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Milling Time Effects on the Thermal Degradation, Density, and Porosity of Coconut Shell-Reinforced Epoxy Biocomposites

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Polymer biocomposites are sustainable and environmentally friendly materials that can be applied to the building, furniture, aerospace, and automotive industries. In this study, biocomposites made of coconut shell-reinforced epoxy resin were prepared and characterised. Initially, the coconut shells were 200 mesh. Then, they were milled by using a ball mill for 10, 20, 30, and 40 h. The biocomposites were manufactured by using a compression method while keeping a constant ratio of filler and matrix at 85 vol.%: 15 vol.%. The effects of ball milling duration on the thermal degradation and physical properties of biocomposites were examined. The thermal degradation of coconut shell biocomposite occurred at 250 – 400 °C. Its thermal degradation temperature increased with the increasing milling times. The density of the coconut shell biocomposite was 1.087 g/cm^3 for 0 h (without milling the fillers). Its density increased to 1.248 g/cm^3 for 40 h of milling duration. Meanwhile, the porosity of coconut shell biocomposite decreased from 17.5% (0 h milling duration) to 12.1% (40 h milling duration). It was found that there was a correlation between thermal degradation and physical properties (density and porosity). This study revealed that the thermal degradation and physical properties of the biocomposites can be enhanced by decreasing the size of the fillers.

Keywords: ball-mill; biocomposite; coconut shell; density; porosity; thermal degradation

I. INTRODUCTION

There are a lot of composite applications such as for building materials, furniture, aerospace, and automotive industries (Motavalli *et al.*, 2010; Ismail *et al.*, 2020; Thomason & Rudeiros-Fernández, 2021). To be applicable in such areas, the composites must perform remarkable durability, high strength-to-weight ratios, stability in various circumstances, low thermal conductivity, and outstanding fatigue characteristics (Motavalli *et al.*, 2010). Many composites are fabricated using synthetic materials, such as fibreglass, carbon fibre, aramid fibre, and polyethylene fibre. These synthetic fibres provide high performance but have detrimental effects on the environment and health (Chawla, 2012). Thus, the natural-based composite is one of the solutions for providing sustainable and eco-friendly composite materials (Mohanty *et al.*, 2018).

Lately, the interest in using natural fibres as a filler in composite fabrication has increased. Researchers are trying to utilise agro-industrial residues in the development of biocomposites (Mohanty *et al.*, 2018). Natural fibres offer many advantages in terms of a sustainable and healthy environment. They are abundant, low-density, unpolluting, renewable, and low-cost (Ismail *et al.*, 2020; Jumaidin *et al.*, 2017; Mawardi *et al.*, 2022). Many studies on biocomposites have been conducted. For instance, natural fibre-based composites have been derived from rice straw, cogon grass, seaweed, and coconut (Jumaidin *et al.*, 2020; Li *et al.*, 2010; Motavalli *et al.*, 2010; Tawasil *et al.*, 2021).

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The results show that natural fibres are promising for biocomposites in the future. Nonetheless, it is quite challenging to produce a biocomposite having great mechanical properties (Mohanty *et al.*, 2018) and high thermal stability (Jones *et al.*, 2018; Nurazzi *et al.*, 2021).

The use of natural fibre in the composites can change the stability and trigger decomposition when a material is working under certain conditions, including heat. Thus, biocomposites are dealing with problems in degradation caused by exposure to heat (Nurazzi *et al.*, 2021). When the biocomposite is subjected to heat, it will change mass, density, shape, and cracks. As a result, the mechanical and other properties are altered (Ray & Cooney, 2018). Some studies have evaluated the filler contributions to thermal stability (Rojas *et al.*, 2019; Darni *et al.*, 2021; Koffi *et al.*, 2021; Panaitescu *et al.*, 2021). Previous research reported that particle size is essential in composite performance. Not only mechanical performance but also thermal degradation is affected. The research reported that nanoparticles enhance the thermal stability of nanocomposites (Abdullah *et al.*, 2021; Ismail *et al.*, 2022). The nanofiller prevents degradation by becoming a physical network barrier toward oxygen transportation (Ray & Cooney, 2018). Therefore, nanoparticles can be used as fillers for improving the physical, mechanical, and thermal properties of composites (Abdullah *et al.*, 2021; Ismail *et al.*, 2022).

