

Composite Materials Based on UPE Resin and Coffee Husks

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ABSTRACT

In this work, two series of composite materials based on unsaturated polyester (UPE) resin and coffee husk powder were fabricated by a hot pressing method using methyl ethyl ketone peroxide (MEKP) as an initiator. The gel time of UPE resin is 32 ± 2 min with 0.5 wt % of MEKP was determined according to ASTM D2471. The differential scanning calorimetry (DSC) reveals that the curing process should be post-cured. The composite panels were fabricated with the size of 17x17x4 mm. With a bulk density of 1.35 g/cm³, two series of the composite material with two types of coffee husk sizes in the range of 0.150-0.315 mm (CH1) and 0.315-0.630 mm (CH2) were investigated. In each series, the coffee bean husk content varies by 45, 50, 55, 60, 65, and 70 wt %, respectively. The obtained composite materials were evaluated for mechanical properties such as flexural and tensile strength according to ASTM D790 and D638, respectively. The results show that the mechanical properties at the reinforcement content of 50% are the best with the flexural strength, flexural modulus, tensile strength and tensile modulus of the CH1 are 8.5, 616.0, 3.9, and 999.8 MPa, respectively. Meanwhile, they are 18.7 MPa, 1888.5 MPa, 8.6 MPa, 8.6 MPa, and 1889.0 MPa, respectively for the CH2.

KEYWORDS

Composite material;
UPE resin;
Coffee husk;
Gel time;
Post-curing;
Mechanical properties.

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1. Introduction

Composite materials are materials made from two or more different materials, with each component having its unique mechanical, chemical, and physical properties. When combined, they form a completely new material with properties superior to the original materials [1]. The two main components of composite materials are usually the matrix and the reinforcing materials. In addition, there may be some additives such as flame retardant, anti-flow agent, anti-UV, anti-foam, and anti-oxidation agent.

For a long time, coffee has become a popular beverage all over the world [2]. According to the International Coffee Organization, about 2.3 billion cups of coffee are consumed every day and coffee production is about 7.5 million tons (2002) and about 10.5 million tons (2020) per year [3, 4]. The production of coffee beans generates a huge amount of agricultural waste. Which, the most is coffee husk representing 18% of coffee fruit [5]. This number is not small and it requires appropriate treatment measures to combat environmental pollution. Recently, researchers have focused on using agricultural waste from the coffee industry to reduce environmental impact such as use as animal feed [6], producing organic compost [7], use as fuel pellets [8], production of activated carbon [9], extraction of antioxidants [10], production of biodiesel [11]...

In recent years, green technology and sustainable development have become popular and interested to many researchers around the world. The coffee husk (CH) as an agricultural waste from industrial coffee has been investigated as a filler in reinforced polymer composites. Most of these studies used thermoplastic such as polyhydroxybutyrate [12], polyethylene [13], polypropylene [14] – [15], polyurethane [16]. In these reports, there are no studies on the use of coffee husk for thermosetting polymers. The potentially attractive properties of composite materials based on thermosetting polymers for processing and use are low bulk density, good thermal insulation, excellent mechanical properties, sustainability, low price, and ease of production [17]. Common thermosetting polymers that can be listed include unsaturated polyester (UPE), vinyl ester, and epoxy resin...

In this work, two series of composite materials based on unsaturated polyester (UPE) resin and coffee husk powder were fabricated by the hot pressing method using methyl ethyl ketone peroxide (MEKP) as an initiator. The curing process of the UPE resin and the mechanical properties of the coffee husk reinforced composite materials were evaluated.

2. Materials and Methods

The UPE resin 6120 as a matrix resin was purchased from En Chuan Chemical Industries Co. (Taichung, Taiwan). Coffee husk material was provided by Elite Coffee joint-stock company (Daklak, Vietnam). MEKP as an initiator was supplied by Aldrich Chemical Corp (Saint Louis, MO, USA). Toluene and ethanol as solvents were purchased from Xilong Scientific Co. (Guangdong, China). All reagents were used as received without any further purification.

