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Mechanical and rheological properties of carbon nanotube-reinforced polyethylene composites

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Abstract

This paper investigates some mechanical and rheological properties of low density polyethylene (LDPE) composites reinforced by multi-walled carbon nanotubes (MWNTs). It was found that the Young's modulus and tensile strength of the composites can increase by 89% and 56%, respectively, when the nanotube loading reaches 10 wt%. The curving and coiling of MWNTs play an important role in the enhancement of the composite modulus. It was also found that the materials experience a fluid–solid transition at the composition of 4.8 wt%, beyond which a continuous MWNT network forms throughout the matrix and in turn promotes the reinforcement of the MWNTs.
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1. Introduction

Both theoretical and experimental studies have shown that the elastic modulus of a carbon nanotube (CNT) is in the range of 1–5 TPa [1–4], which is significantly higher than that of a carbon fiber of 0.1–0.8 TPa [5]. Such a superior property makes CNTs a promising reinforcing material. However, recent results showed that CNTs, when incorporated into polymer matrix, do not necessarily warrant enhanced mechanical properties. Bhattacharyya et al. [6] investigated a melt-blended single-walled carbon nanotube (SWNT)/PP composite and observed a slight drop in tensile strength, elastic modulus and fracture strain with an addition of 0.8 wt% CNT. In a CNT/PMMA composite system, Jia et al. [7] found a decrease in tensile strength, toughness and hardness when untreated CNTs were used. Some other studies showed a moderate increase in mechanical properties, for example, 24% increase in elastic modulus but slightly lower fracture load in CNT/epoxy film with 0.1 wt% MWNTs [8]; about 10% increase in tensile stiffness

and a slight increase in tensile strength of MWNT/PS rod samples prepared by extrusion [9]; 20% increase in storage modulus of CNT/epoxy at room temperature with 0.30 wt% of fluorinated SWNT [10]; about 20% increase in tensile and compressive moduli of a CNT/epoxy composite with 5 wt% CNT [11]; etc. On the other hand, a significant improvement of the mechanical properties was also reported by a few investigators. Ganguli et al. [12] showed that the ultimate strength and fracture strain of a bifunctional epoxy were increased by 139% and 158%, respectively, after adding 1 wt% MWNTs. Allaoui et al. [13] reported that the Young's modulus and yield strength of a MWNT/epoxy composite have been doubled and quadrupled with an addition of 1 or 4 wt% CNTs. The elastic modulus and yield strength of nylon-6 polymer were found to increase by 214% and 162%, respectively, when 2 wt% MWNTs were used [14]. It was also concluded that the interface chemical bonding between CNTs and matrix plays a critical role in determining the properties and performance of a CNT composite [15].

Some common methods for the preparation of CNT/polymer composites include in-situ filling-polymerization [7], solution mix [16,17] and melt blending [18–20]. The

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composites prepared by the first two methods may result in contaminations because of the residual monomer or solvent. However, those by melt blending are essentially free of such contaminations. In addition, the tendency of CNTs to form aggregates may be minimized by appropriate application of shear during melt mixing [20,21]. These advances make the melt blending method a promising technique to produce CNT/polymer composites. Therefore, in recent years, there has been an increasing interest in the investigation of the behavior of CNT composites by melt blending [22–25].

A few investigations on dynamic frequency sweeps [26–30] have been reported using melt processed thermoplastic polymer/CNT composites, whose matrices include polycarbonate [26–28], polypropylene [29], and polyamide-6 and its blends with acrylonitrile/butadiene/styrene [30]. These studies found that the complex viscosity continuously decreases with increasing frequency while storage modulus G' and loss modulus G'' increase. A characteristic change in the rheological behavior with increasing the nanotube content was also observed at temperatures well above the glass transition or melting temperature, referred to as the percolation threshold or gelation point in relation to fluid-to-solid, fluid-to-gel transition or a combined nanotube-polymer network.

The mechanical properties of low density polyethylene (LDPE) composites have been widely investigated in the past decades with varying reinforcements from carbon, glass and natural fibers to metal and non-metal particles [31–36], however, it seems that results on the MWNT reinforced LDPE have not been available . The present paper will investigate some key properties of a low density polyethylene (LDPE) polymer reinforced by MWNTs with varying nanotube contents.

