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Extraction of reinforced epoxy nanocomposite using agricultural waste biomass

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Abstract. The growing awareness and concern of having greener and biodegradable materials has promoted researchers over the world to focus their attention on studies related to natural fibre reinforced polymer composites. In this study, the mechanical and thermal properties of the coconut shell powder and lignin obtained from different extraction methods such as Alkaline and Organosolv, on the epoxy composites were studied. The composite was fabricated using hand lay-up method, where the coconut shell and lignin fibers of 1, 2, 3 and 4 wt.% were mixed with the matrix consisting of epoxy resin and hardener in the ratio of 10:3. The obtained result showed that the usage of coconut shell powder and lignin as reinforcing fillers enhances the tensile strength and Young's modulus of composite when compared to neat epoxy composite by 16.4%, 14.6%, 9.70%, and 31.4%, 25.3%, 17.2% respectively at filler content of 3 wt. % but reduced the elongation at break up to 49.9% with respect to higher content of filler. Similarly, the flexural strength and Young's modulus was enhanced by 13.5%, 10.0%, 6.57% and 49.6%, 39.1%, 19.6% respectively at filler content of 3 wt.% but reduced the elongation at fracture up to 19.0% with respect to higher filler content. Structural characterization was also carried out where fillers were proven to enhance the purity and strength of the lignin.

1. Introduction

Polymers utilization has reliably developed globally in the past decade by playing an important role in many aspects of our daily lives, observing an increase of 45 million tonnes to 202 million tonnes in between 2005 till 2013, with an expectation of a further 40 million tonnes by 2017 [1]. Polymer composites are typically utilized due to advantages such as being able to be processed easily, and has a high rate of production with a reduction in cost they offer in comparison to conventional materials [2]. One drawback concerning the usage of polymer composites is that the unsustainable consumption of fossil fuels and raw materials, such as petroleum, coal and natural gas. The huge consumption of fossil fuels causes greenhouse gas emission that harms the environment, affecting changes in climate and global warming such as the rising of sea levels, rising of average global temperatures, decrease of the polar ice cap, and the rapid depletion of petroleum resources [3-6]. In the recent decade, industries have been using renewable energy that is obtained from potential sources of materials; including residues obtained from forestry, biomass, and agriculture, and are used as natural filler raw materials for polymer composite industries. Typically, in today's market, conventional fibres such as glass and carbon have been the reinforcement of choice due to its abundant presence and low cost. However, many industries are now using natural fibres as reinforcement materials in composite, mainly due to the increase in the thought of obtaining a green environment.

Besides that, the usage of natural fibres in polymer composites is also due to their advantageous assets for instance, being eco-friendly, biodegradable, renewable, cost effective, economically feasible, having low density with a specific strength, and a greater recovery of energy [2]. Some of the common natural fibres includes hemp [7], bamboo [8], jute [9], kenaf [10], and coconut [11]. In the context of this study, coconut shell is chosen as the biomass due to its absence in commercial uses.

Coconut (Cocos nucifera) tree is primarily a plantation corp in some of its origin tropical countries like India, Malaysia, Thailand and Sri Lanka [12]. Usually, the coconut shell is discarded after the fruit and water is consumed. These discarded coconut shells are known as bio waste, which today contributes, to more than 60% of the national waste volume [13]. Coconut shell comprises of organic substances such as cellulose (a glucose polymer), hemicellulose (a sugar polymer mainly containing pentoses) and lignin (a polymer of phenols) [14]. Lignin is an abundant polymer and important organic substance that is present in lignocellulosic biomasses. Lignin is deposited in the walls of certain specialized plant cells, which undergoes secondary wall biosynthesis, making them rigid and water impermeable [15]. It has potential to be converted into desired high quality phenolic products that can be used as a replacement of products that are derived from petroleum and fossil fuels [16]. Soda process [17], Kraft process [18], Sulfite process [19] Organosolv process [20], and steam explosion [21] are methods that can be used to extract lignin from a lignocellulosic biomass.

The field of polymer nanocomposites is presently one of the utmost popular scopes of research and development among researchers from different backgrounds. The term nano specifically refers to the smallest length lower than 100 nm [22], whereas the combination of two or more materials with certain properties that forms a new material that has higher properties is known as a composite. Generally, composites have three basic physical phases, where one phase in known as matrix, the other is known as reinforcement, and the final one is known as composites interphase [23] (Durowaye et al., 2014). A nanocomposite is formed when a filler is reinforced into a matrix in a nanometre (nm) scale (10-9 m) [24].

Natural fibres used as fillers are often the desired choice for reinforcements. Natural fillers are advantageous to the environment in comparison to conventional fillers as they decrease the dependency on non-renewable sources, which usually causes pollution and green house emission [11]. As natural fillers are of natural fibres, they too have similar properties of natural fibres such as they are cheaper, tougher, lower density, has a good specific strength properties, does not corrode easily, and a reduced tool wear [25]. However, they also do have disadvantageous in a sense that, they have got low tensile strength, low melting point, unfit for high temperature uses, poor surface adhesion to hydrophobic

polymers, uneven filler sizes, and they tend to degrade by moisture [26]. Therefore, to amend these disadvantageous, chemical treatments are carried out to alter the properties of the fibre surface [26].

The aim of this study shows the different extraction methods of obtaining lignin from coconut shell fibre, which is the Alkaline and Organosolv process. The lignin that is obtained is used as reinforcement in a nanometre scale, while, epoxy resin is used as the thermosetting polymer matrix, where the epoxy resin matrix acts in bonding the reinforcement particles together.