One of the agricultural wastes available in large amounts is coconut shells. In 2019, worldwide coconut production was approximately 61 million tons (Laura W., 2019). Besides being biodegradable and absent of health hazards, coconut shells have a high modulus and excellent lignin (more than 30%) (Ikumapayi *et al.*, 2020; Tawasil *et al.*, 2021). Several studies of the biocomposite from coconut shells have been carried out (Ismail *et al.*, 2020; Ismail *et al.*, 2022). Previous work showed that the biocomposite of nano coconut shell particles filled in the epoxy resin had excellent mechanical and physical properties (Ismail *et al.*, 2020). However, there is no information available in the literature to date about the thermal degradation of the coconut shell epoxy resin biocomposites. Meanwhile, the thermal degradation properties of biocomposites are very important to know so that these materials can be widely used (Jones *et al.*, 2018; Koffi *et al.*, 2021).

This work aimed to investigate the thermal degradation of coconut shell particle-reinforced epoxy resin biocomposite. Its density and porosity were also examined. The particle size of coconut shells was varied by varying the duration of milling (ball-mill). The effect of milling duration on the performance of the biocomposites was evaluated.

II. MATERIALS AND METHOD

A. Materials

The coconut shell particles (200 mesh) were supplied by Indratma Sahitaguna Company, Indonesia. Commercial epoxy resin was produced by PT Avian, Indonesia.

B. Preparation of Fillers

The size of the fillers (coconut shell particles) was initially 200 mesh. Then they were milled by a planetary ball mill with a ball-to-powder ratio of 10:1 (wt.) at a speed of 350 rpm. The planetary ball mill was manufactured by Fritsch Germany. The milling duration varied from 0, 10, 20, 30, and 40 hours.

C. Preparation of Biocomposites

The biocomposites were fabricated with a compression moulding technique. The ball-milled particles were mixed with epoxy resin for 15 minutes using a mixer. The sample composition was constant at 15 vol.% epoxy resin and 85 vol.% coconut shell particles for each ball-milled particle. The mixture was moulded in the dimension of 150 mm in length, 150 mm in width, and 10 mm in thickness. The moulded biocomposites were subjected to a 9 tons load for 60 min. A photo (taken by a regular camera) of a biocomposite sample prepared from this work is shown in Figure 1.

Figure 1. The photo of the coconut shell biocomposite sample taken by a regular camera

D. Characterisation

Thermal degradation was examined by measuring the mass changes as a function of temperature. The measurement was performed by using a thermogravimetric analyser (TGA) made in Shimadzu, type DTG–60 (Japan). The examination was conducted in an N_2 atmosphere with a heating rate of 20 ˚C/min. The gas flow was 20 ml/min from 25-600 ˚C. The microstructure of biocomposites was examined by using Scanning Electron Microscope (JOEL JSM 6510 LA, Japan).

The density (ρ) of the biocomposites was calculated by using Equation (1).

$$Density = \frac{m}{V} \quad (1)$$

Where m and V are the mass and volume of the sample, respectively. The porosity of the biocomposite was calculated by using Equation (2).

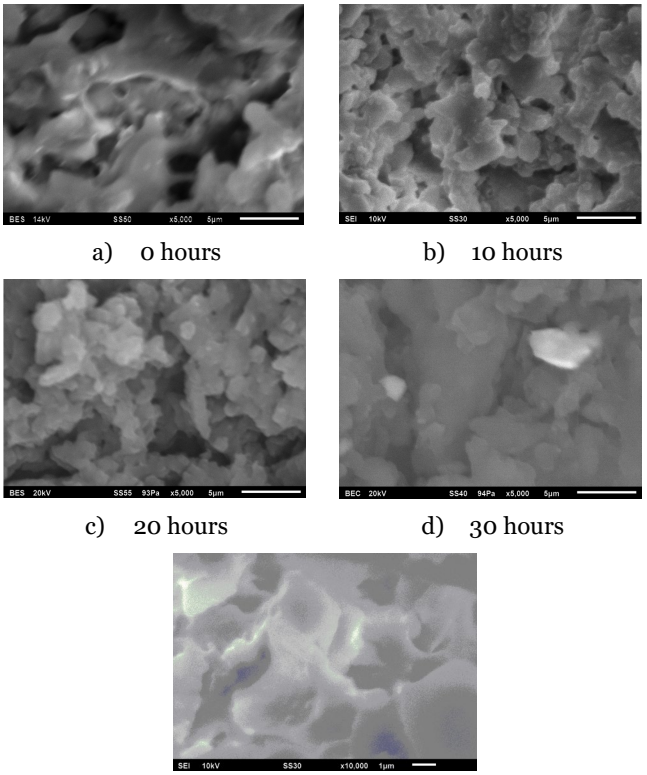
$$Porosity = \frac{m_w - m_d}{V_t} x \frac{1}{\rho_{water}} x100\% \quad (2)$$

Where V_t is the sample volume; m_d is the dry sample mass; m_w is the wet sample mass after being immersed in water for 24 hours; and ρ_{water} is the water density.