2. Experiment

MWNTs used in the present experiments were prepared by chemical vapor deposition (provided by Nanolab) with diameters ranging from 10 nm to 20 nm and lengths varying from 1 μm to 5 μm. The raw granules of LDPE were provided by Qenos Pty Ltd, Australia. LDPE and various amounts of MWNTs were mixed at 140 °C for 20 min using a mechanical mixer at the speed of 120 rpm. The mixed samples were then compressed in a steel mold under a pressure of about 8 MPa at 140 °C for 5 min using a hydraulic press.The resultant composite was cut to small pieces (about 2 mm), mixed, and then molded again at the above mentioned conditions. The molding was repeated for 10 times to improve the dispersion of the nanotubes in the matrix [21]. Tensile properties of the molded dogbone specimens were tested according to the D638 standard, using an Instron machine at a crosshead rate of 100 mm/min. The strains were measured using a strain gauge up to 24% and the corresponding failure strains were estimated from crosshead extension.

Rheological measurements were performed on a stress-controlled rheometer with a parallel plate geometry (Physica, MCR300). A gap of 1 mm between two plates was used for all tests and the diameter of the plate was 25 mm. Measurements were taken in both dynamic and steady modes at 125 °C. Frequency sweeps were carried out at low strains (0.1–10%) from 0.1 to 100 rad/s, within the linear elastic range of the composites. Repeated sweeps with increasing and decreasing frequencies produced identical data, showing that the materials were stable under the measurement conditions. Steady shear sweeps were performed in a stepwise manner from 0.1 to 100/s, with the sample being held at each step for 50 s. Specimens were placed between the preheated plates and 10 min were allowed to remove the excessive melt and to reach the thermal equilibrium before starting a test. The obtained values were corrected to the true volume between the plates.

The electron microstructure of the composite was studied by means of the conventional and high resolution transmission electron microscopy (TEM). The conventional TEM studies were performed on a Philips CM12 transmission electron microscope, operating at 120 kV. The HRTEM investigations were performed on a JEOL JEM-3000F transmission electron microscope, operating at 300 kV. Thin TEM samples were prepared by slicing the bulk material on a microtome. The curvature of a nanotube segment is defined as $1/R$, where R is the radius of a corresponding circle. R is determined from three points along 20 nm long tube segment by means of the image analysis system "micrograph". At least 70 CNTs were examined.

3. Results and discussion

3.1. Tensile properties

The stress/strain curves of the MWNT-LDPE composites with varying tube contents are shown in Fig. 1 and the maximum tensile strength σ_f, Young's modulus E_c and failure strain ε_f of the composites are summarized in Table 1, where ε_f is defined as the strain at which the tensile stress starts to drop sharply. The increases in Young's modulus (89%) and tensile strength (56%), when nanotube loading reaches 10 wt%, indicate that an effective reinforcement of the MWNTs. The rapid decrease of ε_f with the increasing CNT loadings, which is normal to composites, is believed to be caused by the premature failure starting at the CNT aggregates. It was noted that there is a moderate jump of Young's modulus when the MWNT content changes from 3 to 5 wt%, as shown in Fig. 2. The structural change of the composites with the increasing tube content is responsible for this, because when the CNT content was increased to 5 wt%, a continuous MWNT network is formed throughout the matrix, as confirmed by the rheological tests to be discussed later. It is understandable that, because of the curving and coiling nature of the MWNTs, strong mechanical interlocking among nanotubes appears and promotes the reinforcement.
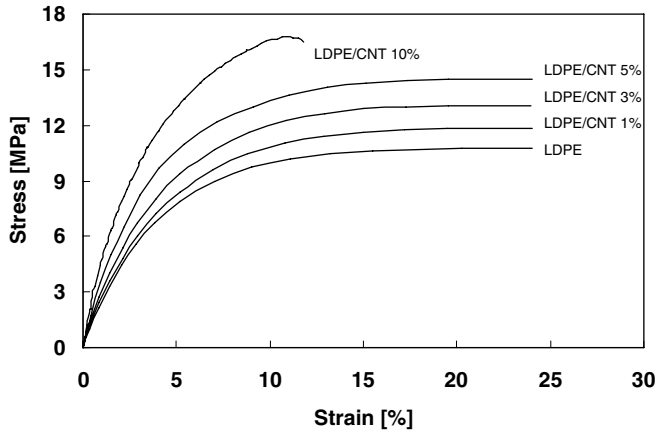
Fig. 1. Stress/strain curves of the composites with varying MWNT content.