2. Materials and Methods

2.1. Materials
Coconut shells purchased from a market in Miri Sarawak. USA brand epoxy resin and hardener purchased from MS Diamond and Cut Rock Trading. Mirror Glaze maximum mold release wax purchased from Poly Glass Aluminium and Construction Works. Chemicals such as ethyl alcohol (C2H6O), sulphuric acid (H2SO4), and sodium hydroxide (NaOH) purchased from Merck Chemicals.
2.2Material preparation

2.1.1 Collection and Processing of Coconut Shell
The preparation of the coconut shell powder was carried out by cleaning the coconut shells thoroughly using normal tap water to remove the dirt from the outer and inner surface of the shells. The coconut shells were then manually hammered using a sledgehammer and dried in the oven at 110°C for 24 hours. This was followed by the grinding of the coconut shells using a ball mill grinder for 12 hours to obtain them in powdery form. Then, the coconut shells powder was sieved using a sieve shaker in the range of 45 to 300 micrometre to fractionate the powder to obtain fine coconut shell powder.

2.1.2 Extraction of Lignin using Alkaline method
The extraction of lignin using alkaline method was first carried out by measuring 20g of Sodium Hydroxide (NaOH). The measured NaOH was mixed into 500mL of distilled water and was mixed thoroughly using a stirring rod. Next, 10g of coconut shell powder (CSP) was added into the solution, and the solution was again mixed thoroughly through constant stirring. When all the NaOH and CSP have dissolved into the distilled water, the mixture was covered and heated for 2 hours using a magnetic stirrer heater at a temperature of 80°C. A magnetic stirrer bar was placed in the mixture and a stir of 200 revolutions per minute (rpm) was set to allow a uniform mixing in the solution. The solution was then allowed to cool. Afterward, 130mL of sulphuric acid (H2SO4) was added into the mixture gradually. The mixture was allowed to stay overnight to allow separation to occur. When separation occurs, two layers can be seen in the solution. The bottom layer contains of the lignin. The solution was then filtered out using a Buchner funnel and a vacuum flask. The washing of the filtered mixture using distilled water until a clear filtrate was obtained followed this. The residue that was obtained is the lignin. The lignin obtained was then placed on a petri dish and put into the oven at a temperature of 80°C, for 24 hours to dry the lignin. When the lignin has dried, a mortar and pestle is used to crush the lignin into powder form. Equation (1) and (2) was used to determine the mass of solid NaOH needed in the solution, and equation (3) was used to determine the volume of H2SO4 needed in the solution.

$$C = \frac{n}{V} \tag{1}$$

Where
      C represents the concentration of the solution (mol/L),
      n represents the no. of moles of NaOH (mol),
      V represents the total volume of the solution (L).

$$m = n \times MW \tag{2}$$

Where

m represents the mass of NaOH (g),
n represents the no. of moles of NaOH (mol),
MW represents the molecular weight of NaOH (g/mol).

$$M_1 V_1 = M_2 V_2 \tag{3}$$

Where
M_1 represents concentration in molarity of the concentrated solution (mol/L),
V_1 represents the volume of the concentrated solution (mL),
M_2 represents the concentration in molarity of the diluted solution (mol/L),
V_2 represents the volume of the concentrated solution (mL).

2.1.3 Extraction of Lignin using Organosolv method
The extraction of lignin using Organosolv method was carried out by mixing ethyl alcohol (C_2H_6O) and distilled water in the ratio of 60:40, respectively. The ethyl alcohol of 300mL was measured out into a 500mL beaker. This was then followed by the addition of 100mL of distilled water, 10g of coconut shell powder (CSP) and 8mL of sulphuric acid (H_2SO_4). The H_2SO_4 here acts as a catalyst. Next, the solution was mixed thoroughly using a stirring rod. When all the C_2H_6O and CSP have dissolved into the distilled water, the mixture was covered and heated for 2 hours using a magnetic stirrer heater at a temperature of 75°C. A magnetic stirrer bar was placed in the mixture and a stir of 200rpm was set to allow a uniform mixing in the solution. The solution was then allowed to cool and to allow separation to occur. When separation occurs, two layers can be seen in the solution. The bottom layer, also known as black liquor was discarded. Here, a centrifuge was used to separate the layers accurately. The centrifuge was run for 10 minutes, and the speed was set at 3500rpm. Afterwards, the filtrate which was obtained from the top layer was precipitated with distilled water until precipitation occurred. The precipitation process was carried out using the filtrate and distilled water in the ratio of 1:3, respectively. The precipitate contains of the lignin. The precipitate was then filtered out using a Buchner funnel and a vacuum flask. The washing of the filtered mixture using distilled water until a clear filtrate was obtained followed this. The residue that was obtained is the lignin. The lignin obtained was then placed on a petri dish and put into the oven at a temperature of 80°C, for 7 hours to dry the lignin. When the lignin has dried, a mortar and pestle is used to crush the lignin into powder form.

2.1.4 Composite fabrication
Hand lay-up technique, also known as open molding, is one of the most common technique used to fabricate the polymer matrix composites. The fabrication was prepared using two different molds, each for their own testing. Three batches of fabrication were carried out with different filler. The first batch was carried out using pure coconut shell powder (1, 2, 3 and 4 wt. %) and was mixed with the matrix consisting of epoxy resin and hardener in the ratio of 10:3. Similarly, the second and third batch was carried out using Alkaline-lignin and Organosolv lignin with the same weight percentage as the CSP and was mixed with the matrix consisting of the same ratio as of the first batch. Table 1 describes the mixing formulation of filler, epoxy and hardener. The fabrication process was started by polishing the molds with an anti-adhesive agent, in this case, wax to prevent the composite from sticking onto the mold upon removal. Then, the required epoxy resin, hardener and filler were measured out in three different paper cups, on an electronic weighing balance. The measured materials were poured into a new paper cup, with the sequence of epoxy resin, hardener, and filler, followed by a constant moderate stirring for 5 minutes using a popsicle stick. It must be ensured not to stir the mixture rapidly as it will trap more bubbles in the solution. Next, the mixture was immersed into an ultrasonic bath filled with 1500mL of water for sonication. The sonication took place for 3 minutes at a temperature of 0°C, with maximum power of 5 and high frequency. This was to enhance the dispersion of filler at the surface of the matrix. The mixture was then immediately placed in a vacuum chamber for 5 minutes to allow degassing process to occur. Degassing process is carried out to remove all bubbles that have been trapped in the mixture during the fabrication of the composites. After that, the mixture was poured into

the molds and left for cool mounting at room temperature for 24 hours until the mixture was hardened. When the composite has hardened, they were cured in an oven at a temperature of 100°C for 3 hours. After the curing, the composites were allowed to cool to room temperature, and then removed from the molds by bringing the mold onto a 30 to 45-degree bend.

