

Enhanced Thermal, Mechanical and Morphological Properties of CNT/HDPE Nanocomposite Using MMT as Secondary Filler

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Abstract—This study explains the influence of secondary filler on the dispersion of carbon nanotube (CNT) reinforced high density polyethylene (HDPE) nanocomposites (CNT/HDPE). In order to understand the mixed-fillers system, Montmorillonite (MMT) was added to CNT/HDPE nanocomposites. It was followed by investigating their effect on the thermal, mechanical and morphological properties of the aforesaid nanocomposite. Incorporation of 3 wt% each of MMT into CNT/HDPE nanocomposite resulted to the increased values for the tensile and flexural strength, as compared to the pure HDPE matrix. The thermal analysis result showed improved thermal stability of the formulated nanocomposites. Transmission electron microscopy (TEM) images revealed that larger aggregates of CNTs were disappeared upon addition of these two components leading to the enhancement of thermo-mechanical properties for such composites.

Keywords—Secondary filler, Montmorillonite, Carbon nanotube, nanocomposite.

I. INTRODUCTION

ADDITION of nanoparticles as fillers in the polymer matrix not only improves the polymer strength, rigidity, and flexibility, but also facilitates the improvement of the polymer light transmission, barrier property, thermal resistance and electrical conductivity [1]-[4]. Several nanoparticles have been used as fillers in the polymer matrix so as to achieve the aforesaid functionalities of polymer nanocomposites. Carbon nanotube (CNT) has been widely explored as a potential filler owing to its larger surface area available to interact with matrix, high aspect ratio, excellent mechanical strength, and electrical and thermal conductivity [5]-[9]. To exploit all the features and properties of CNTs, one needs to ensure good dispersion and distribution of CNTs in polymer matrix along with strong interfacial interaction. In general, the mechanical properties of carbon nanotubes reinforced polymer do not improve significantly mainly due to the weak polymer-CNT interfacial adhesion that prevents the

efficient stress transfer from the polymer matrix to CNT [6], [7], [10], [11]. As a result, nanocomposite having properties much inferior to theoretical expectations is obtained [2], [10], [12]. Among the choice of polymer matrix, polyethylene is widely used due to its attractive properties. It is one of the most common volume thermoplastic with applications in packaging, consumer goods, pipes, cable insulation, etc. [10], [13]-[17].

Recently a strategy has been proposed involving the addition of a second filler/nanofiller working in synergy with CNT, and is defined as mixed (nano-) fillers system [18]-[20]. Addition of secondary filler can be interesting from an application view point since the selection of secondary filler may not only assist the CNT dispersion but might also provide additional functionalities to the polymer matrix. For instance, the addition of nanoclays could modify rheological properties and provide improved barrier properties and fire retardancy to the nanocomposite [20]-[22]. Montmorillonite clay (MMT) has attracted great interest among researchers mainly due to its availability and being “green” filler [14], [23]-[26]. It also offers industrial significance since the use of small amounts of MMT is enough to improve the overall physical properties of a polymer matrix at a relatively low cost [27]. Bao et al. [28] studied the effect of montmorillonite (MMT) on the dispersion of carbon black (CB) into polymer matrix. The study suggested that CB aggregates could adsorb onto MMT platelets thus modifying both the level of CB dispersion and flow properties. Liu et al. [29] studied the effect of addition of nanoclay to single-walled carbon nanotubes (SWCNT)/ epoxy composite. It was explained that SWCNT become more exfoliated and form better networks in such composites, mainly because of its affinity with nanoclay.

Here, attempts have been made to understand the effect of secondary filler on the dispersion and distribution of carbon nanotube reinforced high density polyethylene (CNT/HDPE) nanocomposites. It explains the use of MMT to intercalate CNTs and improve their dispersion into polymer matrix during melt blending. Improvement in dispersion was reflected in terms of enhanced thermo mechanical properties of formulated polymeric nanocomposites.

II. MATERIALS

An injection molding grade of high density polyethylene (HDPE-54) was obtained from local manufacturer in Saudi Arabia. It has narrow molecular weight distribution and high

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flowability (melt index 30.0g/10min at 230°C, 2.16kg). Multiwalled carbon nanotubes used in this study were provided by Bayer Materials, Germany (MWCNT; C 150 P). It has low outer diameter (13-16nm), narrow diameter distribution (5-20 nm) and an ultra-high aspect ratio (length-to-diameter ratio). Organically modified montmorillonite (MMT; NanoMax P-801) enabling them to disperse to nanoscale in polymer resins were supplied by Nanocor, USA.

