Preparation and Characterization of Low Density Polyethylene/Thermoplastic Sago Starch/Kenaf Core Fiber Composites and Their Hybrid Composites with Halloysite Clay

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ABSTRACT

This present work demonstrated the potential of halloysite clay (HC) hybridized with kenaf core fibers (KCF) to reinforce the low density polyethylene (LDPE)/thermoplastic sago starch (TPSS) blends. The effects of HC loading (3-15 phr) on the mechanical, thermal and morphological properties were evaluated. The results depicted that Young’s modulus was improved significantly with the inclusion of HCs. A maximum tensile strength of 7.2 MPa was obtained at 12 phr HC loading. Accordingly, the hybrid composites were characterized by Thermogravimetric Analysis (TGA) and Scanning Electron Microscope (SEM). The thermal stability of hybrid composites was found to be enhanced with the addition of HCs. Morphological findings showed that samples containing 12 phr of halloysite clay had better dispersion.

INTRODUCTION

The never-ended waste disposal crisis caused by the large consumption of plastic materials has been ages debated by researchers, academicians, industries and consumers. It is therefore an urgent task to develop a cheap, renewable-resources based and environmental friendly materials (He et al., 2012). Modification of synthetic polymer with agricultural feedstock like starch has become a subject of interest in order to meet the requirements and to guarantee at least partial degradation [1]. However, it was found that the addition of thermoplastic starch as a minor phase into synthetic thermoplastic matrix as a major phase causes a reduction of the mechanical properties due to the immiscibility between hydrophilic and hydrophobic properties of both constituent [2].

Another interesting attempt to improve the mechanical properties and impart degradation is the use to natural fibers to reinforce synthetic polymer/biopolymer blend. In view of recent global interest, kenaf have drawn special attention due to its good mechanical properties [3]. Since there is great demand for new type of composite materials which can compensate the drawbacks as well as giving advantages to the conventional composite materials, it has brought to the forefront of the development composite material in which reinforcement from two or more types of filler/fibers is combined to produce so called hybrid composite materials [4]. Recently, researchers have been focused on the hybridization of organic and inorganic fillers for reinforcing composites to endeavour the synergistic effect of both types of fillers [5]. This is credited to the low density and biodegradability of organic fibers whereby inorganic fillers have attracted great attention because of their cost efficiency and abundant availability.

The key advantage of these composite materials lies in the possibility of combining physical properties of the constituents to obtain enhanced properties, for example physical and mechanical [4]. Basically, physical properties of composites are greatly affected by the characteristics of fillers such as shape, size and surface nature. Many studies have been conducted to characterize the effect of carbon nanotubes (CNTs), SiO2 nanoparticles, montmorillonite and halloysite nanotubes (HNTs) on the mechanical properties of various polymers [6]. A remarkable improvement on the strength, rigidity, durability and hardness also has been established by the addition of this type of fillers to the thermoplastics [6].


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In recent years, halloysite clays (HGs) have been incorporated as new type of reinforcing filler in polymers [4]. Halloysite clays (HGs) are considered as the promising materials for preparing polymer composites due to the fact that halloysites are rigid materials and that unique crystal structure. Compared with other nanoparticles such as fumed silica, montmorillonite and carbon nanotubes (CNTs), halloysite clays (HGs) are more easily dispersed in polymer matrix by shearing due to their rod-like geometry and limited intertubular contact area. HGs are recognized for their relatively lower hydroxyl density on their outer surface compared with fumed silica and other layered silicates such as montmorillonite [4,7,8] (Ismail & Shaari, 2010; Pasbakhsh et al., 2010; Prashantha et al., 2011). In fact, halloysite clays are readily obtained are much cheaper than other nanofillers such as carbon nanotubes and they are biocompatible [8]. Consequently, it can be seen that, the halloysiteclays are a type of green, unique and promising reinforcing material for thermoplastic [8]. Halloysite, a 1:1 clay mineral chemically similar to kaolinite except in its higher hydrated water content shows tubular morphology but also spherical, platy and semi rolled forms. It is a superfine clay material with the formula (Al₂Si₅(OH)₄·nH₂O) [4] have typical dimensions of 150 nm-2 µm long, 20-100 nm outer diameter and 5-30 nm inner diameter [9].

