Thermal Properties of Jute Fiber Reinforced Chemically Functionalized High Density Polyethylene (JF/CF-HDPE) Composites Developed by Palsule Process

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SUMMARY

Jute fiber reinforced chemically functionalized high density polyethylene composites developed by Palsule process, without using any compatibilizer, and without any fiber treatment exhibit good thermal stability. The initiation of degradation of the JF/CF-HDPE composites is at temperatures intermediate between those of temperatures of initiation of degradation of the fiber and the matrix. The maximum degradation temperature of all the composite compositions are higher that of the matrix, and increase with increasing Jute fiber content. The temperatures of highest rate of degradation of 10/90, 20/80 and 30/70 JF/CF-HDPE composites are 483°C, 485°C and 488°C respectively, and at 550°C the composite compositions show the residual mass of 4.3%, 5.8% and 7% respectively.

INTRODUCTION

Natural fiber reinforced polymeric composites are emerging as eco-friendly, green polymer composites and are offering commercial and engineering applications along with techno-economic advantages. These natural fiber polymer composites are also offering environmental advantages, like; materials based on renewable and biodegradable resources; reduced dependence on

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non-renewable sources, reduced pollutant and greenhouse gas emissions and also carbon-di-oxide sequestration, and enhanced energy recovery [1].

In recent years, natural plant based fibers, for example; jute, coconut, hemp, sisal, coir etc., have been used as reinforcing materials for polymeric composites in place of conventional fibers like glass, carbon, aramid, etc. because natural fibers are renewable, non toxic, cost effective, easily available and have acceptable specific properties [2]. Several plant based natural fibers have been used as reinforcement materials for polymeric composite because of their easy availability, low cost, bio-degradability, renewability, recyclability, low density, good physical, thermal and mechanical properties including acceptable specific strength and specific stiffness, reduced tool wear, non-abrasiveness and non-toxic nature [3].

The main components of a plant fiber are; cellulose, hemicellulose and lignin; and hence natural fibers are commonly termed as lingo-cellulosic materials. Jute fibers, obtained from the bast layer of plants, have emerged as important reinforcing fibers for thermoplastic matrix based composites and like all other natural fibers, jute fibers are also lingo-cellulosic in nature with 61-71% cellulose, 14-20% hemicelluloses and 12-13% lignin [3, 4]. These constituents make natural fibers hygroscopic and hydrophilic because of which they have poor compatibility with hydrophobic polymer matrix in natural fiber reinforced polymer composites. Consequently, natural fiber reinforced polymer composites have poor fiber/matrix interfacial adhesion that limits load transfer from the fiber to the matrix and results in poor mechanical, thermal and physical properties of the composites. Strong fiber/matrix interfacial adhesion is necessary in a natural fiber reinforced polymer composite for its good overall properties and high performance. Following three processes have been used to improve fiber/matrix interfacial adhesion in natural fiber reinforced thermoplastic composites: (i) chemical or physical treatment of natural fibers; (ii) use of compatibilizers or coupling agents; and, (iii) Palsule process based on the use of chemically functionalized polyolefin as a matrix (in place of polyolefin).

Several jute fiber reinforced polymer composites have been processed by the first method of fiber modification by chemical or physical treatment to improve fiber/matrix interfacial adhesion. For example, to process the composites, jute fibers have been treated with 2-hydroxyl ethyl methacrylate (HEMA) [5], Silane [6], Sodium periodate [7], 1,4-butenediol diacrylate (BDDA), ethyl hexyl acrylate (EHA) and trypropylene glycol diacrylate (TPGDA) [8], oligomeric siloxane [9], methyl methacrylate (MMA), polyamide (PA) [10], maleic anhydride grafted polyethylene [11, 12]. However, in this process of imparting fiber/matrix interfacial adhesion by fiber surface modification by chemical or physical treatments, several fibers remain untreated due to aggregation of fibers.
Such untreated fibers fail to develop proper adhesion with the matrix in the composite; consequently, the composite materials exhibit limited properties at heavy loadings and at higher temperatures.

