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Reinforcement effect and synergy of carbon nanofillers with different dimensions in high density polyethylene based nanocomposites

A comparative study of unary and binary carbon nanofiller reinforced high density polyethylene (HDPE) composites with 4 wt.% nanofillers was carried out in order to assess the reinforcement effect and synergy of carbon nanofillers with different dimensions. Rheology and resistivity tests indicate that the relative effectiveness of generating rheological and conductive networks is as follows: multi-walled carbon nanotubes (MWCNTs) > carbon black (CB) > graphene nanoplatelets (GNPs), while the reinforcement effect in modulus is: GNPs > MWCNTs > CB, at the same loading. The resistivity of all the HDPE/CB/MWCNT composites is quite close to the that of HDPE/MWCNT composites, indicating CB may be a good replacement for MWCNTs considering the relatively low cost of CB. A synergistic effect in modulus is observed in the HDPE/GNP/MWCNT and HDPE/CB/MWCNT composites due to the formation of nanofiller–polymer–nanofiller network structures.

Keywords: Polymer composites; Carbon nanotubes; Graphene nanoplatelets; Carbon black; Synergy

1. Introduction

Carbon nanofillers, such as carbon nanotubes (CNTs), graphene nanoplatelets (GNPs) and carbon black (CB), are capable of transferring their excellent conductivity to a polymer whilst also enhancing or maintaining its original mechanical and thermal properties etc. Polymer/carbon nanofiller composites are increasingly finding applications in automotive, aerospace and electronics industries for anti-static protection, electrostatic dissipation (ESD) and electromagnetic interference (EMI) shielding and so on, when flexibility or light weight is required [1–3]. In recent years, much work has been carried out on the preparation and characterisation of polymer/carbon nanofiller composites [3–9].

High density polyethylene (HDPE) is an important, low cost commodity thermoplastic that is used in numerous applications from packaging to fuel tanks. The range of appli-

cation areas of HDPE could however be greatly extended if the properties of this material could be improved through the introduction of carbon nanofillers. Morcom et al. [10] investigated the effect of the properties of MWCNTs on the dispersion and reinforcement in a melt mixed HDPE/MWCNT composite. It was found that MWCNTs with a larger diameter provided the highest reinforcement of 66 % and 69 % in elastic modulus and yield strength respectively at 5 wt.% MWCNTs due to a better nanotube dispersion. Verge et al. [11] compared the dispersion state of different types of MWCNTs in various grades of HDPE matrices by melt mixing. It was observed that each combination resulted in a different dispersion state so it is very difficult to universally predict the dispersion of nanotubes in a given HDPE matrix. However, it was found that a unique combination of low viscosity HDPE and low aspect ratio MWCNTs exhibited remarkable properties in their study due to a more homogeneous nanotube dispersion. The thermal stability was improved by 75 °C and the electrical resistivity of the composites decreased to $5 \times 10^2 \Omega \cdot \text{cm}$ with the addition of 3 wt.% MWCNTs in the low viscosity HDPE. Similarly, Yuan et al. [12] also found that a lower viscosity HDPE corresponded to a higher conductivity of HDPE/CB composites due to better dispersion. Jiang et al. [13] investigated the effect of a wax coating method on the electrical conductivity and the flexural properties of HDPE/GNP and HDPE/CNT nanocomposites. It was found that the wax coated GNPs and MWCNTs were much more efficient than the uncoated ones in improving the electrical conductivity and the flexural properties due to the improved dispersion of GNPs and MWCNTs in the polymer matrix. Wang et al. [14] prepared an HDPE/GNP composite with better electrical property by direct melt mixing using an internal mixer without any special processing techniques. This indicates that it is very difficult to predict which method is better to achieve a higher conductivity for polymer/GNP composites because many factors can influence the formation of conductive pathways.

Carbon nanofillers with different dimensional shapes have different reinforcement effect in polymers. Also, a large difference in the reported reinforcement effect of carbon nanofillers in polymer is found because the properties

of composites strongly depend on the polymer matrix and preparation processes etc. It is therefore difficult to compare the reinforcement effectiveness of carbon nanofillers from the experimental results reported in the literature. By way of example, a low electrical percolation threshold (1 vol.%) for polystyrene(PS)/GNP nanocomposites developed via in-situ polymerization was achieved in Srivastava's study [15], but a much higher percolation threshold (>10 vol.%) of HDPE/GNP prepared via melt extrusion was obtained by Jiang [13]. In order to achieve lower cost or a better balance of properties, the incorporation of hybrid carbon nanofillers with different dimensions is a possibility in preparing multifunctional polymer composites. Kim et al. [16] found that the HDPE composites filled with 0.5 wt.% GNPs and 2 wt.% CNTs exhibited a low electrical resistivity of $3.1 \times 10^2 \Omega \cdot \text{cm}$, while the unary carbon nanofiller reinforced composites filled with 0.5 wt.% GNPs or 2 wt.% CNTs alone showed a high resistivity. The synergistic role of CNTs in improving the electrical conductivity of LDPE/GNP composites prepared by melt mixing was also observed in Haznedar's study [17]. At present, a large number of studies of polymer/carbon nanofiller composites have been reported, however much fewer reports have been published on the comparison of the reinforcement effect of carbon nanofillers with different dimensions [14, 18, 19] and polymer composites filled with hybrid carbon nanofillers [16, 17, 20].