For that reasons, it is interesting to investigate the effect of shape, size and surface nature of inorganic fillers, i.e. halloysite clays on the mechanical and physical properties of low density polyethylene (LDPE)/thermoplastic sago starch (TPSS)/kenaf core fiber (KCF) composites. So far as is known, the hybridization of halloysite clays with kenaf fibers in LDPE/TPSS blend has been rarely reported. Incorporation of HNTs is expected to enhance the mechanical and thermal properties of the composites.

**MATERIALS AND METHODS**

Sago starch (13 % moisture) was obtained from the Land Custody Development Authority (LCDA), Sarawak, Malaysia. It had an average particle size of 20 µm and decomposition temperature of 230°C. Glycerol (plasticizer) was an analytical grade reagent, purchased from Merck Chemicals (Malaysia) and used as received. Low density polyethylene (LDPE, LDF 260GG) with melt flow index of 5 g/10 min was obtained from Titan (M) Sdn. Bhd. (Malaysia). Kenaf fiber (core) with average length of 5 mm was supplied by National Kenaf and Tobacco Board (LKTN), Pasir Puteh, Kelantan, Malaysia. The fibers were subjected to grinding process which yields particles approximately 70 to 250 µm in diameter. KCF were then dried for 3 hours at 70°C using vacuum before being used in the subsequent composite fabrication. The HCs, (ultrafine grade) were contributed by Imerys Tableware Asia Limited, New Zealand. Sago starch powder was vacuum dried by heating at 80°C for 24 hours before blending and processing. The dried sago starch was then pre-mixed with glycerol by using a high speed mixer. The weight ratio of sago starch and glycerol was maintained at 65:35 (by weight percent). The blend was stored overnight to allow the diffusion of glycerol into starch granules and would help the melt-mixing process. The HCs filler were dried at 80°C in the convection oven for 24 hour to reduce moisture prior to use. The ratio between LDPE/TPSS/KCF was fixed at 90/10/10 and the HCs loading were varied from 3 phr to 15 phr as shown in Table 1. HC was melt-blended with LDPE, TPSS and KCF using an internal mixer (HaakeRheomix Mixer, Model R600/610) at the temperature of 150 °C at speed of 50 rpm in order to obtain a homogeneous sample. The processed samples were then compression molded in an electrically heated hydraulic press (Kao Tieh Go Tech Compression Machine) at a temperature of 150 °C into a 1 mm thickness sheet before underwent mechanical testing and characterizations.

**Table 1: Composite formulation.**

<table>
<thead>
<tr>
<th>LDPE (wt. %)</th>
<th>TPSS (wt. %)</th>
<th>KCF (phr)</th>
<th>HC (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>10</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>10</td>
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<tr>
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<td>9</td>
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<td>90</td>
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<td>10</td>
<td>12</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

Tensile tests were carried out with a Universal Testing Machine (Instron 3366) according to ASTM D638. Dumbbell specimens of 1 mm thickness were cut from the compression molded sheets with a Wallace die cutter. A crosshead speed of 5 mm/min was used and the test was performed at temperature of 25 ± 3 °C and relative humidity of 60 ± 5 %. Five specimens were used to obtain average values for tensile strength, elongation at break, and Young’s modulus.

LDPE/TPSS/KCF /HGs composite samples were cut into small pieces (5-10 mg), which were then tested using thermogravimetric instruments (Perkin Elmer, Pyris Diamond TG/DTA) under nitrogen atmosphere within a temperature range from room temperature to 550 °C at a heating rate of 15 °C/min. Thermal degradation temperature was reported by the onset degradation temperature where the weight loss started to occur.
Scanning electron micrographs of tensile fracture surfaces of LDPE/TPSS/KCF/ HCs composites were obtained by using a Scanning Electron Microscope (SEM, model ZEISS Supra 35 VP). The samples were sputter coated with a thin layer of carbon to avoid electrostatic charging during the examination. The image results were analyzed to investigate the distribution of hybrid fillers in polymer matrix and their interactions.