Table 1 Mixing formulation of filler, epoxy and hardener

No.	Filler loading (wt. %)	Filler (g)	Epoxy resin (g)	Hardener (g)
1	0	0	70	30
2	1	1	76.2	22.8
3	2	2	75.4	22.6
4	3	3	74.6	22.4
5	4	4	73.8	22.2

2.2 Material Testing
2.2.1 Tensile testing
Tensile testing was carried out on the specimens to determine the tensile properties of the neat epoxy, as well as the pure coconut shell powder (CSP), alkaline-lignin (AL), and organosolv-lignin (OL) reinforced epoxy composites following the ASTM D638-91 test method. The force required to break the sample specimen and the extent to which the specimen elongates to break point were measured. The mold used for this specimen is based on the Type 1 tensile bar dimension and thickness outlined by ASTM international, which was a dog-bone shape mold. The tensile testing was conducted using LLYOD LR 10K Plus Advanced Universal Testing Machine (UTM), with cross-head speed of 20mm/min at the temperature of 25±3°C. The testing was carried out by placing the specimens at a specified grip separation in the grips of the tester and pulled until the specimen fractures.

2.2.2 Flexural testing
Flexural testing was carried out on the specimens to determine the bending strength of the composite materials under three-point loading condition, which indicates the materials stiffness when being flexed, according to the ASTM D790 test method. The mold used for this specimen is based on the flexural bar dimension and thickness outlined by ASTM international. The flexural testing was conducted using LLYOD LR 10K Plus Advanced Universal Testing Machine (UTM), with cross-head speed of 1.3mm/min. The testing was carried out by placing the specimens at a specified grip separation in the grips of the tester and pulled until the specimens reach 5% deflection or fractures before 5% deflection.

2.3 Characterization
2.3.1 Fourier Transform Infrared Spectroscopy
The surface chemistry of the pure and extracted specimens in terms of functional groups attached to the surface was examined using the Perkin Elmer FT-IR Spectrometer Frontier model. The specimens were exposed to infrared radiation, where the range of infrared region was set to 4500 to 500 cm-1. The scanning was regulated at 4 cm-1 resolution performing 50 scans for every specimen. The specimens absorb the radiation of the wavelengths and cause changes of the dipole moment of the sample molecules. The transmittance spectrum was observed in the region ranging of 4500 to 500 cm-1.

2.3.2 Thermogravimetric Analysis
Thermogravimetric analysis (TGA) of the pure and extracted specimens was conducted to examine the thermal degradation and stability by using a thermogravimetric analyzer (Perkin Elmer STA 6000). The testing was conducted by placing a specimen weight of about 10 to 15 mg an open alumina pan under an air flow of 20mL per minute. The specimens were then heated from ambient temperature of 25

to 700°C, at a heating rate of 10°C per minute. The temperature was recorded for further analysis and discussion.

3. Result and Discussion

3.1 Tensile properties

Fig. 1 (a) shows the effect of different filler content on tensile strength of coconut shell powder (CSP)/epoxy composite, alkaline lignin (AL)/epoxy composite and organosolv lignin (OL)/epoxy composite. The tensile strength graph illustrates that, as filler content increase, tensile strength shows a linear increase for all composites from 1 wt. % until 3wt%, and then decreases at 4wt%. A similar trend to the present study can be observed by studies carried out by Abdul Khalil et al. [27] and Tangimul Islam et al. [28]. In both studies, CSP fillers were reinforced to different composites. The tensile strength increases with the filler content up to a certain content, and thereafter decreased at higher filler concentration. In the case of where lignin was used as reinforcing fillers, Behin et al. [29] and Yu et al. [30] both respectively show the same behaviour of tensile strength that increases as filler content increases. Here, we can perceive that despite the different matrixes were used in the studies a similar trend can be observed when CSP or lignin is used as reinforcing fillers. We can deduce that the increase of the tensile strength as filler content increases may be due to the increased packing fraction and the lower void content in the composite [31]. For the lignin fillers, the reason of the increase in tensile strength is due to the effective transfer of stress from the molecular chains to the lignin networks, which shows a good reinforcement by the rigid lignin network [30].

As for the decrease of the strength at weight of 4%, it could be due to the poor surface adhesion of the reinforcing fillers with the epoxy matrix, as there was no coupling or dispersing agents used in the composites [32]. Also, aggregations and agglomerations of the reinforcing fillers due to the increase in interfacial area that may have formed within the epoxy matrix that caused interruption to the filler-matrix bonding [33]. This interruption lead to the reduction of an efficient load transfer from the matrix to the filler phase, which then easily causes the formation and propagation of crack within the matrix of the composite, and thus leads to a reduction of tensile strength of both the CSP and lignin epoxy composites [34]. Moreover, the reduced tensile strength for the lignin indicates the existence of a plasticizing effect of the lignin at 4 wt. %, filler content. The plasticizing effect occurred due to the poor interfacial adhesion between the lignin filler and the epoxy matrix, which caused lack of infusion of the composite [35].

