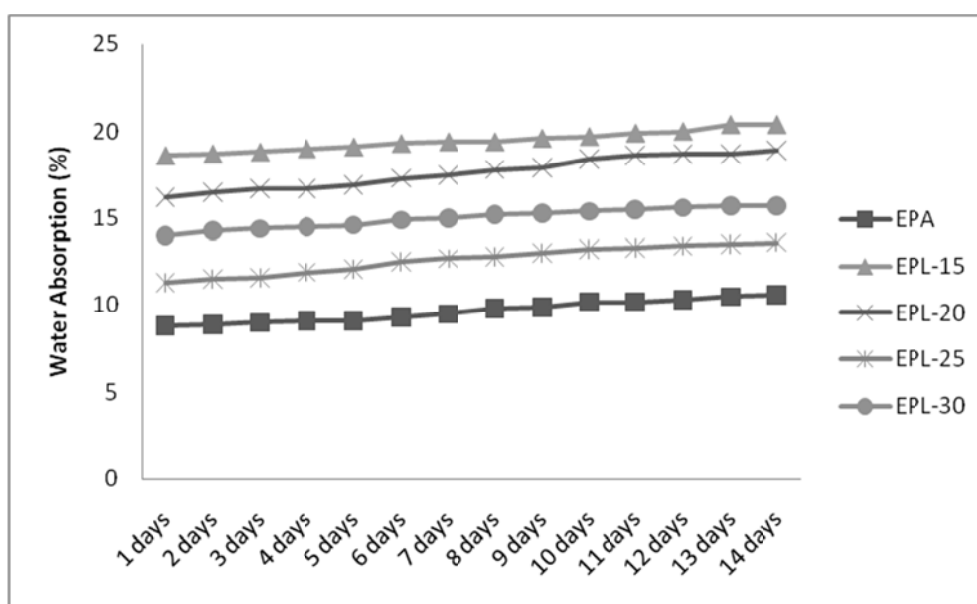


Fig. 12. Water absorption of oil palm EFB composites

CONCLUSIONS

1. Lignin from the black liquor of soda pulping was successfully extracted, and their structures and properties were confirmed by Fourier Transform Infrared Spectroscopy (FTIR), and CHN elemental analysis.
2. The onset degradation temperature for epoxy+15% lignin to epoxy+30% lignin based composites shifted to a higher temperature well over 250 °C compared with the epoxy composite (152 °C), indicating the higher thermal stabilities of the composites.

Increase in lignin contents beyond optimum extent may not necessarily improve the degree of cross linking; instead, it may possibly act as filler.

3. From the overall results of mechanical, physical and thermal properties, it was concluded that the 25 % of lignin in epoxy resin made a higher impact on the strength of the composites as compared to the other composites.
4. This work may provide new opportunities for applications in bioresource-based materials in high performance composites applications, if properly annexed.

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