RESULTS AND DISCUSSION

Tensile Properties:

Figure 1-3 depict the effects of HCladding on the tensile strength, Young’s modulus and elongation at break properties of LDPE/TPSS/KCF composites, respectively. Tensile properties of this hybrid composites are a function of how well the fillers and polymers interact with each other. Figure 1 show that the tensile strength of HCs filled LDPE/TPSS/KCF composite system was increased gradually as the HC loading increases up to 12 phr and then the tensile strength reduces as the loading further increases to 15 phr. The significant improvement of hybrid composites were due to the reinforcing effect of finely dispersed HCs within the matrices which contributed to the effective stress transfer from matrix to the filler. The resulting better load transfer from matrix to filler is subjected to nanotubular structure with high surface area of HCs. Due to this unique crystal structure together with low hydroxyl density on the surfaces, the HCs able to be homogeneously and easily dispersed inside the matrix. In fact, the ability of HCs to react with the kenaffibers in the matrix is believed to allow a more efficient load transfer as well as augment the tensile strength [4]. HC has smaller particle size compared to kenaffiber and generates larger surface area. It will cause a greater interaction between HC and matrix as discussed later in the morphological study [10]. Thus, it is well said that the reinforcing effects of a kind of filler on the mechanical properties of polymer composites depend strongly on its shape, particle size, aspect ratio, surface characteristics and degree of dispersion [11]. While, the tensile strength declined from 7.2 MPa to 6.7 MPa when the loading of HCs in the composite is further increase up to 15 phr (Figure 1). The drop of strength at higher HC loading is due to the bundling effect of HNTs in the composites system. It is believed that, agglomeration of the HCs was the possible explanation for the reduction of tensile strength. It possibly acts as stress concentrator whereby stress applied unable to be transferred from the matrix to the filler and results larger agglomerates tended to initiate voids which resulting failure of the composites [12]. This is further explained in the morphological observations. It is believed that, smaller-sized particles might have an adverse effect on mechanical strength due to generated higher agglomeration than bigger-sized particles [5].

Whereas, the incorporation of HCs was found to increase tensile modulus of LDPE/TPSS/KCF composites as shown in Figure 2. The modulus was increased from 264.6 MPa to 389.9 MPa when 3 to 15 phrHCs were loaded in the composite systems. The addition of HCs was expected to increase the modulus resulting from the inclusion of rigid filler particles in the soft matrix. HCs will stiffen the composite thus increases the Young’s modulus of the composite [13]. This indicates that the improvement of the tensile modulus of hybrid composites related to the strong interaction between fillers and matrices which reduce the elasticity and restrict the movement of polymer chain, resulting in a more rigid and tough composites [4]. It has been reported that, increase in the modulus depends on the perfect bonding of the filler to the polymer matrix, alignment of the polymer and the fraction of the filler packing [14]. This finding is in agreement with the work reported by others elsewhere [4].

![Fig. 1: Tensile strength of hybrid composites at different filler loading.](image)

On the other hand, the addition of HCs into the composite results in immediate transition deformation characteristic, i.e. from ductile to brittle behaviour typically where the elongation at break of HCs filled hybrid composites has been reduced down from 10.33 % to 4.58 % as illustrated in Figure 3. This is in agreement with other report elsewhere [4]. This effect is expected considering that as the amount of HCs increases, the HCs became more dominant and the stiffening effect becomes more obvious which consequently leads to reduced
elongation at break [4]. The presence of HC decreases the polymer chain mobility and deformability of a rigid interface between fillers and matrices which contribute to an inevitable decrease in the degree of ductility. This phenomenon is common for polymer materials with inorganic fillers [1].