III. RESULT AND DISCUSSION

A. Microstructure

The microstructure of coconut shell biocomposites has been evaluated for various milling times of fillers by using the Scanning Electron Microscope (SEM) as shown in Figure 2. There were some porosities and agglomeration observed at the surface of the biocomposite. However, the porosities and size of agglomeration reduced as the fillers (coconut shell particles) were milled. For 30 h and 40 h of milling duration, the porosities and agglomerations in the biocomposite reduced significantly. By improving the milling times, the particle size of fillers is reduced which improves the contact between the fillers and matrix (good blend between fillers and matrix). The surface topography of biocomposite samples becomes smooth, with fewer corrugations. This can improve the properties of biocomposite.



a) 0 hours b) 10 hours

c) 20 hours d) 30 hours

e) 40 hours

Figure 2. The SEM images of the coconut shell biocomposite samples for various milling times

B. Thermal Degradation

Figure 3 and Table 1 display the TGA results of the biocomposites for 0, 10, 20, 30, and 40 hours of milling durations. The biocomposite without milling treatment (0 h milling time), which has 200 mesh of particle size, the decomposition of the biocomposites started at a temperature of 72 °C; the remaining weight of the sample was 95%. At 137 °C, the sample weight was 90%. The decomposition at this first stage was related to the volatile compounds contained in the biocomposite sample (Rojas *et al.*, 2021).

The second stage of degradation occurred at 250 – 400 °C. The sample weight at this stage decreased significantly which was due to the degradation of the natural fibre such as cellulose, hemicellulose, and lignin (Jones *et al.*, 2018; Koffi *et al.*, 2021). The third stage occurred at about 400 °C related to the depolymerisation of biocomposite (Ismail *et al.*, 2022). The weight of the sample was 20% weight left at the temperature of 442 °C.

The decomposition temperature of fibreglass composite (synthetic material) was 350 to 550 °C and its residue was about 50% (weight) at 800 °C (Zhang *et al.*, 2021). The degradation temperature of biocomposite from this study occurred at the temperatures of 250 – 400 °C, which is lower than that of composite from a synthetic material (fibreglass composite). However, biocomposite from natural material is more environmentally friendly, where its residue is much smaller than that from synthetic material composites.

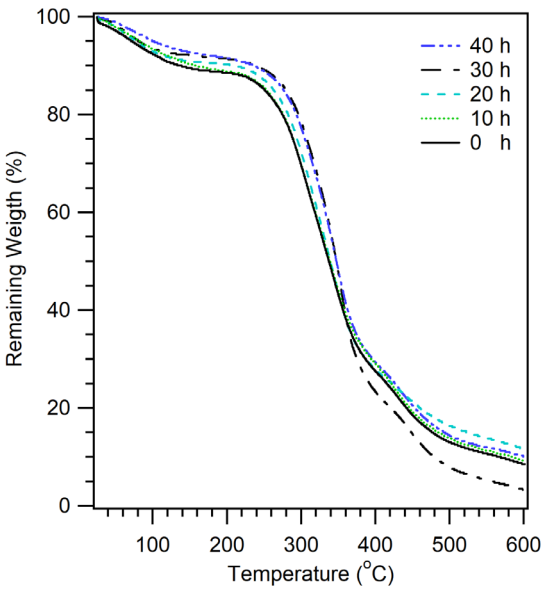


Figure 3. The TGA of biocomposites for various milling durations

Table 1. The TGA results of biocomposites for the various durations of milling (0, 10, 20, 30, and 40 hours)

Remaining Weight of Sample (%)	**Decomposition Temperature (°C)**				
	0	**10**	**20**	**30**	**40**
	(hours)				
95	72	78	78	82	100
90	137	155	203	237	240
80	274	276	282	293	297
70	299	302	305	315	318
50	337	338	340	347	348
20	442	445	459	453	420

