Morphology and Thermal Properties of Alkaline Treated Palm Kernel Nut Shell – HDPE Composites

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Abstract

The shells of the nuts of palm tree an African economic tree was used to reinforce High Density Polyethylene (HDPE) after the particle size was reduced to 300µm with the aid of a Laboratory Ball Mill. Carvers Two Roll Mill was used for compounding of the materials to ensure proper mixing of the two distinct materials. Micro – structure investigation was carried out using Quanta 200 ESEM. The results obtained showed a uniform dispersion of particulates in the polymer matrix and a single fiber pull out for both formulations. Thermal properties of the fabricated composites were also investigated using Palkin Elmer Diamond Differential Scanning Calorimetry (DSC) and Thermo gravimetric analysis (TGA). The results obtained suggest that the fillers incorporated into the polymer matrix influenced the melting and crystallization temperature of the composites though marginally. The melting and crystallization enthalpy were largely reduced by the alkaline treatment of the shell.

Keywords: treated palm kernel nut shell - hdpe composites(TEPK). palm kernel nut shell(PK), high density polyethene(HDPE) and untreated palm kernel nut shell - hdpe composites(EPK)

INTRODUCTION

Plastics when filled with fibers are generally referred to as Fiber Reinforced Plastics (FRP). Presently, polymer matrix composite is the only bridge for harmonizing the need of the present day technology with material property requirement. (Mathews and Rawlings, 1999) The monolithic conventional materials lack some of the desired properties for modern day technology and these properties are only found in Fiber Reinforced Plastics (FRP). Globally, the technology of transforming waste into wealth is a vibrant path to economic growth. In most countries, agriculture plays a pivotal role in its economic growth (Bei, 2004) as such after harvest; large quantities of wastes are generated. These wastes constitute environmental pollution. Today these wastes have found a place in the Reinforced Plastic Industry where value has been added to it. There are quite a number of reasons why agricultural waste is used in composite making. This is because they give composites improved mechanical properties and reduce cost. (Bolton, 1994) Other advantages are related to their cycle of production that is economical and their ease of processing which demands simple equipment and safer handling and working conditions when compared to glass.(Amirhossein,2007 and Malachy et al 2007) A lot of work have been done using different plant fillers, but only few of these researchers have considered shells of these nut which is exceptionally hard with good waterproof property.

Thermoplastic reinforced with special wood fillers have been found to possess unique properties such as good strength and stiffness, (Bledzki et al 1998) Agro wastes such as palm kernel nut shell have proved to possess good compatibility with HDPE; these may be as a result of its constituents like cellulose, lignin and hemicelluloses.(Saira et al., 2007)

Palm tree is grown solely for its oil content. A matured tree can grow up to 20m with leaves 3-5m long. A young tree will produce about 30 new leaves a year while a 10 year-old tree will produce about 20 leaves a year. After flowering, the fruit takes 5-6 months to mature. The reddish fruit grows large bunches. Each fruit contains a single seed called the palm kernel which is surrounded by a soft oily pulp. The oil is extracted from the pulp to produce palm oil. The largest world producer of palm oil today is Malaysia. There are several types of fibers that can be obtained from a palm kernel tree.(Esua, 1977 and George et al 2001) For this study the shell of the palm kernel nut was used.

The interface between the reinforcing agent and the matrix plays a pivotal role in determining the mechanical properties of composite materials. Research efforts have shown that the major problem associated with natural fiber - polymer matrix composite is that of the interface. (Mansour et al,
1983 and Raj et al. 1989) While natural fiber is hydrophilic, HDPE is hydrophobic making it impossible for the two bodies to naturally bond together without any form of treatment. (Shah,1998 al, Bisanda, 1991 and Crawford and Throne, 2000) High density polyethylene (HDPE) which is known as linear polymer or low pressure polymer is selected for this study because of its exceptional environmental stress crack resistance property. (Faulk et al., 2000 and Mizanui and Mubarak 2007)