Besides that, when compared to the tensile strength of neat epoxy composite that shows strength of 49.465 MPa, it can be observed that all the reinforced epoxy composites show a greater tensile strength in the range of lowest 52.483 MPa at 1 wt. % filler content, and highest of 57.575 MPa at 3 wt. % filler contents. Pure CSP, AL and OL composites show the maximum strength of 54.264, 57.575 and 56.674 MPa at 3 wt. % filler content, respectively. AL composite demonstrates the highest tensile strength of all composite with a significant increase of 16.4% compared to the neat epoxy composite. This is followed by OL and CSP, with a significant increase of 14.6% and 9.70% when compared to neat epoxy composite, respectively. From the highest tensile strength at 3 wt. % filler content, we can deduce that all reinforced composites could withstand a stress before it breaks. However, lignin reinforced composites have the best tendency to withstand a stress. The ability of the CSP and lignin to reinforce the epoxy matrix and withstand stress that produces high tensile strength could be due to the intermolecular bonding between the functional groups of the both the filler and epoxy matrix, which results a uniform distribution of the filler on the surface of the epoxy matrix. Moreover, CSP and lignin filler can easily disperse on the surface of matrix at lower filler content, which enables it to improve the filler-matrix interfacial bonding significantly. The good interfacial interaction between the epoxy matrix and filler allow the composite to withstand a great load, which results in a better stress transfer from the matrix to the filler.

Fig. 1 (b) shows the effect of different filler content on tensile Young's modulus of coconut shell powder/epoxy composite, alkaline lignin/epoxy composite and organosolv lignin/epoxy composite. The tensile Young's modulus graph exhibits the same behaviour of the tensile strength graph, where it can be observed that as filler content increase, tensile modulus shows a linear increase for all composites from 1 wt. % until 3wt%, and then decreases at 4wt%. Sarki et al. [25], Wood et al. [35] and Oliveira et al. [36] shows a similar trend of tensile young's modulus in their studies. Sarki et al. [25] reinforced coconut shell particles into the epoxy composite, Wood et al. [35] reinforced lignin into the hemp/epoxy composite, and Oliveira et al. [36] reinforced eucalyptus fibre into the polyester epoxy composites. In all three studies conducted by the respective authors, they observe that the tensile modulus increases with the filler content, but after that decrease at a higher filler concentration. Hence, similarly to the tensile strength, we can perceive that despite the different matrixes were used in the studies a similar trend can be observed when CSP or lignin is used as reinforcing fillers. The increase of the tensile modulus up to 3 wt. % filler contents could be due to the stiffness of the reinforcement which strengthens as the filler content increases. Also, the increase from 1 to 3 wt. % filler contents is due to the fact as the filler increase, it causes a more uniform distribution of the epoxy matrix, resulting in the improved bonding between the matrix and filler interphase. As for the decrease at 4 wt.% filler content of tensile modulus, the reason could be due to the agglomeration of the filler molecules around the matrix, which causes an improper curing of the composite [37]. The decrease could also be due to the increased micropores between the filler and the matrix that weakened the adhesion between the epoxy matrix and the filler interface [38]. It is also understood that fillers at a higher filler content act as flaws due to the lack of resin which wets the fibre surface, and results a weak stress transfer.

Besides that, when compared to the tensile modulus of neat epoxy composite that shows a modulus of 1484.39 MPa, it can be observed that all the reinforced epoxy composites show a greater tensile modulus in the range of lowest 1617.19 MPa at 1 wt. % filler content, and highest of 1950.67 MPa at 3 wt. % filler content. This clearly shows that the reinforcing fillers demonstrate a potential of increasing the young's modulus. Pure CSP, AL and OL composites show the maximum modulus of 1740.27, 1950.67 and 1860.17 MPa at 3 wt. % filler content, respectively. AL composite demonstrates the highest tensile modulus of all composite with a significant increase of 31.4% compared to the neat epoxy composite. This is followed by OL and CSP, with a significant increase of 25.3% and 17.2% when compared to neat epoxy composite, respectively. Here, it can be deduced that AL composite have got the highest resistance to deformation. Furthermore, the increase of the tensile modulus as filler content increases from 1 to 3 wt. % may be due to the improved rigidity of the composite. The rigidity could be improved by the good interfacial bonding between the CSP and lignin fillers and the epoxy matrix. The incorporation of the CSP and lignin filler into the epoxy matrix limited the molecular motion of the epoxy chain. The limitation enables the reduction of the composite deformation.

Fig. 1 (c) shows the effect of different filler content on elongation percentage of break of coconut shell powder/epoxy composite, alkaline lignin/epoxy composite and organosolv lignin/epoxy composite. The tensile elongation illustrates that, as filler content increase, tensile elongation shows a linear decrease for all composites from 1 wt. % until 4wt%. Also, when compared to the tensile elongation at break of neat epoxy composite that shows a 7.217% break, it can be observed that all the reinforced epoxy composites show a lower tensile elongation in the range of lowest 1.675% at 4 wt.% filler content, and highest of 4.654% at 1 wt.% filler content. Pure CSP, AL and OL composites show their maximum elongation at break of 4.654, 4.135 and 3.615% at 1 wt. % filler content, respectively. CSP composite demonstrates the highest tensile elongation of all composite with a significant decrease of 35.5% compared to the neat epoxy composite. This is followed by AL and OL composite with a significant decrease of 42.7% and 49.9% when compared to neat epoxy composite, respectively.