Coffee husk received from Elite is ground into powder by a cutter mill. Controlab Vibratory Sieve Shaker was used to classify coffee husk powder into two dimensions including the range of 0.150 - 0.315 mm (CH1) and the range of 0.315 - 0.630 (CH2) mm. Then, the obtained flour was dried at 103 °C for 24 h to remove completely moisture. The dried flour was then soaked in the mixture of ethanol and toluene (volume ratio is 1:2) for 6 h at 25 °C to remove soluble extracts and dried at 40 °C for 24 h [15].

The bulk density of CHs was determined as follows: pour the obtained CHs into a 50 mL volumetric flask and determine the weight of each component. All tests were performed ten times. The bulk density of CHs was calculated as the following equation:

$$D = \frac{m_1 - m_0}{50} \quad (1)$$

where m_1 is the weight of a full volumetric flask and m_0 is the weight of a free volumetric flask.

The gel time of UPE resin with MEKP as an initiator was confirmed according to the ASTM D2471 method. This process was performed as follows: 30 g of UPE was poured into a cylinder vessel at room temperature. Drop slowly MEKP at a ratio of 0.25, 0.5, 0.75, and 1 % wt into the vessel. The mixture was slowly stirred with a stirring rod. Every 15 seconds, probe the center surface of the reacting mass, with the applicator stick perpendicular to the material surface. When the reacting material no longer adheres to the end of a clean probe, record the gel time as the elapsed time from the start of mixing. All test was performed three times.

The curing reaction of UPE resin was also further investigated by the differential scanning calorimetry (DSC, Netzsch Polyma 214, Germany). This process was conducted as follows: 10 mg of reaction mixture containing UPE resin and 0.5 % wt of MEKP was tested for isothermal DSC at 30 °C for 90 minutes. The gel time resin in the DSC system of a sample (t_1) was determined at the maximum exothermic point. The total gel time includes the time of operation outside the DSC system (t_0) and t_1 . Then, the reaction mixture was continued to test DSC at the heating rate of 5 °C/min in the temperature range of 30-150 °C. The post-cure temperature was confirmed at the maximum exothermic point. The reaction heat of each stage was calculated as areas of the DSC curves.

The chemical bonds of the UPE and cured-UPE resin were determined by the FTIR instrument (FT-NIR/MIR, PerkinElmer Frontier, USA) within 4000-400 cm^{-1} with a scan resolution of 4.00 cm^{-1} . Background measurements were performed and subtracted for all the samples.