![Fig. 2: Young’s modulus of hybrid composites at different filler loading.](image)

**Fig. 2:** Young’s modulus of hybrid composites at different filler loading.

![Fig. 3: Elongation at break of hybrid composites at different filler loading.](image)

**Fig. 3:** Elongation at break of hybrid composites at different filler loading.

**Thermal Properties:**

Thermogravimetric analysis was carried out to examine thermal stability and degradation temperature of neat LDPE/TPSS/KCF composites and its hybrid composites. The TGA profiles for LDPE/TPSS/KCF and hybrid composites are revealed in Figure 4 and the data are summarized in Table 2. For LDPE/TPSS/KCF composite samples, TGA profiles demonstrated that thermal degradation of the samples occurred in two steps degradation process. Initial mass loss from approximately 300 to 370°C was mainly due to the decomposition of starch and volatilization of glycerol as well as the cellulosic substances. The thermal degradation appeared above 400°C was associated with the greatest weight loss, and was due to thermal degradation of the LDPE backbone [15]. Maximum weight loss was found at 97.51%. This is because higher thermal stability of fiber and because of the phase compatibility between TPSS and KCF due to their similar chemical structures, the two structures was linked through hydrogen bonds which will then reduce heat flow to the composite that inhibit the degradation process.

Referring to Figure 4, generally, the addition of 3 phr HNTs into LDPE/TPSS/KCF composites decreased the initial degradation temperature to 299.13 °C and slightly increased the end degradation temperature to 494.13 °C, respectively. And maximum weight loss was reduced to 94.84% in comparison to the one without inclusion of HCs. Accordingly; it is believed that the reduction in weight loss was the result of the improvement in thermal stability [16]. Supposing, the thermal resistance of the HCs itself which then increase char formation are responsible for the improved thermal stability of composites. It was reported that the addition of nanoclay would efficiently raise the char residue of polymers at high temperature [17]. Nanofillers such as HCs are believed to provide a thermal barrier which prevents heat transmit inside the polymer matrix and a mass transport barrier which during the process of degradation forms a char which hinders the escape of the volatile products [10]. In fact, the improvement in thermal stability is also attributable to the hollow structure of HCs which allows the entrapment of degradation products inside the lumens resulting effective delay in mass transfer. From the data highlighted in Table 2, the inclusion of 15 phr HCs into the composite system yield a residual weight of 12.8%. This would suggest that loading of HCs slightly enhances the thermal stability with decreases in characteristic weight loss. However, the increase for thermal stability of the composites by HCs is very limited due to merely slight increment of end degradation temperature in comparison with neat composites. This situation interpreted that the HCs might not favourable for the thermal stability.
Sphericals. Figure (5 % weight loss). It seems that bundling of inorganic fillers is filling in the vacant between polymer matrices and fibers. The tensile fracture morphology results of the composites to initiate cracks. This is further confirmed by the presence of many voids due to pull out of hybrid composites. This is because the HCs are loaded with 15 phrHCs. Interactions are more dominant in comparison with filler interactions. The existence of agglomerates is believed to reduce the tensile strength of the filler to agglomerate [11]. The existence of agglomerates are an indication of insufficient interactions between the filler to matrix. Concurrently, there are microvoids or vacants in between the fibers and matrices.

The SEM micrographs of HC and tensile fracture surfaces of its hybrid composites are depicted in Figure 5 (a)-(g). The SEM images of raw HCs reveal that the majority of HCs exist in a tubular shape and this is evidenced in Figure 9 (a). From the micrograph, it can be observed that HCs presence in the form of short tubular, semi rolled and pseudo-sphericals. Figure 5 (b) whilst illustrated the tensile fracture surface of LDPE/TPSS/KCF (neat composites). It can be observed that, fibers were embedded in the matrix and the fiber surface is wetted by the matrix.LDPE/TPSS/KCF/15 phr HNT. It is well known that the enhancement of mechanical properties of polymer composites significantly depends on the dispersion of filler in polymer matrix. Generally, it is difficult to achieve a good dispersion of inorganic filler in a thermoplastic. And this problem is even worse as the nanoparticles are used due to tendency of the filler to agglomerate [11].

