

# Preparation of Carbon Nanofiber Reinforced HDPE Using Dialkylimidazolium as a Dispersing Agent: Effect on Thermal and Rheological Properties

J. Samuel, S. Al-Enezi, A. Al-Banna

**Abstract**—High-density polyethylene reinforced with carbon nanofibers (HDPE/CNF) have been prepared via melt processing using dialkylimidazolium tetrafluoroborate (ionic liquid) as a dispersion agent. The prepared samples were characterized by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses. The samples blended with imidazolium ionic liquid exhibit higher thermal stability. DSC analysis showed clear miscibility of ionic liquid in the HDPE matrix and showed single endothermic peak. The melt rheological analysis of HDPE/CNF composites was performed using an oscillatory rheometer. The influence of CNF and ionic liquid concentration (ranging from 0, 0.5, and 1 wt%) on the viscoelastic parameters was investigated at 200 °C with an angular frequency range of 0.1 to 100 rad/s. The rheological analysis shows the shear-thinning behavior for the composites. An improvement in the viscoelastic properties was observed as the nanofiber concentration increases. The progress in the modulus values was attributed to the structural rigidity imparted by the high aspect ratio CNF. The modulus values and complex viscosity of the composites increased significantly at low frequencies. Composites blended with ionic liquid exhibit slightly lower values of complex viscosity and modulus over the corresponding HDPE/CNF compositions. Therefore, reduction in melt viscosity is an additional benefit for polymer composite processing as a result of wetting effect by polymer-ionic liquid combinations.

**Keywords**—HDPE, carbon nanofiber, ionic liquid, complex viscosity, modulus.

## I. INTRODUCTION

POLYMER blends and composites received growing interest due to the possibility of attaining tailor-made properties. Commercial polymer composites are designed to improve the properties of virgin polymer components considerably. Compared with conventional polymer composites, polymer nanocomposites have attracted more attention and many combinations of polymers and nanofillers have been made to examine their potential to improve the mechanical strength, thermal properties, flame retardancy, barrier properties and stiffness of virgin polymers with minimal incorporation of nanofillers (<3 wt%) [1]. Organically modified montmorillonite (O-MMT) is one of the inorganic nanofillers that have been widely used for preparing high performance hybrid composites [2]. Successively, carbon nanomaterials with superior properties have been utilized to fabricate polymer nanocomposites. A small amount of carbon

nanotubes (CNTs) and CNFs exhibit the potential ability to produce polymer nanocomposites with good mechanical, thermal and electrical properties [3]-[5]. These composites offer great openings for developing multifunctional polymer composite materials, for electromagnetic interference (EMI) shielding and electrostatic dissipative (ESD) protection applications [6]. However, the overall performance of the polymer nanocomposite mainly depends on the effective dispersion in to the polymer matrix and nanoparticle polymer adhesion [7]. CNFs differ from CNTs in its preparation methods, its unique physical characteristics, and the prospect of low-cost fabrication. Compared to CNTs, CNFs require less purification and are readily available with low cost. Additionally, the grapheme-layered fiber structure of CNF makes it easier to functionalize compared to the tube structure of CNT [8]. Owing to these advantages, CNF is quite attractive for bulk nanocomposite manufacturing and industrial applications. When combined with polymers, the CNFs can induce improvement in the mechanical properties of the neat polymer and improvement dependent upon the type of polymer matrix, the efficiency of dispersion, and processing history [9], [10]. Vapor-grown carbon fibers (VGCFs) are within the class of thick multi-walled CNTs prepared by the catalytic chemical vapor deposition method. Recently many researchers reported the use of VGCFs with polymers and metal oxides to produce nanostructured energy materials in electrochemical energy conversion and storage devices, including lithium ion batteries, and actuator materials [11], [12]. The incorporation of high aspect ratio VGCF in polymer matrix usually exhibits improved mechanical properties with an undesirable processing difficulty. Therefore, evaluating the rheological properties is considered to be an important tool to address the processing behavior. The dispersion and rheological properties of VGCF reinforced polyolefin have been described in a number of publications [13], [14]. The dispersion study of VGCF in ionic liquid reported that the aggregated lump of VGCF completely disappeared in the ionic liquid with longer alkyl chain [15]. Use of ionic compatibilizer has been reported to be a suitable method to improve CNT dispersion in polystyrene matrix [3], [16]. Therefore, more research will be carried out to improve dispersions of VGCF with suitable cationic modifications using a suitable dialkylimidazolium salt, a nonflammable, thermally, mechanically as well as electrochemically stable ionic liquid. Moreover, the presence of long alkyl group present in the ionic liquid enables easy melt processing of polymer