As the coconut shell particles were milled, the decomposition of the biocomposite changed as shown in Figure 4. For example, at 100 °C, the remaining weight of the sample was 92.5% for 0 hours of milling time. For 40 h of milling duration, the remaining weight of the biocomposite sample was 95.0%. This behaviour is similar to other temperatures. At 250 °C, before milling the remaining weight of the sample was 85.0%. However, the remaining weight was 89.0% for 40 hours of milling. The sample became less decomposed as the fillers were milled. This trend occurred significantly at 300 °C where the remaining weight was 69.0% before milling while it was 79.0% after 40 hours of milling. This behaviour was related to the particle size of fillers, and the reduced size of fillers caused by the milling process. The total area contact between fillers and matrix increased as the particle size of fillers was reduced. Coconut shell particles (fillers) mixed well with epoxy resin. So, the biocomposite became less corrugated and had fewer porosities as observed by SEM shown in Figure 2. As a result, the reduction of the size of the fillers resulted in the thermal stability improvement of the biocomposite. This kind of behaviour has been reported in previous studies (Ismail *et al.*, 2022; Ray & Cooney, 2018; Rigana *et al.*, 2021).

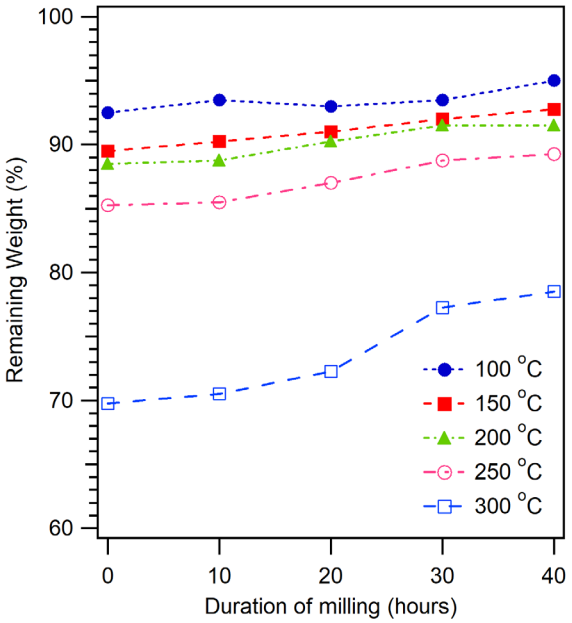


Figure 4. The remaining sample weight at various durations of milling

Figure 5 presents the relationship between the decomposition temperature (DT) and milling duration at the different remaining weights of samples. For 95% of the remaining weight of the sample, the temperature of decomposition was around 72 °C for 0 hour milling time (without the milling process). As the duration of milling was increased to 40 hours, the temperature of decomposition increased to 100 °C. For 90% of the remaining weight, the temperature of decomposition increased from 137 °C to 240 °C after the milling for 40 hours as displayed in Figure 5 (b). This trend is the same for other remaining weights as displayed in Figures 5 (c) and (d). In general, the temperature of decomposition increased significantly as the fillers (coconut shell particles) were milled. This behaviour was due to the reduced size of fillers as the result of milling. As discussed previously, the small size of the fillers increased the surface areas between the matrix and fillers. Thus, the bonding between the fillers and matrix improved; the porosities and corrugations decreased as observed by SEM displayed in Figure 2.

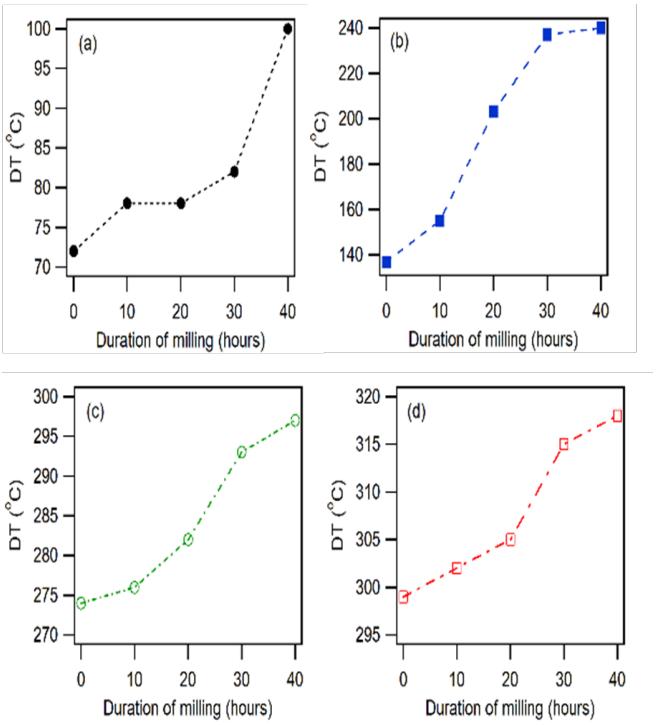


Figure 5. The decomposition temperature (DT) for (a) 95% remaining weight, (b) 90% remaining weight, (c) 80% remaining weight, and (d) 70% remaining weight with various milling times