A compatibilizer acts as a coupling agent between the natural fiber and the polymeric matrix and improves the compatibility and interfacial adhesion between the fiber and the matrix and thus improves the properties of the composites. Following the second method of use of compatibilizers or coupling agents to develop fiber/matrix interfacial adhesion, several jute fiber reinforced composites have been developed using compatibilizers like, maleic anhydride grafted polypropylene varying in 1% to 6% concentration, [13-16], m-TMI grafted polypropylene [17] and several others. In natural fiber reinforced polymer composites processed by compatibilizers, non-uniform distribution of compatibilizer across the composite results in poor fiber/matrix interfacial adhesion and limits the composite properties at heavy loadings and higher temperatures. Reviews on jute fiber/polyolefin composites developed by both methods are available [18, 19].

Palsule [20-22] for the first time demonstrated that the use of chemically functionalized polyolefin, for example, maleic anhydride grafted polyolefin, as a matrix, in place of polyolefin, eliminates the need of any compatibilizer or any fiber treatment for processing natural fiber reinforced chemically functionalized polyolefin composites. This process of using chemically functionalized polyolefin matrix to develop natural fiber reinforced chemically functionalized polyolefin composite has now been termed as Palsule process [21, 22]. Natural fiber reinforced chemically functionalized polyolefin composites, for example banana fiber reinforced chemically functionalized polypropylene composites [21] and jute fiber reinforced chemically functionalized high density polyethylene (JF/CF-HDPE) composites [22], developed by Palsule process have demonstrated good properties due to significantly improved fiber/matrix interfacial adhesion generated in-situ from interactions between the functional groups present on the chemically functionalized polyolefin and the functional groups present on the chemical components of the natural fiber.

Following the studies on structure, morphology and mechanical properties of jute fiber reinforced chemically functionalized high density polyethylene (JF/CF-HDPE) composites by Palsule process; this study reports thermal properties of jute fiber reinforced chemically functionalized high density polyethylene (JF/CF-HDPE) composites developed by Palsule process. Consequently, high density polyethylene (HDPE) has not been used as a matrix in this study, but chemically functionalized high density polyethylene (CF-HDPE), i.e. maleic anhydride grafted high density polyethylene, has been used as matrix. The use of CF-HDPE as the matrix does not require any fiber treatment or any compatibilizers for processing of jute fiber reinforced chemically functionalized
high density polyethylene (CF-HDPE) composites by Palsule process; as the CF-HDPE is expected to develop in-situ fiber/matrix interfacial adhesion with jute fibers due to the presence of maleic anhydride in it. Consequently, the composites processed in this study have been developed by Palsule process, without using any compatibilizer and without any chemical/physical treatment of jute fibers; and this also avoids the problems due to untreated fibers and due to non-uniform distribution of compatibilizer, like, poor fiber/matrix interfacial adhesion, that may limit properties of jute fiber/chemically functionalized polyolefin composites at heavy loadings and higher temperatures.

EXPERIMENTAL

Materials

Matrix Polymer

In this study, high density polyethylene (HDPE) – that requires a compatibilizer or fiber surface treatment- has not been used as matrix; but chemically functionalized high density polyethylene (CF-HDPE) with 1.2% maleic anhydride grafted on it, has been used as matrix for the composites. CF-HDPE was obtained commercially (OPTIM® E-156, Series 300) from Pluss Polymer Pvt. Ltd., India. It is available, commercially, as free flowing granules and is off white to light yellow in appearance. It has a reported density of 0.954 g/cm³, reported melting temperature (T_m) of 132°C and the melt flow index (MFI) of 4.5 g/10 min (190°C, 2.16 kg).

Reinforcing Fiber

Reinforcing jute fibers, of 0.06 mm average diameter, obtained from local market in raw form, were chopped to 3-6 mm length and were used, as received, without any fiber surface treatment. Jute fibers have been termed as JF.