III. METHODS

A. Preparation of HDPE Based Nanocomposites

HDPE, CNT and MMT were dry blended using a co-rotating twin screw extruder (Farrell FTX-20, USA). The twin screw extruder has distributive and dispersive mixing elements with L/D ratio of 35. The extrudates were cooled in a water bath; air dried and then pelletized at the die exit. The pelletized formulations were molded in an Airburg plunger type injection molder (40 tons, Series SM 120, Asian Plastic Machinery) to obtain specimens of ASTM Type I (D638). Table I shows the list of samples and their composition. Neat HDPE polymer is labeled as S1, while S2 is CNT reinforced HDPE at 1 wt. % loading and S3 is 1 wt% of CNT and 3 wt% of MMT.

TABLE I
SAMPLE COMPOSITIONS PREPARED AND USED IN STUDY

Sample	Filler used	Composition
S1	--	Neat HDPE
S2	CNT	S1 (99%) + CNT (1%)
S3	CNT and MMT	S2 (97%) + MMT (3%)

B. Thermal Characterization

Non-isothermal characterization of the neat HDPE and its blend composites was carried out using differential scanning calorimetry (DSC, Shimadzu DSC-60). Samples were heated from room temperature to 200°C at a rate of 10°C/min and held at this temperature for 5 minutes in order to eliminate any thermal history. Subsequently, the samples were cooled down to 50°C at the same rate. The samples were then reheated to 350°C at a rate of 10°C/min. The peak temperature and the area under melting and crystallization curves were recorded to determine melting and crystallization temperature (T_m and T_c , respectively) and the melting and crystallization enthalpies (ΔH_m and ΔH_c , respectively).

C. Mechanical Characterization

The tensile properties of neat HDPE and its blend resins were measured using a Hounsfield H100 KS series tensile testing machine. Dumbbell-shaped ASTM standard samples

(Type I for D638) were used for tensile testing. Tensile tests were performed at a crosshead speed of 100mm/min. Tests were performed in a uni-axial tension mode. Flexural tests were performed using standard ASTM D790 method. The reported measurements for all of the above tests represent the median of three experiments.

D. Transmission Electron Microscopy (TEM)

The Morphological analyses were carried out using a Transmission Electron Microscope (Zeiss Libra 120) with an accelerating voltage of 100 kV and magnification range of 50X to 2 x 106X. The samples for the TEM (around 70nm thickness) were prepared at room temperature with the help of Micro star cryo ultra-microtome having a diamond knife. The injection moulded samples were used for the purpose.

IV. RESULT AND DISCUSSION

A. Thermal Analysis

The endothermic peak of neat HDPE (S1) resin appears at 130°C and increases slightly for other nanocomposites as can be observed as slight shifting of T_m peak towards the right side in Fig. 1. This increase is attributed to the fact that the additives dispersed in the HDPE matrix resisting the conduction of heat to the crystallites until at higher temperatures the heat flow is enough to melt down the crystallites [30],[31]. Thermodynamic properties of all nanocomposites used in this study are shown in Table II. It can be observed that for S2 and S3, there is a gradual increase in T_c with increase in MMT content. This can be attributed to the increased concentration of clay particles causing heterogeneous nucleating effect. In other words, clay acts as a nucleating agent promoting crystallization of the HDPE resin [32]. There was significant reduction in ΔH_c values found for all samples when compared to S1, indicating the imperfect crystallization for the composite upon addition of the additives.

Table II shows the incorporation of CNT to neat HDPE matrix have resulted an increase the T_i and T_d values for S2 nanocomposite. These values were found to have increased further upon addition of MMT, as shown in Table II. This is because of CNT hinders the decomposition at high temperatures and MMT provides the tortuous path by the well distributed silicate layers of clay preventing the passage of the volatile decomposed product throughout the composite [16], [33], [34].

TABLE II
THERMODYNAMIC PROPERTIES OF NEAT HDPE RESIN AND ITS NANOCOMPOSITES

Material	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	T_i (°C)	Temperature of decomposition (T_d) at deferent weight loss (%)			
						20%	40%	60%	80%
S1	115	151	130	-149	265	382	417	432	454
S2	116	135	132	-142	277	421	431	438	455
S3	116	138	131	-132	279	421	431	446	460

B. Mechanical Analysis

The tensile and flexural properties of the neat and formulated nanocomposites are shown in Table III. The data presented are the average of three readings.

TABLE III
MECHANICAL PROPERTIES OF NEAT HDPE RESIN AND ITS NANOCOMPOSITES

Material	Tensile Strength (MPa)	Young's Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)
S1	19	568	32	888
S2	21	576	35	996
S3	22	593	36	1097

When compared to neat polymer resin (S1), the tensile property of S2 nanocomposite is shown to be improved by 12% which could be attributed to the presence of CNTs that stiffen the polymer matrix resulting to significant increase in the elastic modulus of the nanocomposite [12]. Incorporation of MMT to CNT/HDPE nanocomposites (S3) further enhanced the tensile strength by 16%. The enhancement in the tensile strength can be attributed to the fact that MMT layers acts as stress transfer agents and resists breakage, giving better strength to the nanocomposites [35]. Also it can be seen in Fig. 2 (b), that the presence of MMT helps to improve dispersion of CNTs into the HDPE matrix resulting in improved mechanical properties.