C. Physical Properties

The density of biocomposites was quantified. The measurement results are shown in Figure 6. In general, the density of the composites increased gradually by increasing milling time durations. For the milling time of 0 h, the biocomposites density was 1.087 g/cm^3. The density increased to 1.122 g/cm^3 at 20 h milling duration. The composites gained a higher density of 1.202 g/cm^3 at 30 h milling time. For the milling time duration, 30 h and 40 h, the density increased to 1.228 g/cm^3 and 1.248 g/cm^3, respectively. Increasing the milling time duration provided particle size reduction of coconut shells. Figure 2 (SEM images) shows that the biocomposite sample becomes fewer porosities and fewer corrugations as the milling time was increased (particle size of fillers reduced). As a result, the biocomposite sample becomes dense and its density increases.

In line with the density increase, the porosity of the biocomposites decreased significantly as the duration of milling was increased (see Figure 7). In this study, the highest porosity was 17.5% which occurred at a specimen

without ball milling treatment. The lowest porosity was 12.1%, obtained at 40 h of milling duration. The porosity dropped to 16.4% after being subjected to a ball-milling process for 10 h. For a 20 h milling duration, the sample reached a 2.3% of porosity reduction from 16.4% to 14.1%. A slight decline occurred from 20 h until 40 h milling duration where the porosities reduced from 12.6% to 12.1%. Milling duration influenced the porosity of biocomposites where the porosities of biocomposite decreased significantly as the duration of milling was increased, see Figure 2 (SEM images).

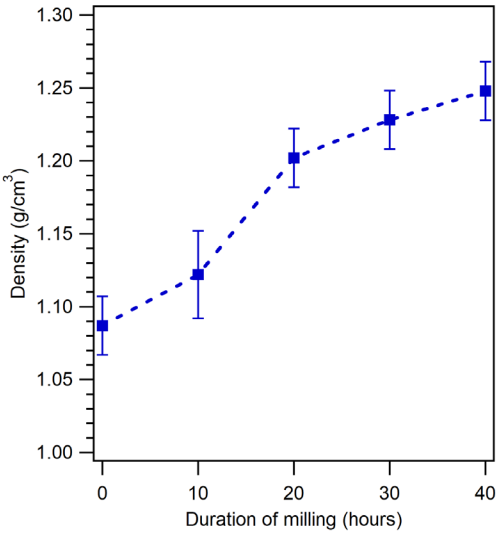


Figure 6. The density of biocomposites for various durations of milling

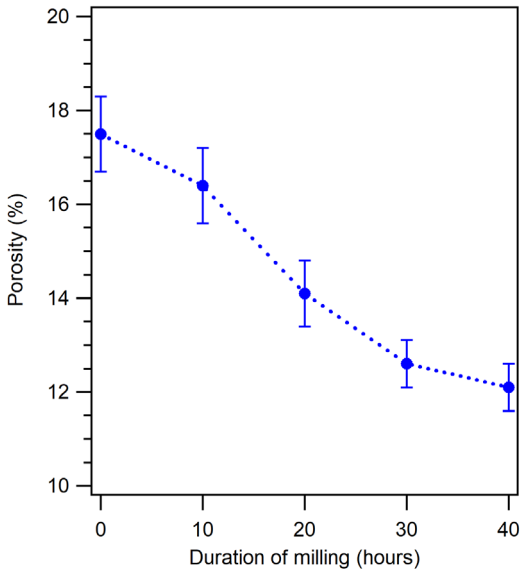


Figure 7. The porosity of biocomposite for various durations of milling

D. Correlation between Thermal Degradation and Physical Properties

The increase in the decomposition temperature of the biocomposites shown previously can be attributed to their physical properties. Figure 8 displays the correlation between the remaining weight of the sample and its density. As the density of biocomposite increased the percentage of remaining weight increased. This shows that the thermal stability of the biocomposite increased as its density increased. It has been discussed previously that decreasing the particle size causes an increase in the biocomposite density. The higher density causes a better bond between the filler and matrix.