In this study, HDPE nanocomposites filled with GNPs, CB or CNTs alone or in binary combinations were prepared at a total filler concentration of 4 wt.% via melt extrusion under the same processing parameters. The effect of the inclusion of unary and binary carbon nanofillers on the rheological, mechanical and electrical properties of nanocomposites was then systematically investigated in order to assess the reinforcement effect and possible synergistic effect of carbon nanofillers with different dimensions. To the best of our knowledge, this study presents the highest known enhancement in modulus reported for a melt processed HDPE/carbon nanofiller to date. It also provides valuable guidance for the development, processing and property optimization of multifunctional polymer/carbon nanofiller composites.

2. Experimental procedure

2.1. Materials

High density polyethylene (HTA-108) with a density of $0.961 \text{ g} \cdot \text{cm}^{-3}$ was sourced from ExxonMobil. It has a high intrinsic viscosity ($MFI = 0.7 \text{ g} \cdot 10^{-1} \text{ min}^{-1}$) and an average molecular weight of $123\,400 \text{ g} \cdot \text{mol}^{-1}$. Graphene nanoplatelets (xGNP-15), consisting of short stacks of graphene sheets, were purchased from XG Sciences. Carbon black

(Carbon ECP600JD) was obtained from AkzoNobel. Multi-walled carbon nanotubes (NC7000) were kindly supplied by Nanocyl SA. The related parameters of these carbon nanofillers are presented in Table 1 [21, 22].

2.2. Preparation

The HDPE pellets were ground into a powder using a Wedco SE-12 plant grinder at room temperature. Then the HDPE powder was premixed at a speed of $2000 \text{ rpm} \cdot \text{min}^{-1}$ for 2 min with different unary and binary carbon nanofillers at a fixed total content of 4 wt.% using a high speed mixer (PRISM Pilot 3). It should be noted that the binary carbon nanofillers mentioned above consist of three different ratios of weight fraction, which are 3:1, 2:2 and 1:3 respectively. Subsequently, the dry blends containing different carbon nanofillers were melt-mixed in a twin-screw extruder (Collin ZK 25) at 150 rpm with a temperature profile of 175, 220, 220, 215, 210, 200°C from zones 1 to 6. The extruded strand was cooled in a water bath and pelletized. The extruded pellets were compression moulded in a steel mould of 1 mm thickness at 200°C and 100 bar for 5 min followed by a slow cooling at approximate $20 \text{ K} \cdot \text{min}^{-1}$ using a Collin P200P platen press in order to produce plaques for material characterisation.

2.3. Characterisation

The morphology and dispersion of carbon nanofillers in the HDPE matrix were examined using a JEOL 6500F scanning electron microscope (SEM) with an operating voltage of 5.0 kV. The samples were first plasma etched for 1 minute at an etching power of 100 W using a reactive ion etching system (STS Cluster C005) to remove the amorphous phase of polymer matrix and then gold sputtered in order to observe the morphology of nanofillers more clearly. Transmission electron microscopy (TEM) was conducted using a FEI Tecnai G2 Spirit TEM at 100 kV. Ultrathin sections with a thickness of less than 100 nm were cryo-ultramicrotomed using a Leica EMUC6 ultramicrotome. A Perkin-Elmer DSC model 6 was used to measure the percentage crystallinity, melting and crystallisation behaviour of the materials under an inert nitrogen atmosphere. Samples with a mass of $7 \sim 10 \text{ mg}$ were cut from the middle of the compression moulded sheets. The samples were heated from 30°C to 200°C at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$, held at 200°C for 3 min to remove the thermal history, followed by a cooling process from 200°C to 30°C at a cooling rate of $10 \text{ K} \cdot \text{min}^{-1}$. Then the samples were reheated to 200°C again at $10 \text{ K} \cdot \text{min}^{-1}$. Three repeated tests were conducted for each sample. In this work, the heat of fusion of 100% HDPE crystal (ΔH_m°) was taken as $293 \text{ J} \cdot \text{g}^{-1}$ [23], and then the degree of crystallinity (X_c) was calculated using

Table 1. The related parameters of the GNPs, CB and MWCNTs.