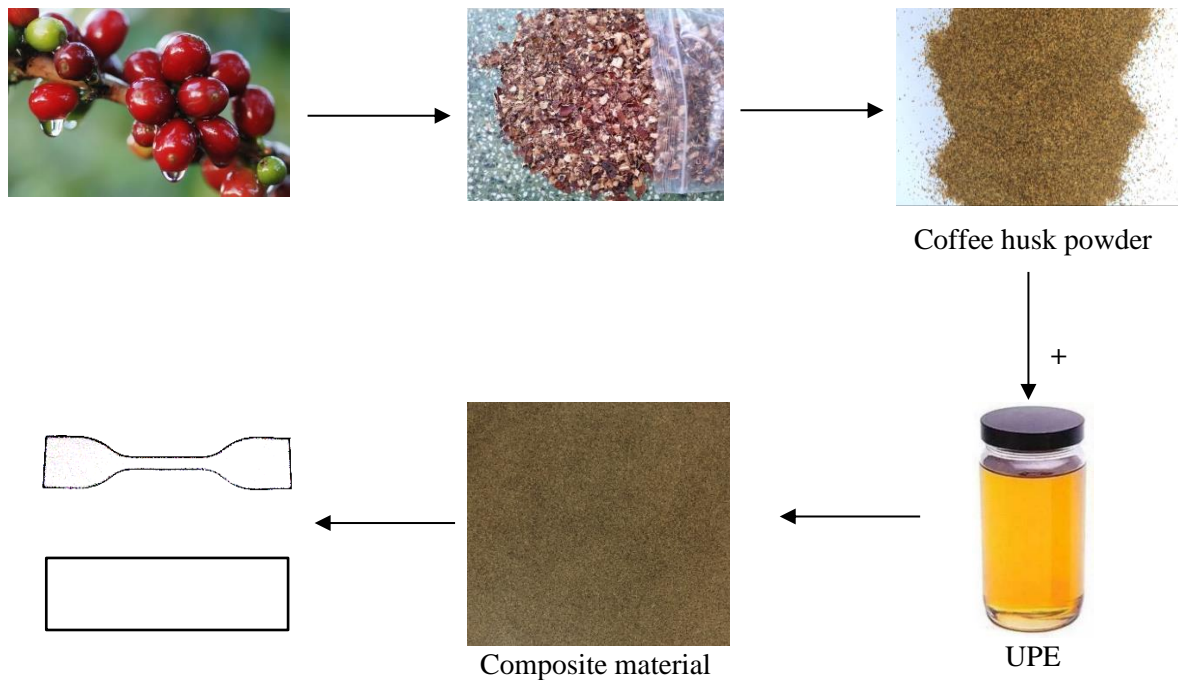
Composites with the bulk density of 1.35 g/cm^3 of the UPE resin and CHs were prepared using the process as illustrated in Scheme 1 at room temperature. The UPE resin, MEKP (0.5 % wt of UPE), and CHs were mixed in the specific ratios depending on the research design by an overhead stirrer (IKA R20, Germany) in about 15 minutes. Then, each composition of composite plates with a size of 17x17x4 mm was fabricated by a hot pressing machine (Yasuda, Japan). The details of the fabrication are as follows: the mixed sample was spread evenly on the mold surface. The mixture is spread evenly on the mold surface. In the first stage, the pressure was increased to 10 kg/cm^2 and held for 3 minutes. Release full pressure to remove air bubbles. Then, the pressure was increased to 20 kg/cm^2 and kept for 30 minutes to polymerize all resin. In the second stage, the temperature of mold cheeks was increased to 100 °C in about 2 hours for post-curing. In the final stage, the samples were de-molded and stabilized

for about 2 days at room temperature before using for further investigation. The feeding of raw materials in this work is summarized in Table 1.

The obtained composite materials based on CH1 and CH2 were tested flexural and tensile properties by methods according to ASTM D790 and ASTM D638, respectively.

Table 1. *The feeding of raw materials of composite materials*

Reinforcement Content (% wt)	Coffee Husks (g)	UPE resin (g)	MEKP (g)
45	70.2	85.8	4.29
50	78.0	78.0	3.90
55	85.8	70.2	3.51
60	93.6	62.4	3.12
65	101.4	54.6	2.73
70	109.2	46.8	2.34



Scheme 1. *Illustrative scheme of the fabrication of composite materials based on CHs and UPE resin.*

