A Preliminary Investigation on Processing, Mechanical and Thermal Properties of Polyethylene/Kenaf Biocomposites with Dolomite Added as Secondary Filler

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In this preliminary investigation, dolomite was added to the low-density polyethylene/kenaf core fiber (LDPE/KCF) biocomposites by using an internal mixer at 150°C, followed by compression molding at the same temperature. The dolomite contents were varied from 0 to 18 wt.%. The processing and stabilization torques, the stock and stabilization temperatures, the tensile and impact strengths, and the thermal decomposition properties of the prepared biocomposites have been characterized and analyzed. The processing recorder results of the LDPE/KCF biocomposites indicated that the stabilization torques and stabilization temperatures have increased with the addition of dolomite. Mechanical testing results showed that the presence of dolomite has increased the tensile stress, tensile modulus, and impact strength of the LDPE/KCF biocomposites. Thermogravimetric analysis results displayed that the thermal decomposition properties of the biocomposites have also increased with the increase of the dolomite content. This research led to the conclusion that the addition of dolomite in lower amounts (<20 wt.%) could act as a secondary filler for improving the processing, mechanical and thermal properties of LDPE/KCF biocomposites without surface treatments of the natural fiber.

1. Introduction

The use of natural fibers as an alternative primary filler for polymer biocomposites has become attractive to researchers and industries. Natural fibers can replace synthetic fibers, such as glass, aramid, and carbon, since they have low cost and low density, nonabrasive, and renewable and have fairly good mechanical properties (high toughness and high specific strength) [1–4]. Moreover, natural fibers have a low manufacturing energy demand compared to commonly used synthetic fibers as well [5]. This indirectly would produce polymer composites with a very low production cost. Besides that, like biopolymers, natural fibers also do not produce any byproducts or residues that might be harmful to humans and the environment during manufacturing or disposing of the biocomposites [6–8].

On the other hand, although natural fibers can reduce the production cost of the biocomposite products, they are also can lessen the performance of prepared polymer composites [9]. This is due to the poor compatibility between natural fibers and synthetic polymers, particularly polyethylene [10]. Therefore, surface treatments of the natural fibers by using chemicals have been proposed to overcome this problem [11, 12]. However, there are some limitations of using chemicals, since they are expensive, and require more energy and time to carry out, and so forth [13]. In this preliminary investigation,
a secondary filler such as a mineral has been used to evade the surface treatments of natural fibers. This secondary filler is important for the production of organic-inorganic fillers hybrid polymer composites and it could also assist the primary filler in the reinforcement of the biocomposites as well [14].

The use of a mineral like dolomite as a secondary filler in biocomposite systems is very promising as its abundance in nature, low cost, nontoxic, and environmentally friendly [15]. The high stiffness and thermal stability of this mineral could lead to the improvements in the mechanical and thermal properties of the biocomposites [16, 17], and this would give much better results than the uncontained ones. Besides, the improved polyethylene/natural fiber biocomposites may also be used in the production of diverse products without significantly increasing their weight due to a low content of the mineral is used (<20 wt.%). The main purpose of this preliminary investigation is to determine the effects of dolomite as a secondary filler on the processing, mechanical and thermal properties of polyethylene/kenaf biocomposites.

2. Materials and Method

2.1. Materials. The polymer matrix used is a low-density polyethylene, LDPE (coating grade), purchased from Lotte Chemical Titan Sdn. Bhd., Malaysia. The primary filler of the biocomposites is kenaf core fiber (Hibiscus cannabinus L.), abbreviated as KCF (420 μm), acquired from the National Kenaf and Tobacco Board (NKTB), Malaysia. The secondary filler used is a calcium magnesium carbonate (mineral dolomite, 177 μm) which is procured from Dolomite Kangar Manufacturing Sdn. Bhd., Malaysia. All materials were consumed as attained without further refinement.

2.2. Preparation of LDPE/KCF Biocomposites Containing Dolomite. The biocomposites were prepared through melt mixing by using a Brabender internal mixer equipped with a real-time processing recorder. The mixing was carried out at a temperature of 150 °C, and the rotor speed was fixed at 60 rpm. LDPE (24 g) was added into the Brabender mixing chamber at the beginning for 3 min, followed by KCF (16 g) for 6 min and dolomite for 3 min. Then, the mixing time was continued for another 3 min, where the plateau torque was reached. The duration of the whole process was 15 min. The mixed biocomposites obtained from the internal mixer were converted into a 1 mm sheet via the compression molding technique by using a hydraulic hot press machine [18]. The molding procedures involved preheating at 150°C for 7 min, compression at the same temperature for 2 min, and then water cooling at 20°C [19] for 5 min [20]. The resultant biocomposites were dried in an oven at a temperature of 70°C for at least 24 hours prior to characterizations. The contents of the dolomite were varied from 3 to 18 wt.%. The biocomposite containing only LDPE and KCF has also been prepared for comparison purposes.