Carbon nanoparticles	Tensile modulus (GPa)	Length (μm)	Diameter/thickness (nm)	Surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Density ($\text{g} \cdot \text{cm}^{-3}$)
GNP	250 [21]	15	6~8	120~150	2.2
CB	10 [22]	—	68	1400	1.8
MWCNT	200 [10]	1.5	9.5	250~300	1.85

Eq. (1). The rheological behaviour of nanocomposites was investigated using an AR-G2 oscillatory rheometer at 200 °C. Circular specimens with a diameter of 25 mm and 1 mm thick from the compression moulded sheets were used in the rheological analysis. Dynamic strain sweeps were first carried out to determine a linear viscoelastic region up to 100 % strain at 10 rad · s⁻¹. Dynamic frequency sweeps were then performed at a strain of 1 % with the sweep frequency being varied from 0.1 to 100 rad · s⁻¹. Volume electrical resistivity measurements were carried out for the composites. For the samples with a high resistance (>10⁸ Ω), circular samples with a diameter of 70 mm and 1 mm thick were tested using a Keithley 6517A electrometer equipped with a Keithley 8009 resistivity test fixture according to ASTM-D257. For more conductive composites (≤10⁸ Ω), the two-point probe method for strips with dimensions of 50 mm × 10 mm × 1 mm was performed using a Keithley DMM 2000 multimeter. Silver paste was introduced to minimise contact. Two specimens for each type were tested. Tensile testing was conducted on the nanocomposites using an Instron 5564 Universal Tester (2 tension/compression load cells with capacity of 2 kN and 10 N, respectively) according to BS EN ISO 527:1996.

Young's modulus was determined using a clip-on extensometer at a crosshead speed of 5 mm · min⁻¹. Tensile strength and elongation were taken at a crosshead speed of 50 mm · min⁻¹. Five dumb-bell samples with approximate dimensions of 75 mm × 10 mm × 1 mm were tested for each type and average values were calculated.

$$X_C = \frac{\Delta H_m}{(1 - M_f)\Delta H_m^0} \times 100\% \quad (1)$$

where ΔH_m is the enthalpy of fusion of sample (J · g⁻¹); M_f is the weight fraction of carbon nanofillers.

3. Results and discussion

3.1. Dispersion and morphology

Figure 1a–c shows SEM images of compression moulded HDPE/carbon nanofiller composites with 4 wt.% MWCNTs, GNPs or CB respectively. It can be observed in Fig. 1a–c that these individual and agglomerated nanofillers are distributed uniformly in the polymer matrix. The stacked layers of the GNPs are not broken into single layers by the melt mixing

Fig. 1. Dispersion and morphology of the unary and binary carbon nanofiller reinforced composites: (a–c) SEM images of HDPE/MWCNT, HDPE/GNP and HDPE/CB composites, respectively.

Fig. 1 Continued: (d–f) SEM and (g–i) TEM images of HDPE/GNP/MWCNT (2 wt.% GNPs + 2 wt.% MWCNTs), HDPE/CB/MWCNT (2 wt.% CB + 2 wt.% MWCNTs) and HDPE/GNP/CB (2 wt.% GNPs + 2 wt.% CB) composites, respectively.

due to the strong van der Waals force and the additional interplanar π - π interactions between the individual graphene sheets [24, 25], as shown in Fig. 1b. The branched CB clusters in Fig. 1c form a so-called “high structure”, which may facilitate the formation of conductive pathways [20, 26]. Figure 1d–f shows the SEM images of compression moulded binary carbon nanofiller reinforced composites with 4 wt.% nanofillers in total (the ratio between the two types of nanofillers is 2:2), in which a homogeneous dispersion of the nanofillers in the HDPE matrix can be also observed. The GNPs and CB are bridged by the MWCNTs in Fig. 1d and e respectively, and the GNPs are surrounded by the CB in Fig. 1f. The SEM results agree well with the TEM results in Fig. 1g–i. It can be seen in Fig. 1i that the CBs do not bridge the GNPs due to the low aspect ratio of the CB.

3.2. DSC

The crystallisation and melting behaviour of the unary and binary carbon nanofiller reinforced composites were investigated using DSC. The crystallinity (X_c) and melting temperature (T_m) in the second heating stage and crystallisation temperature (T_c) are shown in Table 2. It can be seen that the crystallinity and melting temperature are barely changed, regardless of the type and combination of carbon nanofillers. The crystallisation temperature increased by about $1.5 \sim 2^\circ\text{C}$ due to the nucleation effect of carbon nanofillers [27, 28]. A higher T_c for the HDPE/MWCNT and HDPE/GNP/MWCNT composite indicates that the one dimensional nanotubes may more effectively facilitate the nucleation of HDPE, while the CBs show the weakest nucleation effect.

3.3. Rheology

The rheological properties of the unary carbon nanofiller reinforced composites with 4 wt.% nanofillers were compared, as shown in Fig. 2. The rheological behaviour of nanocomposites is mainly determined by three different interactions in the system, which are polymer–polymer, polymer–nanofiller and nanofiller–nanofiller interactions