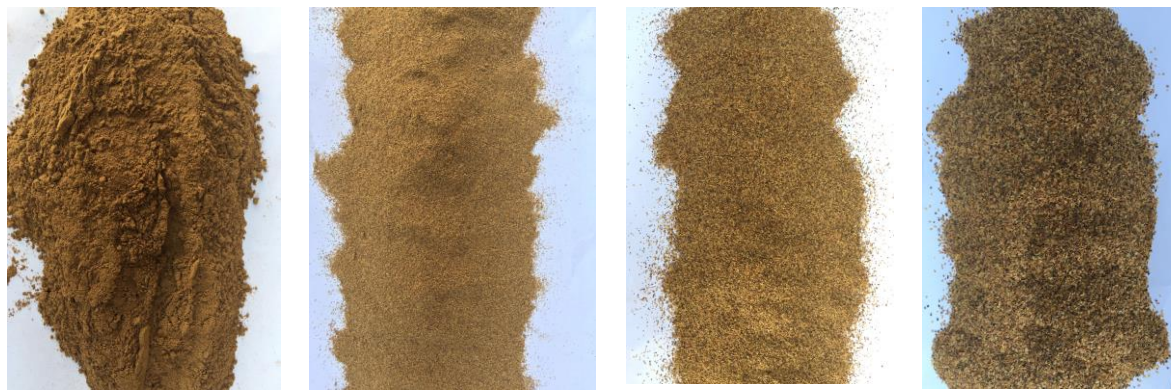
3. Results and Discussion

3.1. Pre-processed coffee husk (CH)

The 16.5 kg of grinded CH was graded using a Controlab vibrator sieve with sieve sizes of 0.63, 0.315, and 0.15 mm. The mass and bulk density of the classification results are presented in Table 2. The morphology of CHs was shown in Figure 1. The results show that the size of CHs is quite diverse. CH from Elite Vietnam Coffee Joint Stock Company is processed by the dry method. Therefore, there will be 2 layers in the coffee skin: outer and silver skin. A force applied by the mill on two different hardness shells will create irregular shell sizes. Table 1 also shows a decrease in the size of CHs leading to increasing in bulk density. This may be explained by the closer pack of the smaller CHs particles (like spherical particles). We chose CHs with particle sizes of $0.150 < d < 0.315$ (CH1) and $0.315 < d < 0.630$ mm (CH2) for further investigation because the size in these ranges was precisely controlled at the upper and lower bounds.

Table 2. *The pre-processed coffee husks*

Sizes (mm)	Mass (kg)	Bulk Th, g/mL
d > 0,630	2.51	0.43 ± 0.03
0.315 < d < 0,630	5.24	0.50 ± 0.05
0.150 < d < 0.315	2.72	0.55 ± 0.06
d < 0.150	5.55	0.62 ± 0.08
Loss	0.48	-
Total	16.5	



(a)

(b)

(c)

(d)

Figure 1. *The morphology of CHs with the size of (a) $d < 0.150$ mm; (b) $0.150 < d < 0.315$ mm; (c) $0.315 < d < 0.630$ mm and (d) $d > 0.63$ mm*

3.2. The curing reaction of UPE resin

3.2.1. The gel time

The gel time of UPE resin was confirmed by ASTM D2471. The results were shown in Table 3. As clearly seen, the gel time decreased gradually with the increase of MEKP content. Increasing the MEKP promoter content leads to an increase in the number of free radicals, creating more active sites. Each of these active centers develops into a polymer chain. This leads to an increase in the polymerization reaction rate and a decrease in gel time. Based on this result, we decided the MEKP content was 0.5% wt with gel time of about 32 ± 2 minutes for further investigation and fabrication of composite materials by hot pressing method.

Table 3. *The gel time of UPE according to ASTM D2471*

MEKP (% wt)	Gel time (min.)
1	17 ± 1
0.75	23 ± 2
0.5	32 ± 2
0.25	96 ± 3

3.2.2. The curing reaction

The mixture of UPE resin and 0.5 wt% of MEKP was tested isothermal DSC at 30 °C for 90 minutes. Then, the heating rate of 5 °C/min to 150 °C was used to evaluate the curing reaction. The DSC curves are shown in Figure 2(a, b).