Based on the observation of the percentage of elongation at break, the elongation attributes are inversely proportional to the Young's modulus from 1 until 3 wt. % filler contents. This is because the stiffness of the sample affects the percentage of the elongation, and thus we can make a hypothesis that the stiffer the specimen, the lower the percentage of elongation at break of the tested specimen. Besides that, we can deduce that the decrease of the tensile elongation as the filler content increases may be due to the

formation of agglomeration that lead to low adhesion between the epoxy matrix and the filler reinforcement, and consequently caused the composite to be brittle [39]. In other words, as the filler content increases, the composite becomes tougher, and therefore, the chain mobilization in the matrix reduces. The reduction of the chain mobility, where the forming of the cross-linked network in the polymer chain is restricted by the high attractive force, causes the brittleness of the composites to increase [28].
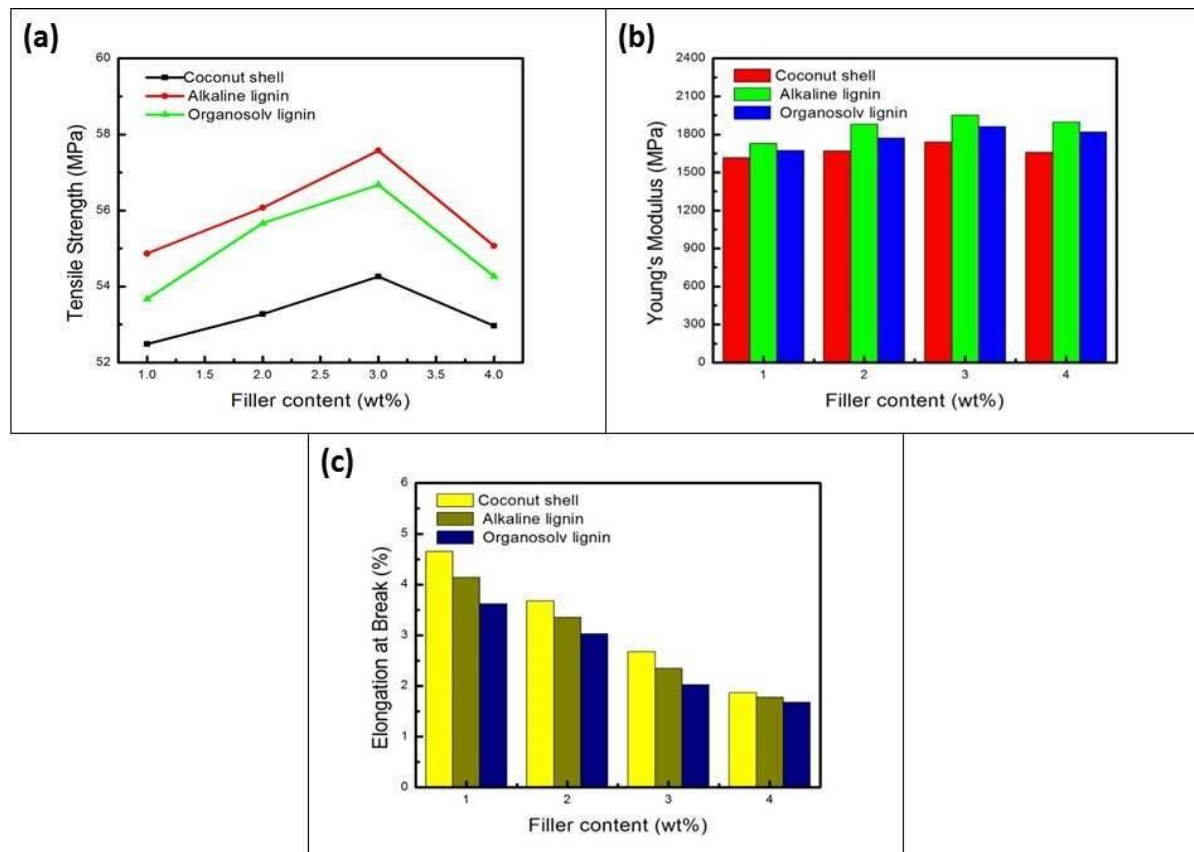

Fig. 1: (a) Tensile strength versus filler content, (b) Tensile Young's modulus versus filler content, and (c) Elongation at break versus filler content

3.2 Flexural properties

Fig. 2 (a) shows the effect of different filler content on flexural strength of coconut shell powder (CSP)/epoxy composite, alkaline lignin (AL)/epoxy composite and organosolv lignin (OL)/epoxy composite. The flexural strength graph illustrates that as filler content increase, flexural strength shows a linear increase for all composites from 1 wt. % until 3wt%, and then decreases at 4wt%. The same was reported by Tangimul Islam et al. [28] that studied the effect of filler from 0 to 100% and revealed that as filler content increases, flexural strength was observed increasing from 0 to 30%, and decreasing afterward. The increase of flexural strength from 1 to 3 wt. % filler contents could be due to strong interfacial bonding caused by the compatibility of the fillers and the polymer matrix. The high strength could also indicate good mixing and infusion of the reinforcing fillers. As for the decrease at 4wt%, the reason could be due to the weak interfacial adhesion to transfer the stress, or the presence of the pores at the surface interface of the filler and the matrix. Moreover, voids content and dispersion problem, and other factors like the size, shape and type of reinforcing filler may cause the strength to decrease Tangimul Islam et al. [28].

Besides that, when compared to the flexural strength of neat epoxy composite that shows strength of 110.58 MPa in Table 1, it can be observed that all the reinforced epoxy composites show a greater flexural strength in the range of lowest 112.89 MPa at 1 wt. % filler content, and highest of 125.47 MPa at 3 wt. % filler contents. This clearly shows that the reinforcing fillers demonstrate a role of increasing the flexural strength. Pure CSP, AL and OL composites show the maximum strength of 117.85, 125.47 and 121.64 MPa, at 3 wt. % filler content, respectively. AL composite demonstrates the highest flexural strength of all composite with a significant increase of 13.5% compared to the neat epoxy composite. This is followed by OL and CSP, with a significant increase of 10.0% and 6.57% when compared to neat epoxy composite, respectively. Here, it can be deduced that AL composite have got the highest ability to resist bending. Based on the observation of the flexural strength graph, the composites with filler content of weight 3% displayed greater load carrying ability and deflection. This indicates that the composites are less brittle and undergoes a slow rate of crack propagation [40].