Compounding and Processing of JF/CF-HDPE Composites

Chemically functionalized high density polyethylene (CF-HDPE), and 3-6 mm short jute fibers (JF) were dried separately in hot air oven at 50°C for one day, and then at 80°C for 3-4 hours, prior to extrusion to remove the moisture. Calculated amounts of reinforcing JF and CF-HDPE matrix were mixed manually with a view to finally obtain 10/90, 20/80 and 30/70 JF/CF-HDPE composites. Mixtures with appropriate amounts of constituent materials
Thermal Properties of Jute Fiber Reinforced Chemically Functionalized High Density Polyethylene (JF/CF-HDPE) Composites Developed by Palsule Process

were fed into the hopper of the co-rotating twin screw extruder (model JSW TEX 30α). The screw speed of JSW TEX 30α co-rotating twin screw extruder was set at 145 rpm and the temperature profile for nine different zones in the extruder was varied from 155°C to 175°C. In particular, the temperature profiles of the various zones of the extruder for processing JF/CF-HDPE composites were – 155°C-155°C-160°C-160°C-165°C-170°C-175°C-175°C-165°C. The JF/CF-HDPE mixtures, with appropriate amounts of the JF and CF-HDPE, were compounded in the extruder, and the extruded composite compositions, termed as 10/90, 20/80 and 30/70 JF/CF-HDPE composites, were cooled in water. These were then pelletized in a pelletizer to obtain granules that were dried in hot air oven at 80°C for overnight, and were then used to mold test specimens for tensile, flexural and Izod impact tests. To process samples for testing and characterization as per ASTM standards, CF-HDPE matrix and extruded and pelletized JF/CF-HDPE composite granules were molded by injection molding machine [Electronica ENDURA 90] with the feed zone temperature of 145°C and nozzle temperature of 170°C.

**Fibre/Matrix Interfacial Adhesion in the JF/CF-HDPE Composites**

Jute fiber reinforced chemically functionalized high density polyethylene composites developed in this study by Palsule process, without using any compatibilizer, and without any fiber treatment, show good mechanical properties and also develop in-situ fiber/matrix interfacial adhesion due to interactions between the functional groups on the fiber and the matrix. Details of the in-situ fiber/matrix interfacial adhesion and its mechanism and of the mechanical properties of the JF/CF-HDPE composites have been described in literature [22].

**Thermal Characterization of the Reinforcing Jute Fibers, CF-HDPE Matrix Polymer and the JF/CF-HDPE Composites**

The thermal properties of the CF-HDPE polymer matrix, reinforcing jute fibers (JF) and the processed JF/CF–HDPE composites were evaluated by a Thermogravimetric/Differential Thermal Analyzer (TG-DTA SII 6300 EXSTAR). This instrument gives data for TGA, DTG and DTA and three different graphs are obtained: (i) Weight change (%) v/s temperature i.e. TGA, (ii) Weight /Time (µg/min) v/s temperature i.e. DTG, (iii) Heat flux (µV) v/s temperature i.e. DTA (for melting temperature).

TGA, DTG and DTA are the most widely used thermal methods, TGA being the most basic and the simplest of all the thermo-analytical method. The
measurement of the sample may be carried out in presence of inert atmosphere (nitrogen), at constant heating rate, and the change in weight is recorded as a function of increasing temperature. Maximum temperature is selected such that the sample weight is stable at the end. This approach gives important information about the sample, i.e.; the ash content (residual mass), the temperature of maximum degradation and the melting temperature. This technique is effective for quantitative analysis of thermal reactions that are accompanied by mass changes viz. evaporation, decomposition, dehydration, gas absorption and desorption and helps in deciding the end use application of the composites.

In this study, CF-HDPE polymer matrix, reinforcing jute fiber and JF/CF-HDPE composite samples were heated from room temperature to 550°C at heating rate 10°C/min in presence of nitrogen atmosphere.

RESULTS AND DISCUSSIONS

Figure 1a-e shows the TG and the weight loss% of the reinforcing jute fibers, CF-HDPE polymer matrix and all the compositions of JF/CF-HDPE composites in nitrogen atmosphere. TGA evaluates mass loss of a material as a function of temperature. A continuous graph of mass change against temperature is obtained when a sample is heated at a constant rate. A plot of percent mass change v/s temperature is referred to as thermogravimetric (TG) curve.

Figure 1a-e. Thermo-gravimetric curves, in nitrogen atmosphere, of (a) Reinforcing jute fibers (JF), (b) CF-HDPE matrix, and of following JF/CF-HDPE composites – (c) 10/90 JF/CF-HDPE (d) 20/80 JF/CF-HDPE (e) 30/70 JF/CF-HDPE
Figure 1a and b indicates that the JF starts releasing volatile matter (water) at around 70°C, CF-HDPE does not release any volatile matter at lower temperatures; and shows initiation of degradation at around 470°C. Figure 1a and b also show that the residual mass of CF-HDPE at 550°C is 3% and that of JF is 16.1%. Figure 1c-e indicates that the 10/90, 20/80 and 30/70 JF/CF-HDPE composites show initiation of degradation at around 405°C, 380°C and 360°C respectively; and these temperatures are in between the temperatures of initiation of degradation of JF (70°C) and CF-HDPE (470°C). Figure 1c,d and e also shows that the residual mass of 10/90, 20/80 and 30/70 JF/CF-HDPE at 550°C are 4.3%, 5.8% and 7% respectively.