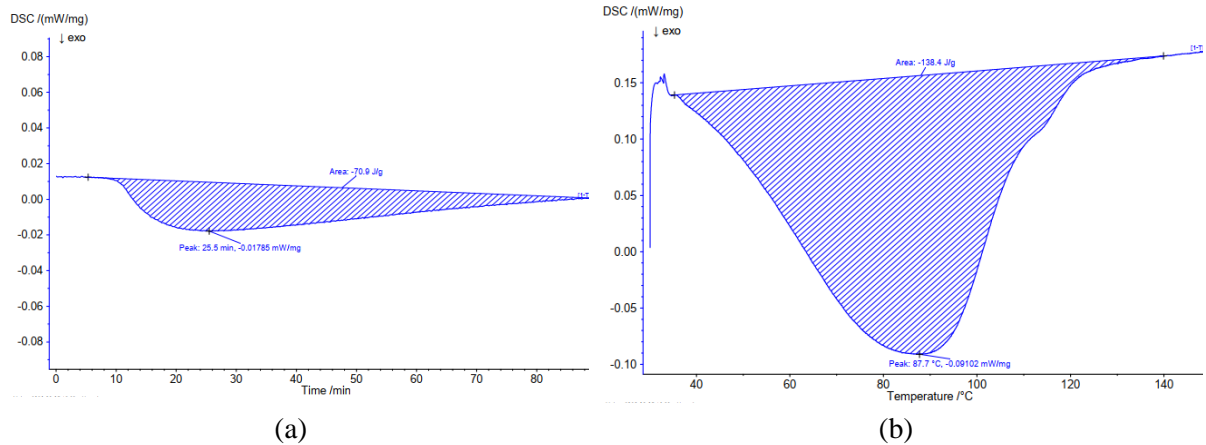


Figure 2. The isothermal DSC (a) and DSC with the heating rate of 5 °C/min of UPE resin contains 0.5 %wt (b).

Figure 2(a) shows the gel time is 25.5 minutes (t_1) and the heat of reaction is -70.9 J/g (ΔH_1). With $t_0 = 8$ min, we defined the gel time in DSC as 33.5 minutes. This result is strongly similar to the ASTM D2471 method. Figure 2(b) shows the polymerization reaction continued to occur as the temperature increased with the exothermal peak at 87.7 °C and the heat of the reaction is -138.4 J/g. This result shows that the polymerization of UPE does not take place completely at 30 °C. The total reaction heat of UPE polymerization is $\Delta H = \Delta H_1 + \Delta H_2 = -209.3$ J/g, in which the curing reaction at 30 °C is only 33.87 %. Therefore, the processing of composite materials based on UPE must be post-cured at a high temperature for the curing reaction to occur completely. Then the mechanical properties of the material are the best.

3.3 FTIR Measurement

The FTIR spectra of the UPE sample before and after polymerization are shown in Figure 3. In the spectrum of uncured UPE resin, the C–H stretching vibration peak of $-\text{CH}_3$ and $-\text{CH}_2-$ was shown at about 2955 and 2890 cm^{-1} , the ester C=O stretching peak was shown at 1742 cm^{-1} , the C=C stretching peak was shown at 1652 cm^{-1} , the C-O-C vibration peak was shown at 1266 cm^{-1} , the C-O stretching peak (for ancol or ester group) was shown at 1124 cm^{-1} , the C-H stretching vibration peak of $\text{CHR}=\text{CHR}$ was shown at 982 cm^{-1} and the C=C peak in vinyl group for styrene monomer was shown at 912 cm^{-1} . After polymerization, the spectrum of cured UPE resin showed an absence of the peak at 912, 982, and 1652 cm^{-1} , indicating that the C=C was transformed completely into C-C. This result indicates that the curing of UPE resin by MEKP initiator has been successfully performed [17].

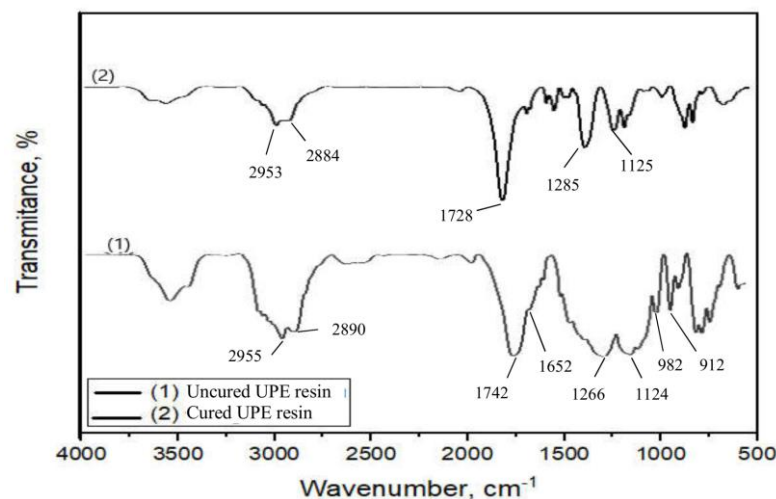


Figure 3. FTIR spectra of uncured (1) and cured UPE (2) resin.