ordered with increasing intensity [8]. It can be observed in Fig. 2a and b that the complex viscosity (η^*) and storage modulus (G') of HDPE/CB and HDPE/MWCNT composites increased at low frequencies compared to the unfilled HDPE, while those of HDPE/GNP composite decreased slightly. The details of complex viscosity and storage modulus at a frequency of $0.1 \text{ rad} \cdot \text{s}^{-1}$ for the unary carbon nanofiller reinforced composites are shown in Table 3. The slightly reduced viscosity ($26560 \text{ Pa} \cdot \text{s}$) and storage modulus (1142 Pa) of the HDPE/GNP composite compared to the unfilled HDPE may be attributed to interlayer slip, as a result of a low surface friction, in the GNP platelets [29, 30]. A clear deviation from a linear relationship at low frequencies for the HDPE/CB and HDPE/MWCNT composites can be seen in the Cole–Cole plots shown in Fig. 2c, indicating a transition from liquid-like to solid-like (or pseudo-solid) behaviour and the formation of a rheological percolation network in the CB and MWCNT filled composites with the presence of numerous polymer–nanofiller and nanofiller–nanofiller interactions. In addition, there appear to be more rheological network structures formed in the HDPE/MWCNT composite compared to the HDPE/CB composite according to the greater increase in the η^* and G' and deviation in the Cole–Cole plots at low frequencies. Changes in the viscoelastic behaviour of HDPE with the addition of different carbon nanofillers were quantitatively analysed by examining the crossover frequency (ω_c) plots of G' and G'' as a function of sweep frequency. In general, the unfilled HDPE and filled HDPE present a G'' superior to G' at low frequencies, indicating that the material has predominantly liquid-like behaviour. However, an inversion occurs and the values of G' are greater than those of G'' at a certain ω_c , which means that the material exhibits solid-like behaviour [2, 31]. By way of example, Fig. 2d shows the plots of G' and G'' as a function of frequency for the HDPE/GNP (4 wt.%) composite, and the corresponding value of ω_c ($50.1 \text{ rad} \cdot \text{s}^{-1}$) from the plots can be seen in Table 3. Other plots of G' and G'' as a function of frequency for the HDPE/MWCNT (4 wt.%) and HDPE/CB (4 wt.%) composite are not shown. A marked decrease in the ω_c for the HDPE/CB composite with 4 wt.% CBs reflects indir-

Table 2. Crystallisation and melting data of unary and binary carbon nanofiller reinforced composites.

Sample ^a	X_c (%)	T_m ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)
HDPE	70.4 ± 1.3	134.1 ± 0.1	114.0 ± 0.2
CNT4	70.7 ± 2.4	134.3 ± 0.2	116.0 ± 0.2
GNP4	70.3 ± 2.7	134.5 ± 0.2	115.6 ± 0.2
CB4	68.6 ± 0.8	134.6 ± 0.4	114.5 ± 0.3
GNP3CNT1	70.7 ± 1.4	134.5 ± 0.1	116.1 ± 0.2
GNP2CNT2	72.9 ± 2.8	134.0 ± 0.5	116.2 ± 0.2
GNP1CNT3	69.7 ± 2.1	134.2 ± 0.3	116.3 ± 0.3
CB3CNT1	70.9 ± 2.5	134.4 ± 0.1	115.5 ± 0.1
CB2CNT2	70.6 ± 3.0	134.5 ± 0.2	115.7 ± 0.2
CB1CNT3	69.6 ± 1.8	134.5 ± 0.2	115.8 ± 0.2
GNP3CB1	70.8 ± 3.4	134.6 ± 0.2	115.6 ± 0.3
GNP2CB2	70.5 ± 3.0	134.5 ± 0.2	115.6 ± 0.4
GNP1CB3	70.0 ± 1.0	134.4 ± 0.1	115.4 ± 0.2

^a The composite sample with 4 wt.% MWCNTs was denoted as CNT4, and so forth.

actly the formation of a percolated network (Table 3). For the HDPE/MWCNT composite, the ω_c is not available because G' is always higher than G'' within the range of sweep frequencies examined. It indicates the existence of more rheological network structures in the HDPE/MWCNT composite compared to the HDPE/CB composite as stated earlier. Also, this reveals that it may be more difficult to process CNT filled polymer in some forming methods such as injection moulding.

Figures 3–5 show the rheological properties of the HDPE/GNP/MWCNT, HDPE/CB/MWCNT and HDPE/

GNP/CB composites with 4 wt.% nanofillers, respectively. The details of complex viscosity and storage modulus at a frequency of $0.1 \text{ rad} \cdot \text{s}^{-1}$ and crossover frequency ω_c for the binary carbon nanofiller reinforced composites are also shown in Table 3.

It can be observed in Fig. 3 that the increase in complex viscosity (Fig. 3a) and storage modulus (Fig. 3b) and the deviation from a linear relationship in Cole–Cole plots (Fig. 3c) at low frequencies are enhanced steadily for the HDPE/GNP/MWCNT composites with increasing MWCNT loadings compared to the unfilled HDPE, indicat-

Fig. 2. (a) Complex viscosity and (b) storage modulus versus frequency, and (c) Cole–Cole plots for the unary carbon nanofiller reinforced composites with 4 wt.% nanofillers; (d) the crossover frequency for the HDPE/GNP (4 wt.%) composite.

ing that the addition of MWCNTs facilitates the formation of a percolated network. Figure 3d shows an example of the plots of G' and G'' as a function of frequency for the HDPE/GNP/MWCNT composites containing 2 wt.% GNPs and 2 wt.% MWCNTs. A steady decrease in the ω_c for the HDPE/GNP/MWCNT composites with increasing MWCNT loadings also reflects indirectly the formation process of the rheological network in Table 3. A clear deviation from a linear relationship in the Cole–Cole plot and a low ω_c value for the HDPE/GNP/MWCNT composite with 2 wt.% GNPs and 2 wt.% MWCNTs indicates the formation of a rheological network. For the HDPE/GNP/MWCNT composite with 1 wt.% GNPs and 3 wt.% MWCNTs, the ω_c is not available because G' is always higher than G'' within the range of sweep frequencies examined due to a very evident “pseudo-solid” like behaviour.