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nanocomposites. The use of imidazolium-intercalated CNTs is highly beneficial to prepare well-distributed polymer nanocomposites through  $\pi$ -cation interactions [17], which creates an ordered imidazolium salt into a layered crystalline phase. This paper looked into dependence of both VGCF and ionic liquid content on physical properties in HDPE, one of the polyolefins most widely used in structural, packaging applications. The objective is to explore the possibility of preparing VGCF/HDPE composites with improved processability. The mechanical behavior of the resultant thermoplastic composites will be further assessed with the help of rheological analysis. From material design point, not only dispersion and compatibility but also other synergic properties will be addressed to develop polymer nanocomposites with balanced properties.

## II. EXPERIMENTAL

### A. Materials & Sample Preparation

HDPE (EMDA-6200) with a melt index (I2.16) 0.4 g/10 min from EQUATE Petrochemical Company was used in this study. EMDA-6200 is used for producing containers for packaging household and industrial chemicals and food products. It is also suitable for producing thin-walled parts, sheets and profiles including corrugated drainage pipes. Commercially available CNFs (>98% carbon basis, D  $\times$  L 100 nm  $\times$  20-200  $\mu$ m (produced by vapour-grown method) were obtained from Aldrich Co. Ionic liquid and 1-hexadecyl-3-methylimidazolium tetrafluoroborate > 98% was supplied by Iolitec.

In the first stage, the CNF powder and HDPE pellets with different filler ratios (0, 0.5 and 1 wt.%) with and without ionic liquids were carefully mixed to ensure an adequate distribution of the particles at the macroscale level. The mixture was then melt-mixed at 180–200 °C in a laboratory scale twin screw extruder at a rotor speed of 100 rpm. Neat component of HDPE was also treated under the same mixing condition for comparison

### B. Characterization

The thermal profile (Differential Scanning Calorimetry; DSC) of the HDPE and its nanocomposites was evaluated using DSC 60 A plus Shimadzu with a heating rate of 10 °C/min starting from 30 to 220 °C. Thermal degradations were performed in a TGA analyzer (Discovery TGA). Degradations were performed from 40 up to 700 °C, in a nitrogen atmosphere and at a heating rate of 10 °C/min. The TGA and differential thermogravimetric (DTG) curves were plotted and the % weight loss of samples at various temperatures was tabulated. The rheological analysis of CNF/HDPE composites was performed by a hybrid oscillatory rheometer (DHR-3) with a magnetic bearing, force rebalance transducer (FRT), and optical encoder dual reader. The measurements were accomplished using a parallel-plate with a geometry gap of 1 mm and the samples were set between the preheated parallel plates. The influence of frequency, and nanofiber concentration were evaluated. These frequency sweep tests were conducted under different frequency conditions (0.1 up to 100 Hz) with 5 data points per decade. The measurements

were conducted under a constant temperature (200 °C), and an amplitude of deformation of 2% applied to obtain rheological parameters. The parameters corresponding to frequency sweep such as storage modulus ( $G'$ ), loss modulus ( $G''$ ), damping factor ( $\tan \delta$ ) and complex viscosity ( $\eta^*$ ) were measured.