The micrograph in Figure 5 (d) reveal that, with increasing amount of HCs up to 12 wt. %, the fracture surface observed exhibits evidence of significant matrix tearing. The rougher surface indicates that the resulted matrix tearing has contributed to the increase of tensile strength as HCs amount increased although there are some detachments of fillers as a result of poor adhesion onto the matrix [4]. It is further justified in Figure 5 (g) that samples have quite good dispersion of HCs within the polymer matrix, indicating the ability of HCs to disperse homogeneously. It is also observed that, the HCs being wrapped in the matrix and no debonded tubes and cavities can be seen [2]. Due to the straight and tubular structure of the HCs, they can be homogeneously and easily dispersed inside the matrix.

On the contrary, SEM micrographs in Figure 5 (e) exhibits many agglomerates and it seems that, filler-filler interactions are more dominant in comparison with filler-matrix interaction when composite systems were loaded with 15 phrHCs. The existence of HC agglomerates is believed to reduce the tensile strength of hybrid composites. This is because the HC matrix can act as a stress concentration point and increase the ability of the composites to initiate cracks. This is further confirmed by the presence of many voids due to pull out of HC agglomerates from the matrix. The tensile fracture morphology results of the composites are in agreement with the tensile result discussed earlier.

### Table 2: Thermogravimetric analysis of hybrid composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T&lt;sub&gt;f&lt;/sub&gt; (% weight loss) (°C)</th>
<th>Weight loss (%) (Max) (°C)</th>
<th>T&lt;sub&gt;Max weight loss&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE/TPSS/KCF</td>
<td>305</td>
<td>97.51</td>
<td>494.26</td>
</tr>
<tr>
<td>LDPE/TPSS/KCF/3 phr HNT</td>
<td>299.13</td>
<td>94.84</td>
<td>494.13</td>
</tr>
<tr>
<td>LDPE/TPSS/KCF/15 phr HNT</td>
<td>284.26</td>
<td>87.2</td>
<td>494.26</td>
</tr>
</tbody>
</table>

**Fig. 4:** TGA profiles of hybrid composites with different filler loading.

**Morphological Properties:**

The SEM micrographs of HCs and tensile fracture surfaces of its hybrid composites are depicted in Figure 5 (a)-(g). The SEM images of raw HCs reveal that the majority of HCs exist in a tubular shape and this is evidenced in Figure 9 (a). From the micrograph, it can be observed that HCs presence in the form of short tubular, semi rolled and pseudo-sphericals. Figure 5 (b) whilst illustrated the tensile fracture surface of LDPE/TPSS/KCF (neat composites). It can be observed that, fibers were embedded in the matrix and the fiber surface is wetted by the matrix. Concurrently, there are microvoids or vacants in between the fibers and matrices.

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Fig. 5: SEM micrographs of (a) raw HNTs, (b) LDPE/TPSS/KCF, (c) LDPE/TPSS/KCF/3 phrHCs, (d) LDPE/TPSS/KCF/12 phrHCs, (e) LDPE/TPSS/KCF/15 phrHCs, (f) bundling of HCs and (g) embedded HCs in polymer matrix.

Conclusions:
The inclusion of HNT inorganic fillers in LDPE/TPSS/KCF composites and its effect on the physical and mechanical properties were established. It was found that, the hybridization of fillers could effectively improve the tensile strength and modulus of the composites. As expected, elongation at break showed the reversal effect. Generally, the addition of HNTs responsible for the improvement in thermal stability and thermal degradation temperatures of LDPE/TPSS/KCF composites. Morphological studies provided by the SEM micrographs whereas revealed that aggregated HNTs largely affected the interfacial interaction between fillers and matrices.

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