Figures 2a and b show the DTG (relative weight change as a function of temperature) of JF and CF-HDPE matrix and it was observed that the temperature of highest rate of degradation of JF is 359°C and that of CF-HDPE is 480°C. Figures 2c-e indicates that the temperatures of highest rate of degradation of 10/90, 20/80 and 30/70 JF/CF-HDPE composites are 483°C, 485°C and 488°C respectively.

Figure 2. DTG Curves (relative weight change as function of temperature) of (a) JF and (b) CF-HDPE

The maximum degradation temperature of all JF/CF-HDPE composite compositions is higher than the maximum degradation temperature of CF-HDPE matrix and the maximum degradation temperature of the composites increases with increase in jute fiber content in composite compositions, indicating higher thermal stability of all the JF/CF-HDPE composites than that of the CF-HDPE matrix.
Figure 2. DTG Curves (relative weight change as function of temperature) in nitrogen atmosphere of (c) 10/90 JF/CF-HDPE, (d) 20/80 JF/CF-HDPE (e) 30/70 JF/CF-HDPE
Melting Temperatures of CF-HDPE Matrix and JF/CF-HDPE Composites

The melting temperature of the CF-HDPE matrix and all the compositions of JF/CF-HDPE composites are recorded in the Figure 3 (DTA) and in Table 1. The peak melting temperature (Tm) of CF-HDPE matrix and of the 10/90, 20/80 and 30/70 JF/CF-HDPE composites evaluated from the DTA curves (Figure 3) recorded in Table 1 indicate that the melting temperature of the CF-HDPE is 132.4°C and of the various JF/CF-HDPE composites are in the range of 132.7°C to 135.1°C. This indicates that the T_m of the different compositions of the JF/CF-HDPE composite are not exactly the same (132.4°C) as that of the CF-HDPE matrix, but are within the limits of experimental errors, probably, either because of the measurement limitations of the instrument, or probably because of some very minor interference of the fiber with the polymer matrix structure. Thus, there is no appreciable change in the melting temperature of the JF/CF-HDPE composites, as compared to CF-HDPE matrix, because in principle, the CF-HDPE is the only component of JF/CF-HDPE composite that actually melts, and the JF would not melt, but would degrade.

Figure 3. DTA curve indicating melting temperature (T_m) of (a) CF-HDPE matrix, (b) 10/90 JF/CF-HDPE, (c) 20/80 JF/CF-HDPE and (d) 30/70 JF/CF-HDPE composites
Table 1. Melting temperature of CF-HDPE matrix and of all the JF/CF-HDPE composites

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Temperature $T_m$ (°C)</th>
</tr>
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<tbody>
<tr>
<td>CF-HDPE</td>
<td>132.4</td>
</tr>
<tr>
<td>10/90 JF/CF-HDPE</td>
<td>133.6</td>
</tr>
<tr>
<td>20/80 JF/CF-HDPE</td>
<td>132.7</td>
</tr>
<tr>
<td>30/70 JF/CF-HDPE</td>
<td>135.1</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Good thermal stability is demonstrated by jute fiber reinforced chemically functionalized high density polyethylene composites developed by Palsule process, without using any compatibilizer, and without any fiber treatment. The maximum degradation temperature of all the composite compositions are higher that of the matrix, and increase with increasing jute fiber content. The initiation of degradation of the JF/CF-HDPE composites is at temperatures intermediate between those of temperatures of initiation of degradation of the fiber and the matrix; and the temperatures of highest rate of degradation of 10/90, 20/80 and 30/70 JF/CF-HDPE composite compositions are 483°C, 485°C and 488°C respectively, and at 550°C the composite compositions show the residual mass of 4.3%, 5.8% and 7% respectively.

REFERENCES