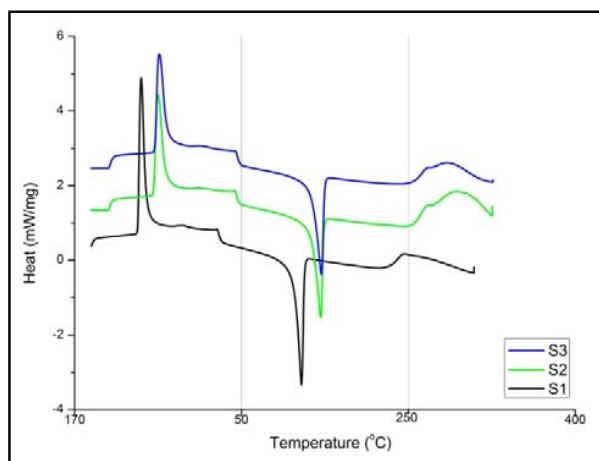


Fig. 1 Exothermic and Endothermic thermograms of the neat HDPE (S1) and its nanocomposites

C. Transmission Electron Microscopy

TEM analysis was carried out to investigate the morphology of HDPE nanocomposites prepared using different fillers and its correlation with the microstructure as shown in Figs. 2 (a), (b). Fig. 2 (a) shows the morphology of S2 nanocomposite (1% CNT loading). It can be seen clearly that the sample lacks ideal dispersion. There are varying regions of CNT aggregates (Fig. 2 (a) inset) and sparse CNTs present in the sample.

Unlike the S2 nanocomposites, the morphology of S3 represents a mixture of phase separation and intercalated morphology with tactoids of various sizes as shown in Fig. 2

(b). Presence of CNT aggregates can be observed for both composite samples S2 and S3 as the bundle regions in Figs. 2 (a) and (b). However the bundled are less in number and smaller in the area for S3 when compared to S2. It can be clearly seen from Fig. 2 (b), S3 has significantly more CNTs embedded as individual tubes or fairly thin CNT bundles present in the polymer matrix and, therefore, have a large surface area available to interact with the polymer matrix. That is why S3 has better mechanical properties when compare to S2 nanocomposites as discussed previously.

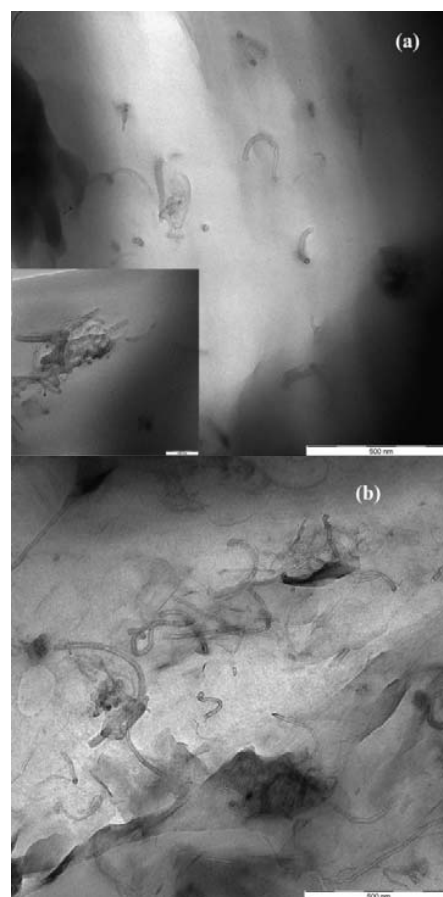


Fig. 2 Transmission electron microscopy for (a) S2 (HDPE+1% CNT) (b) S3 (CNT/HDPE + 3% MMT)

V. CONCLUSION

The incorporation of MMT to CNT/HDPE nanocomposites resulted in improved mechanical properties without affecting the basic thermal properties (crystallization and melting temperatures) of the nanocomposites. Additionally, their incorporation led to improve the thermal stability of the CNT/HDPE nanocomposites. XRD results showed no new crystalline phase is formed during the mixing and molding indicating that no chemical reactions between HDPE and/or CNT or MMT occurred. Furthermore, TEM analysis showed improved dispersion of such nanocomposites. Overall, the incorporation of MMT helps in improving dispersion and

interfacial adhesion of CNT into the HDPE matrix thus resulting in enhanced mechanical properties.

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