For all the compression moulded HDPE/CB/MWCNT composites, a clear increase in the complex viscosity (Fig. 4a) and storage modulus (Fig. 4b) and a marked deviation from a linear relationship in the Cole–Cole plots (Fig. 4c) at low frequencies can be seen, and the tendency appears to be also enhanced with increasing MWCNT loadings. Figure 4d shows the crossover frequency for the HDPE/CB/MWCNT composite with 2 wt.% CB and 2 wt.% MWCNTs. G' is always superior to G'' within the range of sweep frequencies examined for the HDPE/CB/MWCNT composites containing over 2 wt.% MWCNTs, thus the ω_c is not available for them (Table 3). In this study, a “pseudo-solid” like behaviour is evident for all the HDPE/CB/MWCNT composites due to the formation of a rheological network.

It can be observed in Fig. 5a–c that the increase in complex viscosity and storage modulus and the deviation from a linear relationship in Cole–Cole plots at low frequencies are enhanced for the HDPE/GNP/CB composites with increasing CB loadings, but they are not very significant compared to the unfilled HDPE. Figure 5d shows the crossover frequency plots for the HDPE/GNP/CB composite with 2 wt.% GNPs and 2 wt.% CB, which is still at a high frequency ($50.1 \text{ rad} \cdot \text{s}^{-1}$). The ω_c decreases to $31.6 \text{ rad} \cdot \text{s}^{-1}$ for the HDPE/GNP/CB composite with 1 wt.% GNPs and 3 wt.% CB (Table 3), indicating a rheological network

may have just been formed partially in the system. Overall, the HDPE/GNP/CB composites do not exhibit a significant “pseudo-solid” like behaviour in this study.

3.4. Tensile testing

The tensile properties of the compression moulded unary and binary carbon nanofiller reinforced composites with 4 wt.% nanofillers are shown in Table 4. It can be seen from Table 4 that the experimental elastic modulus (E) of composites is improved significantly with the addition of carbon nanofillers. For the unary carbon nanofiller reinforced composites, the composite filled with GNPs, which have the highest aspect ratio, exhibits the highest increase (125.5 %) in modulus as a result of effective stress transfer between the GNPs and HDPE matrix. The modulus only increased by 29.7 % for the HDPE/CB composite due to the low aspect ratio of CB. For the HDPE/CB/MWCNT composites, the modulus increases with increasing MWCNT loadings. Similarly, the modulus of the HDPE/GNP/CB composites increases with increasing loading of GNPs. The increase in modulus (over 114 %) for all the HDPE/GNP/MWCNT composites is higher than that for the HDPE/CB/MWCNT and HDPE/GNP/CB composites due to the high aspect ratios of both GNPs and MWCNTs. The improvement in modulus is not attributable to the crystallinity of the composites as there is no increase in crystallinity with the addition of carbon nanofillers according to the DSC results (Table 2). One can see that the inclusion of carbon nanofillers has a clearly negative effect on the stress at break (σ_b) and strain at break (ϵ_b) due to the presence of agglomerates, regardless of the dimensionality and combination of the nanofillers. The stress at break of CB and MWCNT filled HDPE composites decreased by about 40 %. The stress at break of the HDPE/GNP/MWCNT composite containing 2 wt.% GNPs and 2 wt.% MWCNTs decreased by only 9.7 % compared to the unfilled HDPE, but its strain at break decreased significantly by 98.7 %.

The experimental values of modulus were compared with the theoretical values (E_r) from a randomly aligned Halpin–Tsai model [32] expressed in Eq. (2) to further assess the reinforcement effectiveness of carbon nanofillers. The theo-

Table 3. Complex viscosity and storage modulus at a frequency of $0.1 \text{ rad} \cdot \text{s}^{-1}$ and crossover frequency for the unary and binary carbon nanofiller reinforced composites.