3.4 Mechanical properties

The photograph of composite materials based on 50 %wt CH1 and CH2 are described in Figure 4(a), (b), respectively. The obtained composite materials have a smooth surface, uniform color, and no

warping. It can be explained by the UPE resin that is enough to cover the entire CH in the sample. In addition, it also shows that the in-mold hot pressing technique is suitable for the fabrication composite materials based on UPE and CH powder. Then, composite panels are cut to samples according to ASTM D638 and D790 for mechanical properties assessment.



Figure 4. The photographic images of composite materials based on 50 %wt of CH1 (a), and CH2 (b).

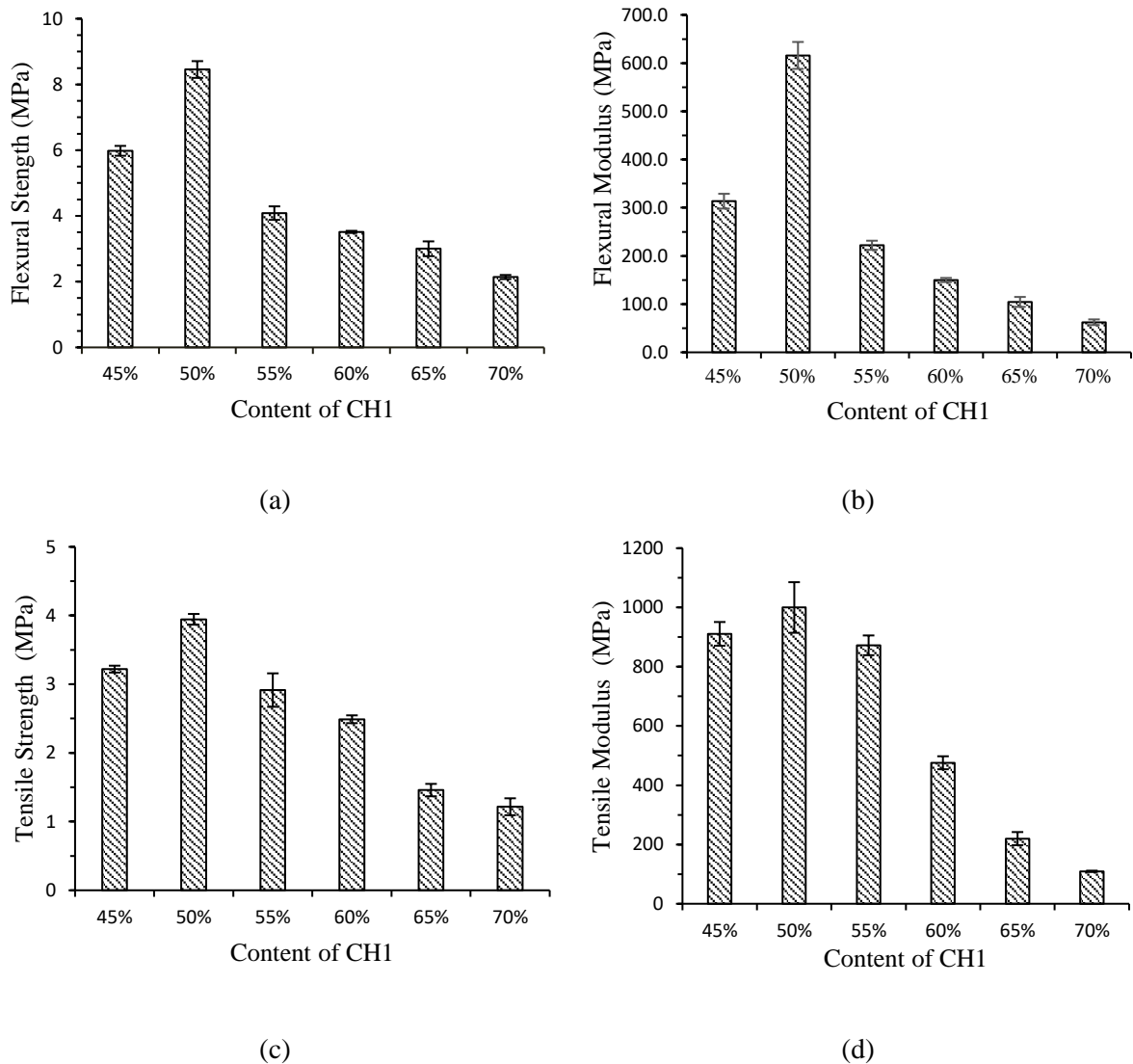


Figure 5. Mechanical properties of composite materials based on CH1: flexural strength (a), flexural modulus (b), tensile strength (c), and tensile modulus (d).

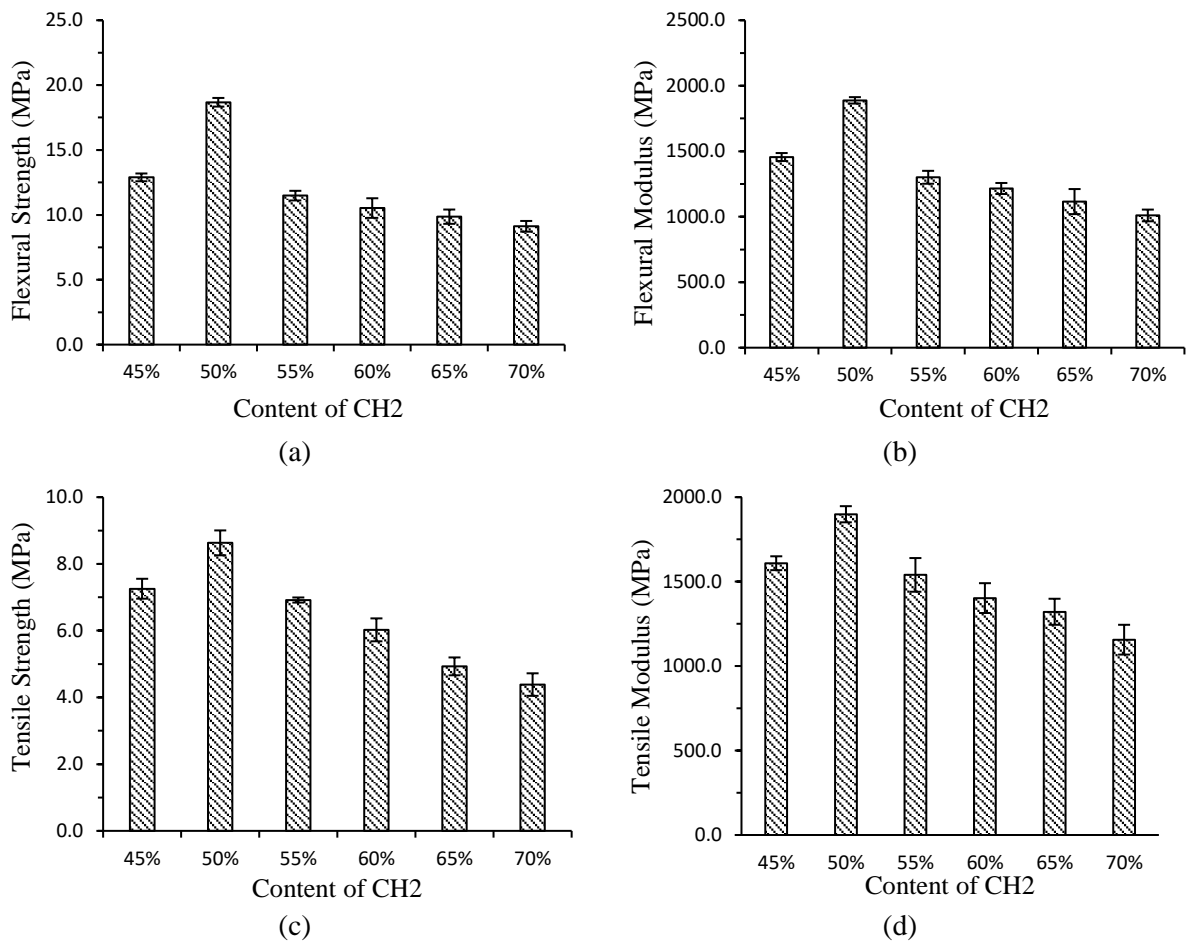


Figure 6. Mechanical properties of composite materials based on CH2: flexural strength (a), flexural modulus (b), tensile strength (c), and tensile modulus (d).