Moreover, when compared to the flexural strength of neat epoxy composite that shows strength of 110.58 MPa, it can be observed that all the reinforced epoxy composites show a greater flexural strength in the range of lowest 112.89 MPa at 1 wt. % filler content, and highest of 125.47 MPa at 3 wt. % filler content. This clearly shows that the reinforcing fillers demonstrate a role of increasing the flexural strength. Pure CSP, AL and OL composites show the maximum strength of 117.85, 125.47 and 121.64 MPa, at 3 wt. % filler content, respectively. AL composite demonstrates the highest flexural strength of all composite with a significant increase of 13.5% compared to the neat epoxy composite. This is followed by OL and CSP, with a significant increase of 10.0% and 6.57% when compared to neat epoxy composite, respectively. Here, it can be deduced that AL composite have got the highest ability to resist bending. The enhancement of the surface roughness enables the lignin to have a better fibre-matrix adhesion. Besides that, based on the observation of the flexural strength graph, the composites with filler content of weight 3% displayed greater load carrying ability and deflection. This indicates that the composites are less brittle and undergoes a slow rate of crack propagation.

Fig. 2 (b) shows the effect of different filler content flexural Young's modulus of coconut shell powder/epoxy composite, alkaline lignin/epoxy composite and organosolv lignin/epoxy composite. The flexural Young's modulus graph exhibits the same behaviour of the flexural strength graph, where it can be observed that as filler content increase, flexural modulus shows a linear increase for all composites from 1 wt. % until 3wt%, and then decreases at 4wt%. Gopinath et al. [41] and Vasu et al. [42] shows a similar trend of flexural young's modulus in their studies. Gopinath et al. [41] reinforced jute fibre particles into the polyester and epoxy matrix, and Vasu et al. [42] reinforced coconut shell powder into the propylene composites. Both authors, each in their own respective study showed the results of the flexural modulus that increases with the filler content, however decreases at a higher filler concentration. Here, we can observe that despite the different matrixes and reinforcing fillers were used in the studies, a similar trend can be observed when CSP or lignin is used as reinforcing fillers. The increase of the flexural modulus is due to the stiffness of the reinforcement which strengthens as the filler content increases. As for the decrease of the modulus at 4 wt. %, the reason may be due to the poor mixing and infusion of the filler and matrix, or in other words, improper wetting of the matrix and filler which caused the epoxy matrix deficiency, and thus agglomeration.

Besides that, when compared to the flexural modulus of neat epoxy composite that shows a modulus of 3324.05 MPa, it can be observed that all the reinforced epoxy composites show a greater flexural modulus in the range of lowest 3724.85 MPa at 1 wt. % filler content, and highest of 4973.64 MPa at 3 wt. % filler content. This clearly shows that the reinforcing fillers demonstrate a potential of increasing the young's modulus. Pure CSP, AL and OL composites show the maximum modulus of 3973.76, 4973.64 and 4624.75 MPa at 3 wt. % filler content, respectively. AL composite demonstrates the highest flexural modulus of all composite with a significant increase of 49.6% compared to the neat epoxy composite. This is followed by OL and CSP, with a significant increase of 39.1% and 19.6% when compared to neat epoxy composite, respectively. Here, it can be deduced that AL composite indicates the highest value of stiffness, and thus have got the highest resistance to deformation which is closely followed by organosolv-lignin and CSP. Both the lignin's show higher modulus compared to CSP,

which could be due to the fact that during the extraction of the lignin, the lignin fibres may have undergone swelling which was caused by the water absorption. The water absorption crowds the space between the fibre and the epoxy matrix, which led to an increase in the mechanical properties of the composites [43].

Fig. 2 (c) shows the effect of different filler content on elongation percentage of fracture of coconut shell powder/epoxy composite, alkaline lignin/epoxy composite and organosolv lignin/epoxy composite. The flexural elongation illustrates that, as filler content increase, flexural strength shows a linear decrease for all composites from 1 wt. % until 4wt%. Also, when compared to the flexural elongation at break of neat epoxy composite that shows a 18.713% fracture, it can be observed that all the reinforced epoxy composites show a lower flexural elongation in the range of lowest 13.218% at 4 wt.% filler content, and highest of 16.157% at 1 wt.% filler content. Pure CSP, AL and OL composites show their maximum elongation at break of 16.157, 15.635 and 15.158% at 1 wt. % filler content, respectively. CSP composite demonstrates the highest flexural elongation of all composite with a significant decrease of 13.7% compared to the neat epoxy composite. This is followed by AL and OL composite with a significant decrease of 16.5% and 19.0% when compared to neat epoxy composite, respectively. This clearly shows that the reinforcing fillers decrease the elongation percentage at fracture of the composites, which may be due to the reduction of polymer component inside the composite.
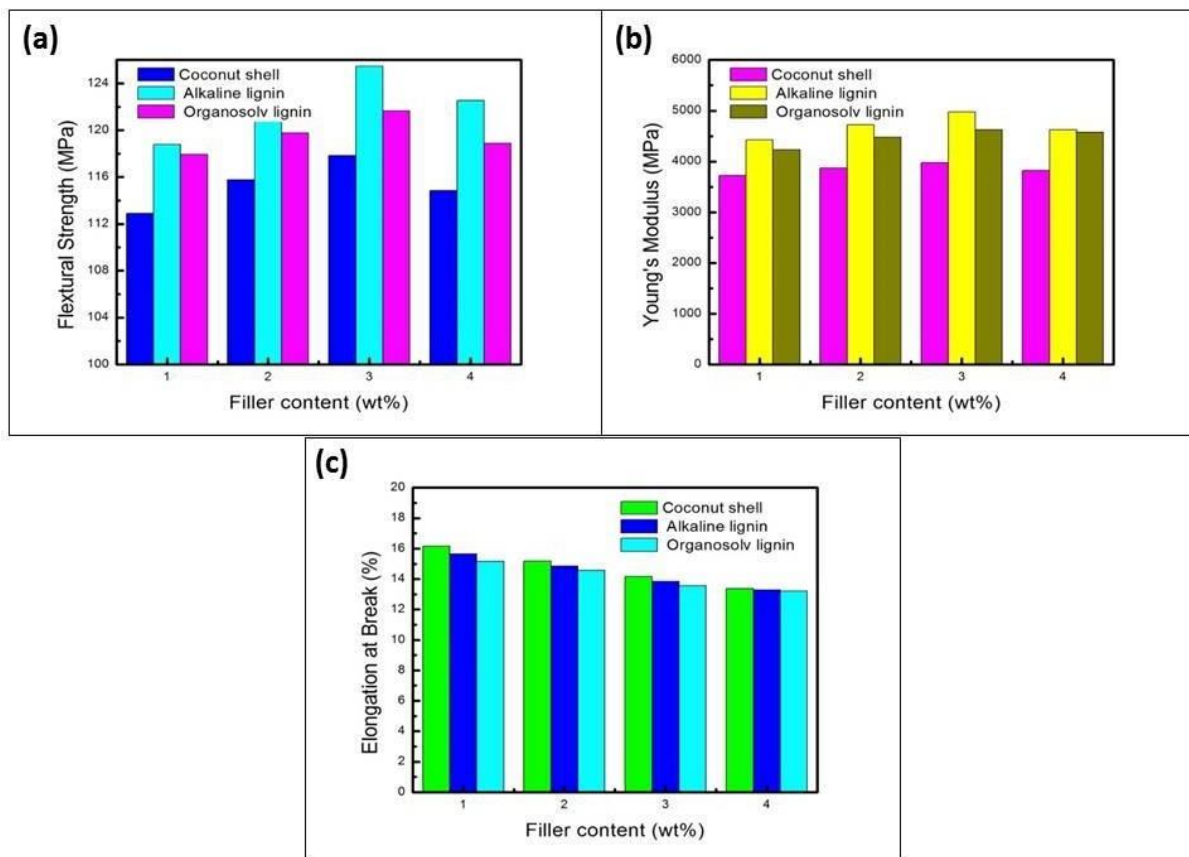