Sample	η^* at $0.1 \text{ rad} \cdot \text{s}^{-1}$ (Pa · s)	G' at $0.1 \text{ rad} \cdot \text{s}^{-1}$ (Pa)	ω_c (rad · s ⁻¹)
HDPE	30 200	1 279	63.1
GNP4	26 560	1 142	50.1
CB4	75 550	5 746	10.0
CNT4	242 000	20 780	–
GNP3CNT1	41 410	2 171	39.8
GNP2CNT2	72 440	4 873	15.9
GNP1CNT3	122 900	9 753	–
CB3CNT1	94 530	7 266	4.0
CB2CNT2	120 800	9 822	–
CB1CNT3	166 600	14 340	–
GNP3CB1	30 900	1 328	50.1
GNP2CB2	34 150	1 633	50.1
GNP1CB3	47 900	2 831	31.6

retical values of modulus are also shown in Table 4. As we can see, the experimental values agree reasonably well with the theoretical values for all the unary carbon nanofiller reinforced composites, particularly for the MWCNT filled composite. It can be observed in Table 4 that the theoretical modulus of HDPE/GNP composite is slightly higher than the experimental value, while the experimental modulus is 19% higher than the theoretical value for the HDPE/CB composite. This may be attributed to the fact that the high structure CB used with a high surface roughness (high surface area $1400 \text{ m}^2 \cdot \text{g}^{-1}$) are not of perfect spherical structure, thus their practical aspect ratio is higher than the as-

pect ratio of 1 which was used in the theoretical model. More importantly, a high surface area of the dispersed phase may be presented to the continuous phase with consequences for surface adsorption and immobilization of the polymer [33]. Interestingly, the experimental modulus of the HDPE/GNP/MWCNT composite containing 2 wt.% GNPs and 2 wt.% MWCNTs is higher than the theoretical modulus and the modulus of the composite containing 4 wt.% GNPs (Table 4), which can be attributed to a synergistic effect arising from nanofiller–polymer–nanofiller network structures formed in the system enhancing the stress transfer between the polymer and nanofillers [34,

Fig. 3. (a) Complex viscosity and (b) storage modulus versus frequency, and (c) Cole–Cole plots for the HDPE/GNP/MWCNT composites with 4 wt.% nanofillers; (d) the crossover frequency for the HDPE/GNP/MWCNT (2 wt.% GNPs + 2 wt.% MWCNTs) composite.

35]. The network structure is generated due to numerous entanglements between the polymer chains and nanofillers, and the polymer chains acting as a “bridge” via polymer-wrapping of carbon nanofillers. The formation of a nanofiller–polymer–nanofiller network structure is also supported indirectly by the rheological results discussed earlier. To the authors’ best knowledge, this increase of 167 % in modulus with the addition of 2 wt.% GNPs and 2 wt.% MWCNTs is the largest reinforcement in the modulus of melt processed HDPE/carbon nanofiller composites at this low loading to date. A slightly weaker synergistic effect is observed for the HDPE/GNP/MWCNT composite with

1 wt.% GNPs and 3 wt.% MWCNTs, which may be attributed to the decreased GNP content (GNPs exhibit the most efficient reinforcement in modulus compared with MWCNTs and CB). A similar synergistic effect is also observed in the HDPE/CB/MWCNT composites. All the experimental values of modulus of the HDPE/CB/MWCNT composites are higher than the theoretical values, particularly for the composites with less MWCNT content. The modulus of the composite containing 3 wt.% CB and 1 wt.% MWCNTs significantly increased by 46 % compared to the composite containing 4 wt.% CB. It is just 10 % lower than that of the composite containing 4 wt.%

Fig. 4. (a) Complex viscosity and (b) storage modulus versus frequency, and (c) Cole–Cole plots for the HDPE/CB/MWCNT composites with 4 wt.% nanofillers; (d) the crossover frequency for the HDPE/CB/MWCNT (2 wt.% CB + 2 wt.% MWCNTs) composite.

MWCNTs. However, the synergistic effect is absent for the HDPE/GNP/CB composites probably due to the lack of nanofiller–polymer–nanofiller network structures. A schematic diagram of nanofiller–polymer–nanofiller network structure is shown in Fig. 6. Although the nanofiller–polymer–nanofiller network structures are probably formed in the HDPE/MWCNT composite containing 4 wt.% MWCNTs as well, the introduction of abundant nanotubes would generate some agglomerates which will reduce the effective aspect ratio and thus reinforcement effect. As a result, the experimental modulus the HDPE/MWCNT composite is not statistically higher than the theoretical modulus.

$$\frac{E_r}{E_m} = \frac{3}{8} \left[\frac{1 + \zeta \eta_L \phi_f}{1 - \eta_L \phi_f} \right] + \frac{5}{8} \left[\frac{1 + 2\eta_T \phi_f}{1 - \eta_T \phi_f} \right] \quad (2)$$

where

$$\eta_L = \frac{E_f/E_m - 1}{E_f/E_m + \zeta}$$

$$\eta_T = \frac{E_f/E_m - 1}{E_f/E_m + 2}$$

E_f and E_m are the elastic modulus of the nanofiller and matrix, respectively. ϕ_f is the volume fraction of nanofiller. ζ is the shape factor depending on the filler geometry. η_L and η_T are the efficiency factors of the fillers along and perpendicular to the tensile direction, respectively. For the MWCNT and CB filled composites, ζ is 2α for E_r . For the

Fig. 5. (a) Complex viscosity and (b) storage modulus versus frequency, and (c) Cole–Cole plots for the HDPE/GNP/CB composites with 4 wt.% nanofillers; (d) the crossover frequency for the HDPE/GNP/CB (2 wt.% GNPs + 2 wt.% CB) composite.