2.3. Characterizations. The tensile stress, tensile modulus, and tensile strain properties were ascertained according to the ASTM D638 [21] at room temperature by using an Instron universal testing machine (model 5567) equipped with a 30 kN load cell. The crosshead speed was 5 mm min \(^{-1}\) with a 40 mm gauge length. The biocomposite samples of 1 mm thickness were cut into a dumbbell shape using a type V die cutter. Ten samples from each composition were tested to determine the mean values, and the standard deviations were reported to show the error range.

The impact strength of the biocomposites was measured according to the ASTM D4812 by using a CEAST impact testing machine (model 9050) via the Izod impact test method. The samples for the impact test were cut into a rectangular bar with a nominal size of 60 × 13 × 1.0 mm\(^3\) by using a scroll saw machine, and then they were notched up to 1 mm depth. The samples were supported by a vertical cantilever beam and they were broken by a single swing of the 0.5 joule pendulum. The average data from ten samples of each composition were calculated and the corresponding standard deviations were also reported.

Thermogravimetric analysis (TGA) was performed by using a TA Instruments TGA (model Q500) to investigate the initial and maximum decomposition temperatures of the prepared biocomposites. The analysis was conducted with a heating rate of 10°C min \(^{-1}\) and the temperature ranged from 30 to 800°C. A sample of 10 to 11 mg of the prepared biocomposite was heated in the sample pan in an atmosphere of nitrogen gas at a flow rate of 50 mL min \(^{-1}\).

3. Results and Discussion

3.1. Processing Characteristics. Figure 1 demonstrates the processing torque-time curves of the LDPE/KCF biocomposites with different contents of dolomite. Processing torque is one of the processing behaviors which was recorded during the processing of the samples by using a Brabender processing recorder. Furthermore, processing torque amongst samples at equal temperature is suggestive of melt viscosity distinctions [22]. At around the first minute, the sharp increase peaks in the processing torque curves were acquired for all samples during the mixing process. This is due to the increase of resistance exerted on the internal mixer rotors by the unmelted LDPE. As the melting of LDPE took place, the peaks started to decrease with the increase of the mixing time. At around the fourth minute, the processing torques began to rise again to higher peaks immediately after the addition of KCF to all samples. This is due to the fact that the dispersion of the KCF filler in the molten LDPE needed more forces. As the KCF became very well dispersed in the LDPE matrix, the torques significantly started to decrease [20]. For the sample with 0 wt.% dolomite, the processing torque has decreased and remained almost unchanged at a particular level until the end of the total mixing time as the KCF dispersion completed. An upward peak was recorded at around the ninth minute, caused by the dolomite that was added to the mixer. For the samples from 3 to 9 wt.% dolomite, the slight increases of the processing torques at around the tenth minute reflected that there was a small amount of friction from the dolomite acting on the molten
biocomposites. Nevertheless, the significant increase in the processing torques of the samples from 12 to 18 wt.% dolomite implied that there was a large amount from the friction of dolomite acting on the molten biocomposites. The torques gradually started to decrease as the dispersion of the dolomite was accomplished, and this is because of the decrease in the melt viscosity of the LDPE/KCF biocomposites. After the twelfth minute, the torques of all samples remained stable until the end of melt processing.

Figure 2 shows the effects of dolomite content on the stabilization torque of the LDPE/KCF biocomposites. The torque values at the end time of the mixing process, at exactly the fifteenth minute are regarded as the stabilization torque values. In all cases, the different stabilization torque values were obtained due to the fact that the addition of dolomite into the mixing chamber are distinct from each other. The stabilization torques have slightly increased for the samples with the addition of dolomite from 3 to 9 wt.%. Nonetheless, for the samples from 12 to 18 wt.% dolomite, their stabilization torques continuously increased as the dolomite content in the biocomposites increased. The significant increases are caused by the weight proportion between the LDPE and the KCF that has been fixed to 60/40 when the dolomite was added. This resulted in the increase of the stabilization torque values, since the mobility of the LDPE molecular chains was reduced [20]. The increase in the viscosity of the molten biocomposite samples has also improved their stabilization torques, which was caused by the addition of dolomite. Moreover, it can be seen that the highest stabilization torque value was observed for the sample with 18 wt.% dolomite, followed by samples with 15 and 12 wt.% dolomite. Hence, the increases of the stabilization torque values are correlated with the dolomite content in the biocomposite systems. Furthermore, the biocomposites with more dolomite content necessitated higher torques for stabilization than the biocomposites with less dolomite or without dolomite at a similar LDPE/KCF loading.