Fig. 2: (a) Flexural strength versus filler content, (b) Flexural Young's modulus versus filler content, and (c) Elongation at fracture versus filler content

3.3 Fourier Transform Infrared Spectroscopy

The Fourier Transform Infrared Spectroscopy (FTIR) spectrum for the coconut shell powder, alkaline lignin and organosolv lignin in this study is shown in Fig. 3. From the figure, it can be observed that different absorption bands ranges in the spectrum from 4000 to 300 cm-1. The absorption band around 3350 cm-1 is due to the hydroxyl (O-H) stretching vibration. According to Ibrahim et al. [44] that have quoted Khan et al. [45] in his study, the O-H stretching may be due to the absorbed alcohols that are found in cellulose, hemicellulose, lignin, extractives and carboxylic acids. Also, the relatively small O-H stretching band may be due to the limited reactive efficiency of the hydroxyl at the coconut shell and lignin fiber surface. This signifies the capability of easier surface water desorption, as well as hemicellulose/lignin decomposition for the CSP. The absorption band around 2950 cm-1 is due to the carbon-hydrogen (C-H) stretching, which is a characteristic of any natural fiber. The presence of the band which is only an indistinct peak in the spectrum is observed at around 2650 cm-1. However, this band could not be identified with any molecular origin. It is also observed that the bands in the range of 2350 cm-1 and around 2020 cm-1 may be related to carbonyl (C=O) stretching. As for the bands in the range of 1750 to 1300 cm-1, Ibrahim [46] suggested that this range is due to the deformation of the carbon-hydrogen (C-H) stretching. Ibrahim [46] also suggested that the deformation of the C-H and carbon-oxygen (C-O) are due to the ether linkage. In this spectrum, the deformation of C-H and C-O is noticeably observed to be at 1080 cm-1. This accentuated band could represent the difficulty for the ether radicals to decompose.
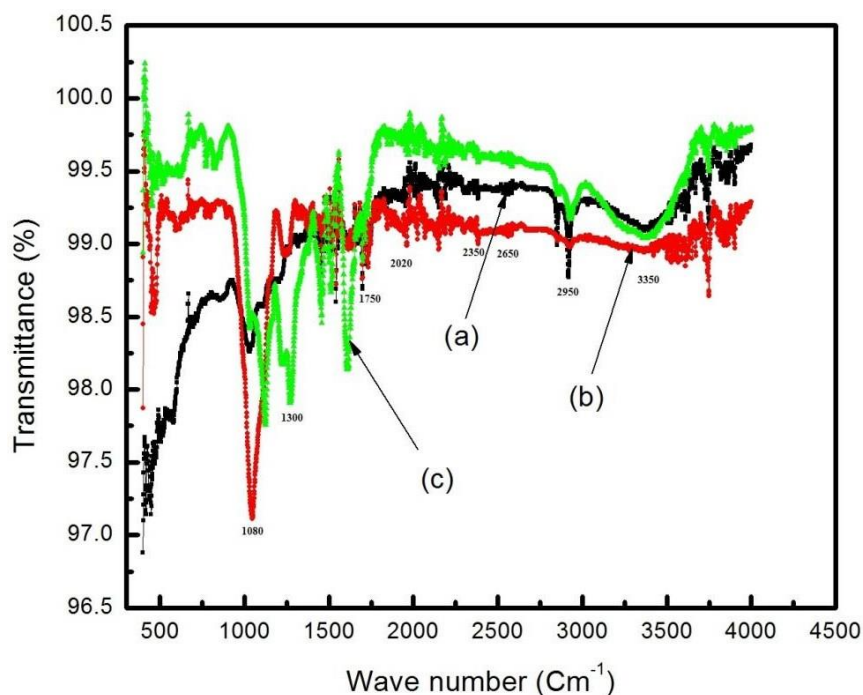