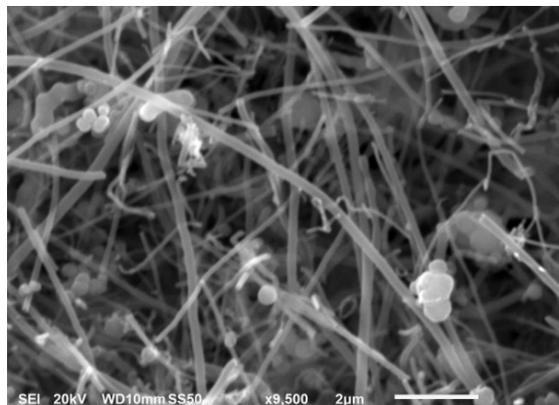


Fig. 1 SEM image of CNFs

## III. RESULTS AND DISCUSSION

### A. TGA

The effect of CNF loading and wetting effect by ionic liquid on the thermal behavior of HDPE nanocomposites was analyzed by TGA. The TGA parameters are stated in Table I and traces are shown in Figs. 2 and 3. The thermal stability of the HDPE/CNF nanocomposites was increased by increasing the CNF content. The onset degradation temperature ( $T_{onset}$ ) values of the samples blended with ionic liquid showed a considerable improvement. The maximum degradation temperature ( $T_{dmax}$ ) was increased by 20 °C compared to pure HDPE (Table I). The improved thermal stability of HDPE/CNF/IL composite may be attributed to the better dispersion of CNFs in the polymer matrix, which increases the interfacial contact between the CNF and HDPE matrix, or by an interfacial bonding between filler and matrix. Comparing the results obtained over the thermal degradation showed a clear effect by ionic liquid which was more noticeable during thermal decomposition process. These results and interpretations are in good correspondence with the results found for the thermal and thermal oxidative decomposition of polymer CNT composites. While comparing the derivative curves, it was observed that all the prepared composites degraded via a single step degradation process similar to the neat HDPE sample. HDPE/IL blend also showed a single step degradation process indicating a uniform solubility of IL in the polymer matrix. However, the incorporation of the thermally stable imidazolium salt into polymer matrix induces incombustibility and high thermal stability. The in-situ and maximum decomposition temperatures are shifted towards higher temperature; this effect is explained by the fine dispersion of the nanofibers, which decreases the polymer permeability to volatile decomposition products. Thus the addition of the CNF combined with ionic liquid reduces the

release rate of the decomposed byproducts and hence enhances the thermal stability of the nanocomposites.