EXPERIMENTAL

The composites were prepared using alkaline solution Treated Palm Kernel Nut Shell (TPKS) and Untreated Palm Kernel Nut Shell (UPKS) . The particulates were incorporated into the polymer matrix using Two Roll Mill at a processing temperature of 160°C for 7min. The sodium hydroxide treatment was performed to remove some of the impurities in the shell which is rich in cellulose and lignin. The interfacial bond strength of the two phases was investigated using Quanta 200 Environmental Scanning Electron Microscope (ESEM) while Perkin Elmer Differential Scanning Calorimetry (DSC) and Thermo gravimetric Analysis (TGA) was employed to determine the thermal properties of the fabricated composites.

Environmental Scanning Electron Microscope (ESEM)

ESEM is especially useful for non-metallic and biological materials because coating with carbon or gold is unnecessary, which sometimes conceal small features on the surface of the sample and may reduce the value of the results obtained. The Environmental Scanning Electron Microscope (ESEM) images the sample surface by scanning it with a high - energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's micro - structure , composition and other properties such as electrical conductivity.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature/time. The sample and reference are maintained at the same temperature throughout the experiment. There are two different conventions: exothermic and endothermic reactions in the sample which is shown with a positive or negative peak, depending on the kind of technology used in the experiment. The curve can be used to calculate enthalpies of transitions by integrating the peak corresponding to a given transition. Differential Scanning Calorimetry can be used to measure a number of characteristic properties of a sample such as fusion, crystallization and glass transition temperatures. Chemical reactions such as oxidation can also be studied using DSC.

Thermo gravimetric Analysis

Thermo gravimetric analysis or thermal gravimetric analysis (TGA) is a type of test that is performed on samples to determine changes in weight in relation to change in temperature. This analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. TGA is commonly employed in research to determine the characteristic of materials, to determine degradation temperatures, absorbed moisture content of material and the level of inorganic and organic components in materials. The samples were tested using a Mettler Toledo FP 85 TA cell connected to a FP90 Central processor. This unit is capable of operating up to a maximum temperature of 400 °C. Prepared samples were placed into a 160 µl aluminum crucible for testing. The mass of sample tested was determined by difference in weighing the crucible before and after addition of the sample. Tests were carried out with an open crucible in static air.

<table>
<thead>
<tr>
<th>Step</th>
<th>Starting Temperature</th>
<th>End Temperature</th>
<th>Heating/cooling Rate</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>30</td>
<td>isothermal</td>
<td>5 min.</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>100</td>
<td>5 degree per min.</td>
<td>15min</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>100</td>
<td>isothermal</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>30</td>
<td>5 degree per min.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>400</td>
<td>5 degree per min.</td>
<td>15 min.</td>
</tr>
<tr>
<td>6</td>
<td>400</td>
<td>400</td>
<td>isothermal</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>400</td>
<td>30</td>
<td>5 degree per min.</td>
<td></td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Micro- Structure of the Fabricated Composites

The micro - structures of the various composites were investigated using Quanta 200 ESEM under high voltage of 20kV at 2 different magnifications x500 and x1000. The micrograph obtained showed that there is even distribution of the fillers in the polymer matrix for all the formulation investigated as shown in Figure 1a to 2b. The micrograph suggested formation of good interface between the filler phase and the matrix phase which is a well desired property in composite fabrication. It also showed a satisfactory adherence as a consequence of the fibrous and irregular nature of the fillers.

The observation indicated that the fillers were well dispersed in the HDPE matrix. The shells are covered with a thin layer of matrix linking the filler surface to the matrix as such a better stress transfer may be expected. The filler – matrix interface in the composites when investigated, revealed that the particulates are tightly connected with the matrix. A
considerable adhesion at the interface was observed in the treated palm kernel nut shell – HDPE composites when compared to the untreated palm kernel nut shell – HDPE composites. The image revealed that some of the fibers have matrices on their surfaces.