Table 4. Mechanical parameters of composite materials based on 50% of CHs and UPE resin

Mechanical parameters	CH1	CH2
Flexural Strength (MPa)	8.5 ± 0.2	18.7 ± 0.3
Flexural Modulus (MPa)	616.0 ± 24.7	1888.5 ± 24.5
Tensile Strength (MPa)	3.9 ± 0.1	8.6 ± 0.4
Tensile Modulus (MPa)	999.8 ± 85.3	1899.0 ± 47.8

The CHs contents in the range of from 45% to 70% were used to investigate the effect of the addition CHs powder on the mechanical properties of the obtained composite material. The parameters recorded and evaluated include flexural strength, flexural modulus, tensile strength, and tensile modulus. The results as illustrated in Figure 5 and Figure 6 for composites based on CH1 and CH2, respectively. In general, the mechanical properties increased with CHs content from 45% to 50% but rapidly decreased with a further introducing from 55 to 70%. In the composite materials, reinforced components function as a transporter of load and anti-stress concentration throughout the material, so that low CHs introducing leading to low mechanical parameters due to insufficient carrier content [18]. However, when the reinforcement content is too large, the amount of resin is not enough to wet the CHs component and combine the discrete parts into a continuous phase. This can lead to agglomeration of CHs within the material and prevented load transfer. The increase in flexural and tensile modulus with CHs was

used as reinforcement is in agreement with other reports [15] – [19]. The suitable CHs content for composite materials based on UPE resin is 50 wt%.

In the comparison of the mechanical parameters between composite samples containing 50% CH1 (smaller size) and 50% CH2 (larger size), all these parameters have superior values for CH2 sample. As demonstrated in Table 4, the based-CH1 sample has the values of flexural strength, flexural modulus, tensile strength, and tensile modulus at 8.5, 616.0, 3.9, and 999.8 MPa, respectively. Meanwhile, these values for the CH2-based sample are 18.7, 1888.5, 8.6, and 1899.0 MPa. As seen, the mechanical parameters of the CH2 sample were two to three times higher than that of the CH1 sample. This can be explained by the easier agglomeration of the smaller grain reinforcement. In general, grain-reinforced composites are prone to phase separation and uneven dispersion, so the stress distribution will be poor at the interface between the matrix and the reinforcement, this discontinuity creates a weak structure of the material [21]. Further research to improve the mechanical properties of composite materials based on UPE resin and CHs is being conducted.

4. Conclusions

In this work, CHs have been used as reinforcing fillers for composite materials based on UPE resin which was initiated by MEKP. Sheet composite materials are fabricated in molds by the hot pressing method. The suitable MEKP content for the curing reaction of UPE resin is 0.5 wt% with a corresponding gel time of 32 ± 2 minutes. The DSC revealed the curing reaction needs to be post-cured at a temperature higher than 87.7 °C because at room temperature the reaction occurs only 33.87%. The chemical structure of UPE resins was confirmed by FTIR and suggests that the UPE resin is fully polymerized. The mechanical parameters such as flexural strength, flexural modulus, tensile strength, and tensile modulus of the CH2 ($0.315 < d < 0.630$ mm) sample were two to three times higher than that of the CH1 ($0.150 < d < 0.315$ mm) sample. This work has opened a new potential in the reuse of CHs in line with the goals of green technology and sustainable development. However, due to the specificity of granular fillers, the mechanical properties in this work are not very high. Further research is ongoing to improve the mechanical properties of composite materials based on UPE resin and CHs.

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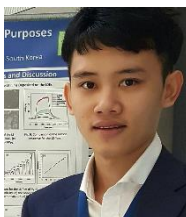
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