Fig. 3: FTIR spectrum of (a) alkaline-lignin, (b) pure coconut shell powder, and (c) organosolv-lignin

3.4 Thermogravimetric Analysis
Coconut shell powder (CSP), alkaline-lignin (AL) and organosolv-lignin (OL) were selected for testing to identify thermal stability and the purity of the composite materials. Fig. 4 shows the comparison for the thermogravimetry analysis (TGA) curves of the particulates for pure CSP, alkaline-lignin and organosolv-lignin. From the figure, it can be observed that there is a thermal degradation at much lower temperature and significant weight with respect to temperature. Fig. 8 depicts the TGA curve of pure

CSP and lignin fibres as a function of temperature. It shows the degradation of all three fibres occurred at three stages. A similar degradation of three stages was observed by Monteiro et al. [47] in his study. The first stage was at a heating range of 25 to 250°C. At this stage, all the fibre films show a relative weight loss, despite the thermal stability improvement of the fibre. The cause of the relative weight loss may be due to the loss of moisture content in the fibres. Here, the loss of moisture is because of the water loss and structural rearrangements with the release of small molecular weight compounds. According to Monteiro et al. [47], temperatures below 250°C usually corresponds to the water loss of the natural fibre, and it also indicates the condensation and splitting of the side chains of the lignin. Second stage occurred at the heating range of 250 to 400°C. At this stage, all the fibre films show a major weight loss. The cause of the major weight loss may be due to the degradation of components of carbohydrates in the CSP and lignin samples, which are converted to volatile gasses such as carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). Third stage occurred at the heating range of 400 to 660°C. Monteiro et al. [47] stated that the decomposition above 400°C of the lignin is associated with a series of degradation and condensation reactions with accumulation of aromatic products. Kabir et al. [48] stated that a greater thermal stability is obtained due to higher decomposition temperatures. Therefore, at this third stage, all the composite films show a significant weight loss. Here, the cause may be due to the degradation of the fibres due to burning and oxidation. The carbon-hydrogen (C-H) and carbon-oxygen (C-O) bonds in the organic coconut shell were cleaved to generate non-condensable volatile components. As for the lignin, the degraded volatile products include phenols, alcohols and aldehyde acids along with the formation of gaseous products that are getting removed. The mass change in this stage was extremely small. Besides that, it can be observed from the TGA curve that the thermal degradation for all the samples did not commence until the materials had adsorbed a certain amount of heat energy. Therefore, the heat initiated the degradation processes, whereas the breaking down of the structure caused the molecular chain to be broken. It can fairly be suggested that the CSP and lignin's thermal properties are dependent on their source.
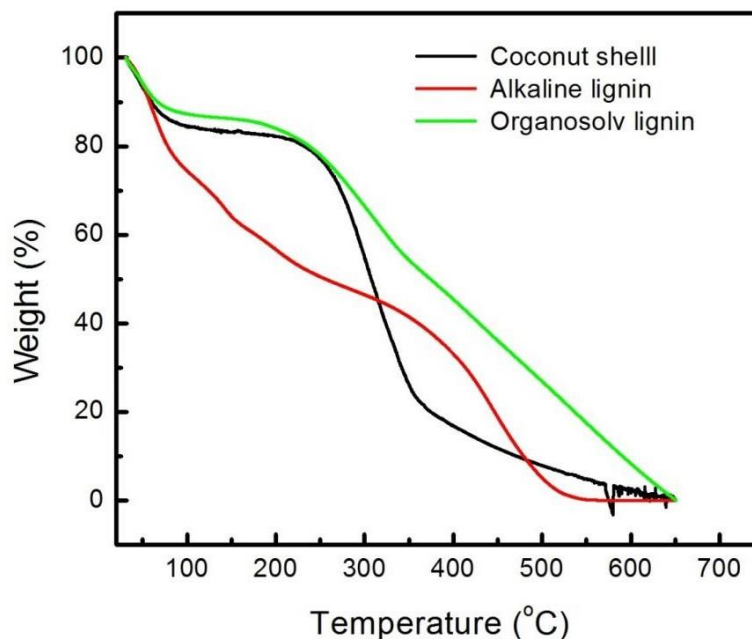

Fig. 4: Weight versus temperature of coconut shell powder

4. Conclusion

The present study investigated the usage of natural fibre polymer composites filler with addition of natural fine fillers into matrix to enhance the properties of the epoxy composite. The incorporation of nano-size reinforcement of functional filler is advisable to compensate with the limitation of the epoxy resin. Functional nanofillers like nanofibers are great filler to modify and improvise the mechanical and thermal properties of polymer matrix resin, like epoxy. The tensile strength, tensile Young's modulus, flexural strength and flexural Young's modulus was observed to increase until 3 wt.% of filler content, however degraded at a higher addition of 4 wt.%. The obtained results showed that the tensile strength of CSP, alkaline-lignin and organosolv-lignin shows a significant increase of 9.70%, 16.40%, 14.6% and the tensile modulus observes an increase of 17.2%, 31.4%, 25.3% when compared to neat epoxy composite. The flexural strength of CSP, alkaline-lignin and organosolv-lignin shows a significant increase of 6.57%, 13.5%, 10.0% and the flexural modulus observes an increase of 19.6%, 49.6%, 39.1% when compared to neat epoxy composite. In addition, the tensile elongation of break of CSP, alkaline-lignin, organosolv-lignin shows a decrease of 35.5%, 42.7%, 49.9% and the flexural elongation of fracture was observed a decrease of 13.7%, 16.5%, 19.0% when compared to neat epoxy composite. The findings of the present study draw the main conclusion that lignin/epoxy composites improve the mechanical and thermal properties of epoxy composite compared to coconut shell/epoxy composite and neat composite.

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