Figure 1a: 30wt.% of PK –HDPE Composite. (×500)

Figure 1b: 30wt.% of PK –HDPE Composite (×1000)

Figure 2a: 30wt.% of TPK –HDPE Composite (×500)

Figure 2b: 30wt.% of TPK–HDPE Composite (×1000)

Thermal Properties of the Fabricated Composites

The thermal stability of the different composites was investigated using TGA and DSC. The TGA curve in Figure 3, 4 and 5 showed complete weight loss in the different steps. An increase in the decomposition temperature resulted in a more thermally stable product. Weight loss for the three systems were observed at different temperature and it showed that the alkaline treatment did not affect degradation process.

Differential scanning calorimeter was used for measuring the exothermic and endothermic heat flow of the different systems. The unfilled HDPE system as indicated in Figure 6 showed crystallization temperature of about 115.19°C and 130.99°C as the melting temperature. Two factors controls the crystallization of polymeric composites system according to Kokta et al (1985). He suggested that additives incorporated into polymer matrix have a nucleating effect that results in an increase in the crystallization temperature, which has a positive effect on the degree of crystallization. In addition, their findings also suggested that additives hinders the movement of polymer molecular chains to the surface of the growing polymer crystal in the composite. This resulted to slight change in the crystallization temperature, which may hinder crystallization.

In this study, the crystallization temperature of the different composites studied increased slightly when compared to the unfilled HDPE. This increase signifies that the cellulosic nature of the shells enhanced migration and diffusion of the HDPE molecular chains to the surface of the nucleus in the composite.

From the curves obtained in Figure 7 and 8 the melting enthalpy and crystallization enthalpy decreased with the addition of fillers. The composite’s Tm and Tc remained consistent with the reference sample (unfilled HDPE). These results suggest that the fillers (shell) significantly affected the crystallization kinetic of the HDPE matrix. The
untreated PK - HDPE composite showed melting temperature at 134.39°C and the treated PK – HDPE composites showed T_m of 133.17°C. The curve obtained in the Figure 8 distinguished the thermal behavior of treated TPK –HDPE composite (TEPK) from that of the untreated PK - HDPE composites (EPK). The cooling curve of EPK after melting temperature was attained, showing steady heat flow before the multiple small peaks which depicts degradation of the small particulates in the composites. The cooling curve showed a single sharp peak of crystallization temperature and then two small peaks.

From Table 2, the treatment decreased the T_m and T_c. ∆H_m and ∆H_c of the TEPK composites when compared with EPK composites were also reduced by more than 40%.

Table B: The DSC Results of the Various Composites

<table>
<thead>
<tr>
<th>Name</th>
<th>T_m (°C)</th>
<th>T_c (°C)</th>
<th>∆H_m (J/g)</th>
<th>∆H_c (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled System</td>
<td>130.99</td>
<td>115.19</td>
<td>180.6582</td>
<td>196.8385</td>
</tr>
<tr>
<td>EPK</td>
<td>134.39</td>
<td>117.13</td>
<td>127.4415</td>
<td>112.8431</td>
</tr>
<tr>
<td>TEPK</td>
<td>133.17</td>
<td>115.95</td>
<td>105.8674</td>
<td>67.2911</td>
</tr>
</tbody>
</table>
CONCLUSION
The thermal analysis using DSC and TGA showed that fillers incorporated into the polymer matrix influenced the melting and crystallization temperature of the composites when compared with the unfilled sample. In other words, the fabricated composites may not be processed at the same temperature for unfilled HDPE system. The alkaline treatment of the shell directly influenced the basic thermal properties of the composites.

The SEM result of both formulations suggested that the fillers were uniformly dispersed, so there was some compatibility of the fillers with the matrix except for some voids observed for EPK which may be as a result of the impurities present in the shell.

REFERENCES