Stock temperature-time curves of LDPE/KCF biocomposites with different contents of dolomite are indicated in Figure 3. Stock temperature is defined as the temperature inside the Brabender mixing chamber which is usually the same as the processing temperature if there is no extensive shearing occurs [23]. Based on the results, most of the samples showed different peaks but an almost similar pattern. The curves demonstrated that during the melting of LDPE, a huge drop in temperatures has been observed. This is because when the LDPE melted inside the mixing chamber, an endothermic process has occurred. The temperatures started to increase again when the LDPE was fully melted. The addition of the KCF filler was done at the third minute and the stock temperatures started to decrease moderately. The modest decreases in the stock temperatures are also caused by a moderate endothermic process. At around the fifth minute, the stock temperatures started to increase more than the processing temperature (150°C). This is due to the increased friction between the molten LDPE/KCF biocomposite sample and internal mixer rotors, which led to an exothermic process. The biocomposite sample with 0 wt.% dolomite showed no change in its stock temperature until the end of the mixing. At around the ninth minute, the dolomite was added to the biocomposite samples from 3 to 18 wt.%, and most of them showed a slight drop in stock temperatures after the addition of dolomite due to the little heat absorption. The stock temperatures started to rise again at around the eleventh minute, implying that an exothermic process took place as well. During the twelfth minute and above, most of the stock temperatures remained almost constant as the dolomite became well-blended with the biocomposites.
The effects of the dolomite content on the stabilization temperature of the LDPE/KCF biocomposites are displayed in Figure 4. The stabilization temperature values are attained from the end time of the mixing process, specifically at the fifteenth minute. The different stabilization temperature values were obtained for all samples largely related to the variation of dolomite content in the mixing chamber. For the sample without dolomite (0 wt.%), the stabilization temperature value is lower compared to the samples with dolomite. Nevertheless, the samples with less than 12 wt.% dolomite showed slightly increased stabilization temperatures of the LDPE/KCF biocomposites compared to the samples with more than 9 wt.% dolomite. For the samples with 3, 6, and 9 wt.% dolomite, their stabilization temperatures are only 169.03, 169.93, and 170.6°C, respectively. Meanwhile, the sample with 0 wt.% dolomite is 168.37°C, which indicated insignificant differences between them. Surprisingly, further addition of dolomite has increased the stabilization temperatures of the biocomposites. It seems like the stabilization temperatures of the biocomposites significantly increased as the content of dolomite increased. The significant increases in the stabilization temperatures are due to the increased heat formation after the addition of dolomite. From the stabilization temperature results, when a higher content of mineral dolomite was added to the biocomposites, higher stabilization temperatures were generated.

3.2. Mechanical Properties. Figures 5(a) and 5(b) indicate the tensile stress and tensile modulus of LDPE/KCF biocomposites with different contents of dolomite. It is clearly seen that the tensile stress and tensile modulus of the sample without dolomite are lower than the other samples, which exhibited low stiffness feature. This proved that the compatibility between LDPE and KCF is extremely low, whilst the biocomposite samples with the addition of dolomite from 3 to 9 wt.% showed an insignificant improvement in their tensile stress, with values of 1.50, 1.53, and 1.60 MPa, respectively. Furthermore, a similar trend was also observed for the tensile modulus of the biocomposites with dolomite added, which did not significantly increased as well. Slight increases in the tensile stress and tensile modulus were expected due to the very small addition of dolomite to the LDPE/KCF biocomposites. Fortunately, the tensile stress and tensile modulus drastically increased as the concentration of dolomite increased. It was found that the addition of dolomite from 12 to 18 wt.% to the biocomposites has caused a significant improvement in their tensile stress and tensile modulus as compared with the other samples. Therefore, dolomite in the biocomposite systems could act as a secondary filler, which enhanced their stiffness characteristic. The abrasive nature of the dolomite could have provided the mechanical interlocking which hindered the sliding of the KCF in the LDPE matrix, this affected the mechanical properties of the LDPE/KCF biocomposites. From these results, it can be seen that this secondary filler is only required less than 20 wt.% of the total biocomposites weight in order to improve the tensile stress and tensile modulus properties.