GNP filled composites, ξ is $(2/3)\alpha$ [21]. α is the aspect ratio of nanofiller. Here α is 2000, 150 and 1 for the GNPs, MWCNTs and CB respectively according to the shape parameters of nanofiller shown in Table 1. In terms of the binary carbon nanofiller reinforced composites containing two carbon nanofillers, the theoretical modulus was obtained based on the fundamental principle of the Halpin–Tsai model and an assumption that the reinforcement of two nanofillers will not affect each other in the matrix. Therefore, the theoretical modulus (E_r) of the HDPE/MWCNT/GNP, HDPE/MWCNT/CB and HDPE/GNP/CB nanocomposites can be calculated according to Eq. (3).

$$E_r = E_m + \Delta E_1 + \Delta E_2 \quad (3)$$

where

$$\Delta E_1 = E_1 - E_m$$

$$\Delta E_2 = E_2 - E_m$$

where ΔE_1 and ΔE_2 represent the contribution of the first and second nanofillers to modulus respectively. E_1 and E_2 are the theoretical modulus of unary carbon nanofiller reinforced composites containing the first and second nanofillers respectively, which can be calculated using Eq. (2).

3.5. Electrical resistivity

The volume resistivity of unary and binary carbon nanofiller reinforced composites is shown in Table 5. It can be seen in Table 5 that the resistivity of HDPE decreases significantly by 16 and 14 orders with the addition of 4 wt.% MWCNTs or CB respectively. The one-dimensional MWCNTs are the most efficient in generating conductive pathways which is likely to be due to the ease with which 1D particles can entangle and form networks. Although the aspect ratio of CB is low, high structure CB tends to form branched clusters (see Fig. 1c) which facilitates the construction of conductive networks [20, 26, 36]. The HDPE/GNP composite contain-

Table 4. Tensile properties of the unary and binary carbon nanofiller reinforced composites with 4 wt.% nanofillers (E and E_r are the experimental and theoretical modulus respectively).

Sample	E (MPa)	E_r (MPa)	ΔE (%)	σ_b (MPa)	$\Delta\sigma_b$ (%)	ε_b (%)	$\Delta\varepsilon_b$ (%)
HDPE	900.6 ± 61.1	–	–	27.9 ± 3.0	–	907.0 ± 58.0	–
CNT4	1905.8 ± 149.3	1856.0	+111.6	16.6 ± 0.3	–40.5	46.9 ± 8.8	–94.8
GNP4	2031.1 ± 96.3	2317.6	+125.5	23.6 ± 1.2	–15.4	12.5 ± 2.1	–98.6
CB4	1167.8 ± 99.5	946.1	+29.7	16.4 ± 0.8	–40.1	27.2 ± 10.4	–97.0
GNP3CNT1	1930.6 ± 118.8	2189.4	+114.4	21.9 ± 0.9	–21.5	17.1 ± 3.0	–98.1
GNP2CNT2	2403.3 ± 100.3	2070.0	+166.9	25.2 ± 1.9	–9.7	11.8 ± 2.8	–98.7
GNP1CNT3	2344.6 ± 43.6	1958.7	+160.3	20.4 ± 0.9	–26.9	43.6 ± 8.7	–95.2
CB3CNT1	1706.6 ± 48.8	1167.5	+89.5	17.0 ± 0.6	–39.1	43.1 ± 11.4	–95.2
CB2CNT2	1787.8 ± 71.9	1393.1	+98.5	16.8 ± 0.6	–39.8	39.5 ± 11.6	–95.6
CB1CNT3	1791.3 ± 57.1	1622.4	+98.9	16.6 ± 0.2	–40.5	42.6 ± 16.1	–95.3
GNP3CB1	1901.9 ± 116.6	1966.8	+111.2	22.4 ± 1.1	–19.7	13.1 ± 4.0	–98.6
GNP2CB2	1639.4 ± 51.2	1621.5	+82.0	21.6 ± 1.5	–22.5	17.4 ± 5.2	–98.1
GNP1CB3	1381.2 ± 128.4	1281.1	+53.4	17.3 ± 0.6	–38.0	31.1 ± 13.2	–96.6

Fig. 6. Schematic diagram of the nanofiller–polymer–nanofiller network structure formed in HDPE/GNP/MWCNT and HDPE/CB/MWCNT composites.

Table 5. Volume resistivity of the unary and binary carbon nanofiller reinforced composites with 4 wt.% nanofillers.