High density confirms low porosity. The low porosity indicates the low presence of voids in the sample (Ismail *et al.*, 2020). Figure 9 shows the tendency of sample weight to decrease with the increase of porosity. At 300 °C, the sample weight decreased from about 79% to 70% as the porosity increased from 12.1% to 17.5%. This means the thermal stability of the biocomposite increased as the porosity decreased, resulting in decreasing in the rate of thermal degradation (Karami *et al.*, 2021).

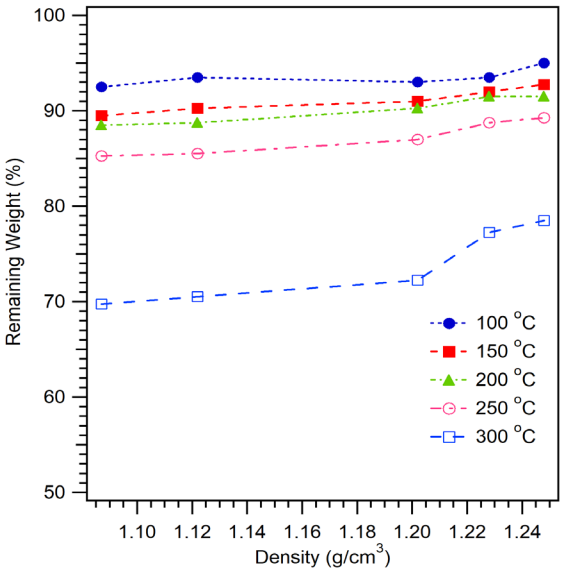


Figure 8. The correlation between sample degradation and the density of biocomposite

The thermal stability of the biocomposites shows a close relationship with the density, porosity, and milling time duration. The milling process has reduced the particle size. Consequently, the density increased, and the porosity

decreased (Ismail *et al.*, 2020). As a consequence, the decomposition temperature of the biocomposites increased which means the stability of the sample was getting better. Thus, the particle size has a notable effect on decomposition temperature (Wang *et al.*, 2014).

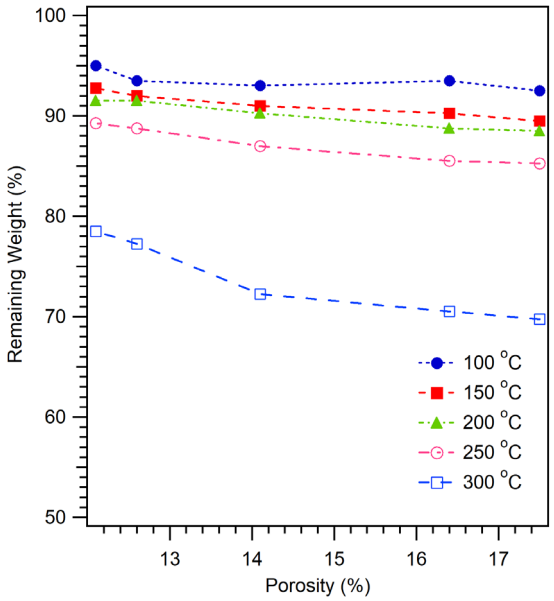


Figure 9. The correlation between sample degradation and the porosity of biocomposite

IV. CONCLUSION

In this study, biocomposites derived from coconut shell particles and epoxy resin as a matrix have been fabricated and examined. The thermal degradation of coconut shell biocomposites significantly occurred at temperatures above 250 °C. The biocomposites experienced a significant increase in degradation temperature as the size of fillers was reduced by increasing the length of milling time. The milling treatment successfully improved the density and porosity of the biocomposite. The biocomposite density increased from 1.087 g/cm^3 at 0 h to 1.248 g/cm^3 at 40 h; while its porosity reduced from 17.5% to 12.1%. The results confirmed that there is a correlation between thermal degradation and physical properties. Low porosity (or high density) biocomposite has good thermal degradation properties. The enhancement of these properties was associated with the improvement of the bonding between the matrix and fillers. Overall, the milling durations significantly improved the thermal degradation properties without reducing the physical performance of biocomposites. This study confirmed that reducing the size of the fillers enhanced the thermal degradation and physical properties of the coconut shell biocomposites.

V. ACKNOWLEDGEMENT

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