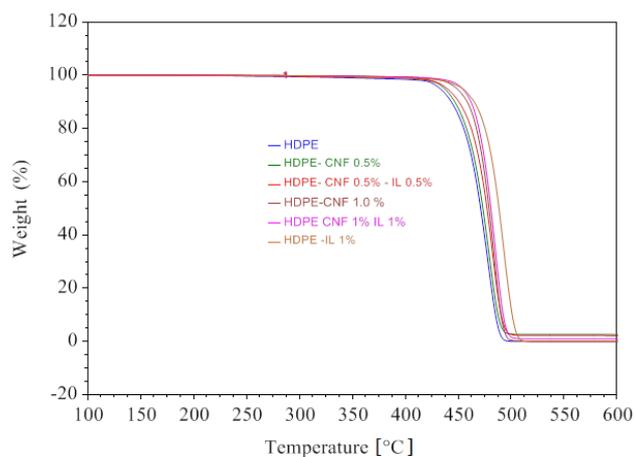


Fig. 2 TGA traces of HDPE/CNF composites

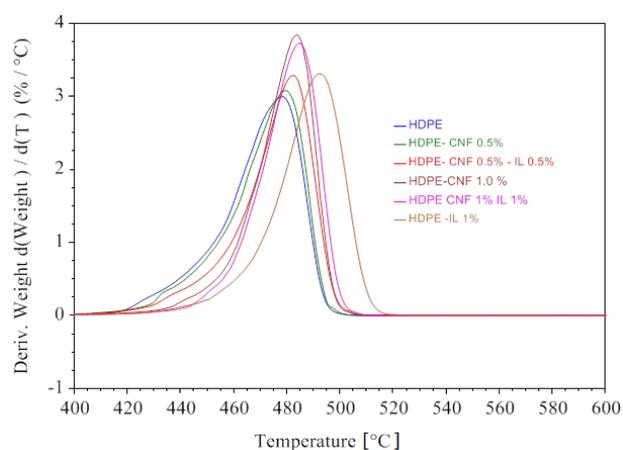


Fig. 3 TGA derivative curves of HDPE/CNF composites

### B. DSC

The heating and cooling curves were recorded for the evaluation of the thermal properties of CNF/HDPE composites (Figs. 4 & 5) and parameters obtained are summarized in Table I. There was small decrease in the melting temperature ( $T_m$ ) of ionic liquid blended HDPE and slight increase upon filler loading. The key challenge in the design of polymer nanocomposites is the monitoring of the distribution of filler particles and other additives for dispersion in the polymer matrix. From the DSC results it was found that the dialkyl imidazolium ionic liquid did not exhibit any melting peak, which could be ascribed to the dispersion effect of the long hydrophobic alkyl chain in the HDPE matrix. The crystallization temperature ( $T_c$ ) for all the prepared materials showed same values of neat HDPE, and this can be explained by the well-dispersed CNF without any nucleation or aggregation in the polymer matrix.

TABLE I  
DSC & TGA CHARACTERISTICS OF HDPE AND ITS NANOCOMPOSITES

Sample	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$T_{dmax}$ (°C)
HDPE	131.65	152.47	114.83	141.60	477.31
HDPE-IL 1%	131.05	157.60	114.61	142.60	492.67
HDPE-CNF 0.5%	130.90	139.30	114.25	133.26	480.14
HDPE-CNF0.5% IL0.5%	131.77	124.57	114.57	126.81	481.47
HDPE-CNF 1.0%	130.78	178.04	114.96	163.94	482.32
HDPE-CNF1.0% IL 1.0%	132.52	115.76	114.11	142.31	484.49

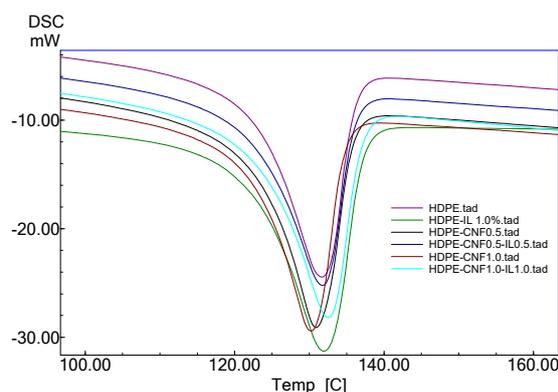


Fig. 4 DSC melting curves of HDPE/CNF composites

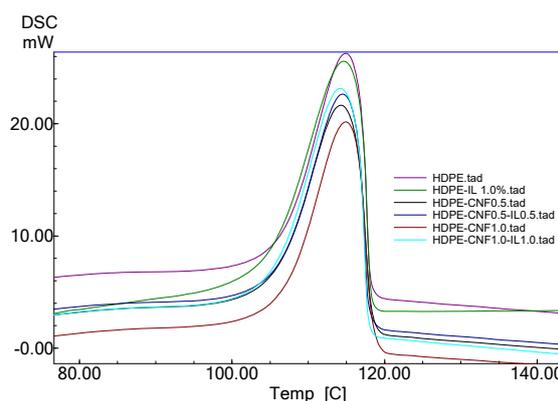


Fig. 5 DSC cooling curves of HDPE/CNF composites

### C. Rheological Properties

The viscoelastic properties of polymers and its composites typically play an important role on the material processing melts. The parameters obtained in this study describe the fundamental behavior of HDPE and HDPE filled with CNF and ionic liquid in processing. The angular frequency dependence of shear storage modulus ( $G'$ ) and shear loss modulus ( $G''$ ) Complex Viscosity ( $\eta^*$ ) at 200 °C are plotted in Figs. 6 and 7. Complex viscosity was observed to increase with the increase in concentration of the CNF content. In a fiber reinforced polymer, the presence of fibrous fillers perturbs the melt flow and obstructs the mobility of chain segments in flow and therefore the viscosity of the filled polymer system increases [3], [9]. Fig. 6 showed that the complex viscosity of the CNF filled HDPE composites