Sample	Volume resistivity ($\Omega \cdot \text{cm}$)
HDPE	$1.3 \times 10^{17} \pm 2.1 \times 10^{15}$
CNT4	$4.5 \times 10^1 \pm 5.9 \times 10^0$
GNP4	$5.1 \times 10^{14} \pm 2.1 \times 10^{15}$
CB4	$2.1 \times 10^3 \pm 1.4 \times 10^3$
GNP3CNT1	$1.6 \times 10^{10} \pm 6.5 \times 10^9$
GNP2CNT2	$1.7 \times 10^3 \pm 8.6 \times 10^2$
GNP1CNT3	$2.6 \times 10^2 \pm 4.9 \times 10^1$
CB3CNT1	$8.9 \times 10^1 \pm 1.6 \times 10^1$
CB2CNT2	$8.8 \times 10^1 \pm 2.5 \times 10^1$
CB1CNT3	$6.9 \times 10^1 \pm 1.9 \times 10^1$
GNP3CB1	$2.8 \times 10^{14} \pm 5.8 \times 10^{13}$
GNP2CB2	$1.6 \times 10^{13} \pm 5.4 \times 10^{12}$
GNP1CB3	$3.8 \times 10^8 \pm 1.2 \times 10^8$

ing 4 wt.% GNPs exhibits a high electrical resistivity, indicating insufficient conductive pathways in the insulating polymer matrix. This poor reinforcement effect with the highest aspect ratio nanofillers may be due to the relatively poorer dispersion and the difficulty in achieving interlacing of the GNPs to produce a conductive network. In addition, the commercial GNPs used in this work may contain some uncondusive graphene oxide [18, 24]. It can be seen in this study that the relative effectiveness of enhancement in electrical conductivity is as follows: MWCNTs > CB > GNPs, at the same loading and processing conditions.

The resistivity of all the HDPE/CB/MWCNT composites with 4 wt.% nanofillers significantly decreased by 16 orders of magnitude compared to that of unfilled HDPE, indicating abundant conductive pathways formed with the addition of MWCNTs and high structure CB. The resistivity of the HDPE/CB/MWCNT composites is quite close to the resistivity of the composite with 4 wt.% MWCNTs, even though the nanofillers consist of 3 wt.% CB and only 1 wt.% MWCNTs. The MWCNTs can provide charge transport over large distances, while the branched CB aggregates formed around MWCNTs help charge transport over small distances [20]. This demonstrates that high structure CB may be a good replacement for CNTs considering its relatively low cost. For the HDPE/GNP/MWCNT and HDPE/GNP/CB composites, the resistivity decreases with increasing loadings of MWCNTs or CB respectively, while it is clear that the 1D MWCNTs with higher aspect ratio are more efficient than the spherical CB in terms of generating conductive networks in the binary carbon nanofiller reinforced systems. By way of example, compared to the composite containing 4 wt.% GNPs, the resistivity decreased by 11 orders of magnitude for the HDPE/GNP/MWCNT composite with 2 wt.% GNPs and 2 wt.% MWCNTs, while it only decreased by 1 order of magnitude for the HDPE/GNP/CB composite with 2 wt.% GNPs and 2 wt.% CB. In this case, the resistivity of binary carbon nanofiller reinforced composites is between that of corresponding unary carbon nanofiller reinforced composites, thus there is no evident synergistic effect in electrical property with a combination of two types of nanofillers. A sy-

nergistic effect in conductivity would be more difficult to achieve than that in modulus, because the formation of conductive pathways requires numerous nanofiller–nanofiller contacts rather than the nanofiller–polymer–nanofiller interactions for synergy in modulus.

4. Conclusions

In this paper, a comparative study of unary and binary carbon nanofiller reinforced HDPE composites with 4 wt.% nanofillers was carried out in order to assess the reinforcement effect and synergy of carbon nanofillers with different dimensions. It is shown that the material crystallinity is not affected by the addition of nanofillers, but the crystallisation temperature increases by $1.5 \sim 2^\circ\text{C}$ due to the nucleation effect of carbon nanofillers. Rheology and resistivity tests indicate that the relative effectiveness of generating rheological and conductive networks is as follows: MWCNTs > CB > GNPs, at the same loading. Both rheological and conductive networks were formed in all the HDPE/CB/MWCNT composites. For the HDPE/GNP/MWCNT and HDPE/GNP/CB composites, the rheological and conductive networks were enhanced with increasing MWCNT or CB loadings, respectively, while increasing MWCNT content in the HDPE/GNP/MWCNT composites better facilitates the formation of rheological and conductive networks compared to increasing CB content in the HDPE/GNP/CB composites. For the unary carbon nanofiller reinforced composites, the composite filled with GNPs, which have the highest aspect ratio, exhibit the highest reinforcement (125.5%) in modulus as expected. The experimental modulus of the HDPE/GNP/MWCNT composite containing 2 wt.% GNPs and 2 wt.% MWCNTs is higher than the theoretical value and that of composite with 4 wt.% GNPs. It is proposed that this is due to a nanofiller–polymer–nanofiller network structure formed in the system enhancing the stress transfer between the polymer and nanofillers. To the authors' best knowledge, the increase of 167% in modulus with the addition of 2 wt.% GNPs and 2 wt.% MWCNTs is the largest increase in the modulus of a melt processed HDPE/carbon nanofiller composite at this loading achieved to date. A similar synergistic effect is also observed in the HDPE/CB/MWCNT composites, but it is not evident for the HDPE/GNP/CB composites due to the lack of nanofiller–polymer–nanofiller network structures.

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