Figures 6(a) and 6(b) show the tensile strain at break and impact strength of the LDPE/KCF biocomposites with different contents of dolomite. From these data, it can be clearly seen that the tensile strain of the biocomposite sample without dolomite is higher than that of the biocomposites containing dolomite. This is due to the ductile behavior of the LDPE/KCF biocomposite, which is higher compared to the other biocomposite samples. After dolomite was added to the biocomposites, their tensile strain decreased due to the decrease in the slippage of the LDPE chains. This is because of the particle size of the dolomite in the biocomposite systems is lesser than that of the particle size of the KCF, which can prevent the slippage of the LDPE chains. Nevertheless, it is clearly perceived that the impact strength result is inversely proportional to the tensile strain result. From this observation, the improvement in the impact strength is due to the ability of the prepared biocomposite samples to absorb the exerted impact energy, especially in the presence of dolomite [16]. Moreover, the addition of dolomite at high content has significantly improved the impact strength of the LDPE/KCF biocomposites, which provided more toughness but less ductility. Therefore, the impact strength of the biocomposite samples has increased in direct proportion to the dolomite content. The increasing trend of this result was shown in both the samples of 15 and 18 wt.% dolomite, with increments of 33 and 50%, respectively. Consequently, the use of dolomite as a secondary filler could also improve the impact strength of LDPE/KCF biocomposites.

3.3. Thermal Characterization. Thermogravimetric analysis (TGA) thermograms of the LDPE/KCF biocomposites with different contents of dolomite are represented in Figure 7. Based on the analysis, it can be observed that there are two stages of weight loss that have occurred. These are associated with the loss of moisture content or water molecules and also their components, whereas Table 1 displays the values of the initial decomposition temperature (at 10% weight loss) and the values of the maximum decomposition temperature of the prepared LDPE/KCF biocomposites. It can be seen that the biocomposite sample without dolomite has low values of the initial and maximum decomposition temperatures in comparison with the dolomite samples. It is known that dolomite could increase the thermal stability of polymer composites [16]. Therefore, in this preliminary
in the biocomposite systems [24]. Hence, it can be deduced that the thermal decomposition temperatures of the overall LDPE/KCF biocomposite samples are also dependent on the thermal stability of their secondary filler, such as dolomite. Therefore, the addition of dolomite is advantageous for improving the thermal decomposition properties of the LDPE/KCF biocomposites as well.

### Table 1: The values of the initial and maximum decomposition temperatures of the LDPE/KCF biocomposites obtained from TGA thermograms.

| Sample | Initial decomposition temperature (°C) | Maximum decomposition temperature (°C) |
|--------|----------------------------------------|----------------------------------------|
| 0%     | 305.45                                 | 467.28                                 |
| 3%     | 306.93                                 | 468.12                                 |
| 6%     | 308.74                                 | 469.96                                 |
| 9%     | 310.14                                 | 470.17                                 |
| 12%    | 311.75                                 | 471.78                                 |
| 15%    | 312.98                                 | 472.14                                 |
| 18%    | 315.20                                 | 472.77                                 |

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**Figure 7:** TGA thermograms of the LDPE/KCF biocomposites with different contents of dolomite.

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**Figure 5:** Effects of dolomite content on (a) tensile stress and (b) tensile modulus of LDPE/KCF biocomposites.

**Figure 6:** Effects of dolomite content on (a) tensile strain and (b) impact strength of LDPE/KCF biocomposites.
4. Conclusions

In this preliminary investigation, the stabilization torques and stabilization temperatures of the LDPE/KCF biocomposites have increased with the addition of dolomite, as indicated by the processing recorder results. The tensile stress, tensile modulus, and impact strength of the biocomposites have increased with the presence of dolomite as shown by the mechanical testing results. The thermal decomposition properties of the biocomposites have also increased with the increase of the dolomite content as displayed in the thermogravimetric analysis results. It can be concluded that the processing, mechanical and thermal properties of the LDPE/KCF biocomposites could be improved with the addition of lower amounts of dolomite (≤ 20 wt.%), which acted as a secondary filler with no surface treatments of the natural fiber required.

Conflict of Interests

The authors have declared that none of them has a direct financial relationship with the commercial products mentioned in this paper that might lead to a conflict of interests for any of the authors.

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