decreased with the increasing frequency. Presence of ionic liquid induced a small decrease in viscosity and followed closely with the neat HDPE, which is attributed to the plasticizing effect of ionic liquid. The complex viscosity values at high frequencies, for filled and neat HDPE samples showed a tendency to merge together. The complex viscosity at low shear rate showed a reduction in the viscosity for the ionic liquid compatibilized filled systems compared to the CNF filled systems. Therefore, the reduction in melt viscosity is a supplementary benefit for polymer composite processing. Fig. 7 showed that the neat HDPE, CNF/HDPE and CNF/HDPE/IL composite systems displayed viscous behavior at low frequencies ( $G'' > G'$ ), and an elastic behavior at high frequencies ( $G' > G''$ ). The crossover modulus values decreased with increasing filler loading. The crossover frequency and modulus values showed a different viscous behavior for the filled systems. The incorporation of CNF fillers in the HDPE matrix induces restrictions in the molecular chain mobility to exhibit pronounced elastic properties as compared to the neat HDPE.

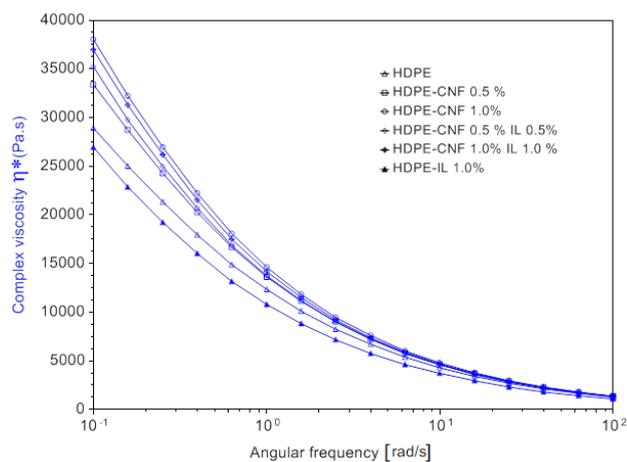


Fig. 6 Variation of complex viscosity with angular frequency

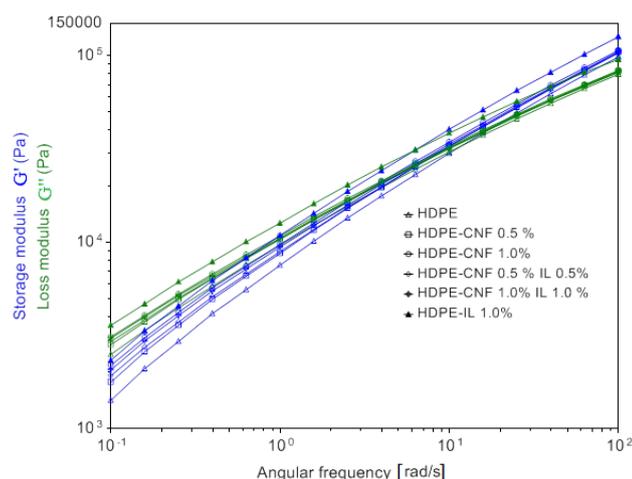


Fig. 7 Variation of storage and loss modulus with angular frequency

#### IV. CONCLUSION

HDPE/CNF has been prepared via melt processing using 1-hexadecyl-3-methylimidazolium tetrafluoroborate dilakylimidazolium tetrafluoroborate (ionic liquid) as a dispersion agent. TGA analysis showed that samples blended with imdazolium ionic liquid exhibit higher thermal stability. DSC analysis clearly indicated the technical compatibility of ionic liquid along with CNF in the HDPE matrix. Melt rheological properties of CNF/HDPE and CNF/HDPE/IL were studied as a function of CNF loading. The complex viscosity of the system was found to increase with fiber loading due to an increased interference to the melt flow. The measurements also showed that ionic liquid incorporated HDPE and CNF/HDPE systems exhibited lower complex viscosity compared with unfilled HDPE, and this could be the molecular motion due to the availability of greater free volume and weaker intermolecular interactions. The composites show stronger shear thinning behavior with increase fiber concentration at higher frequencies, where the addition of ionic liquid to the HDPE brings a variation in processing behavior.

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