Table 1
Tensile properties of the composites and deduced moduli of MWNTs

MWNT content	0%	1%	3%	5%	10%
σ_f [MPa]	10.7	11.8	13.1	14.5	15.6
ε_f [%]	380	320	260	160	12
E_c [GPa]	0.235	0.261	0.284	0.386	0.444
E_{MWNT} [GPa]		27	17	29	22
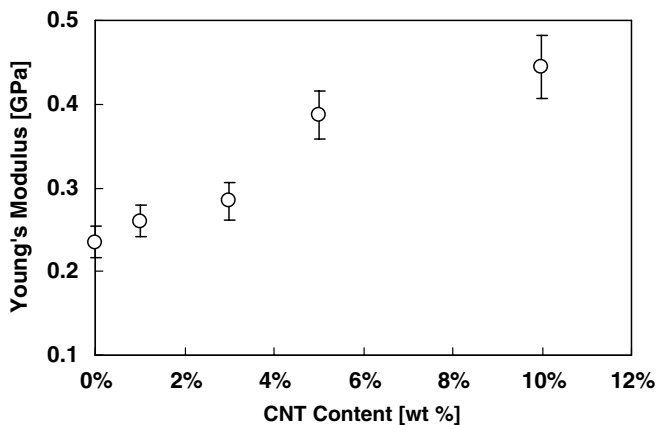
Fig. 2. Young's moduli of the composites as a function of MWNT content.

In the theory of short fiber-reinforced composites, when fibers are randomly distributed, the composite modulus, E_c, is related to the fiber modulus, E_f, by the well-known mixing rule, i.e.,

$$E_c = \eta_1 \eta_0 V_f E_f + (1 - V_f) E_m \tag{1}$$

where E_m is the modulus of the matrix, η_1 and η_0 are coefficients related to the critical fiber length and orientation, and V_f is the volume fraction of fibers. Wagner et al. [37] showed that the critical fragmentation length of MWNTs is less than 500 nm, which is much shorter than the length of the nanotubes (1–5 μm) used in this study. Therefore η_1 was chosen to be 1. If this formula is applied to the CNT

composite systems of this work and choose $\eta_0 = 0.2$ for randomly oriented fibers [38], noting that the volume fraction is about half of the weight fraction [39], then the deduced modulus of MWNTs, $E_{MWNT} = E_f$, given in Table 1, varies from 15 to 30 GPa and is about two orders of magnitude smaller than the previously published data (1–5 TPa [1–4]). This means that the reinforcement ability of the high Young's modulus of MWNTs is not fully exploited in the CNT-composites. A possible explanation for this is the inability of the model to reflect the three-dimensional curving and coiling of the MWNTs in matrix. The electron micrograph of the composites is presented in Fig. 3. It is evident that CNTs are evenly distributed in the matrix, but most of them are curved. The measured curvature distribution of the CNTs is shown in Fig. 4 with a mean value of 0.0074 nm^{-1} and a standard deviation of 0.0009 nm^{-1}.

Fisher et al. [40] demonstrated using a finite element analysis that even a slight curvature of CNTs significantly reduces the effective reinforcement. Further, the critical length of curved nanotubes could be much longer than that of the straight ones as reported in [37]. It seems clear that the above theory of fiber-reinforced composites cannot be applied directly to the CNT-composites. A further development should at least take the curving and coiling of CNTs into account.

Fig. 5 shows a high resolution TEM picture of MWNTs in LDPE. It is seen from Figs. 3 and 5 that MWNTs and matrix form close interfaces without gaps. This implies a good wetting of MWNTs. The mismatch in the coefficients of thermal expansion between CNT and polymer leads to a compressive radial residual stress along the tube when the polymer is cooled down from its melt [41]. However, no tube collapse in this study was observed, indicating that
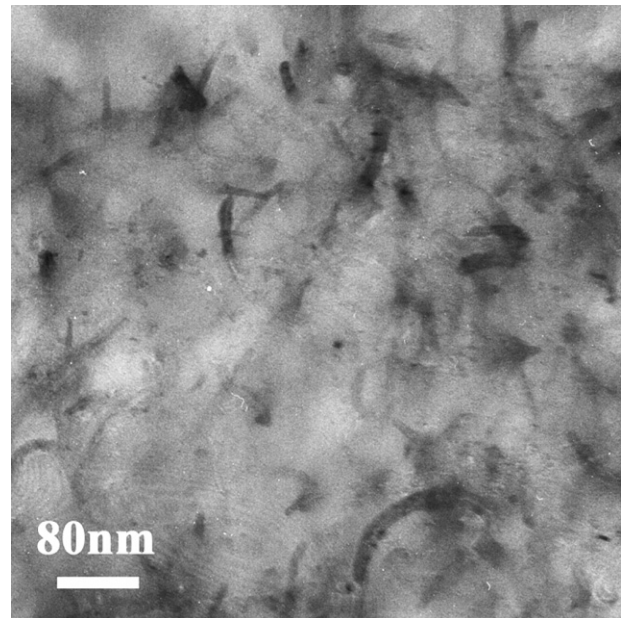

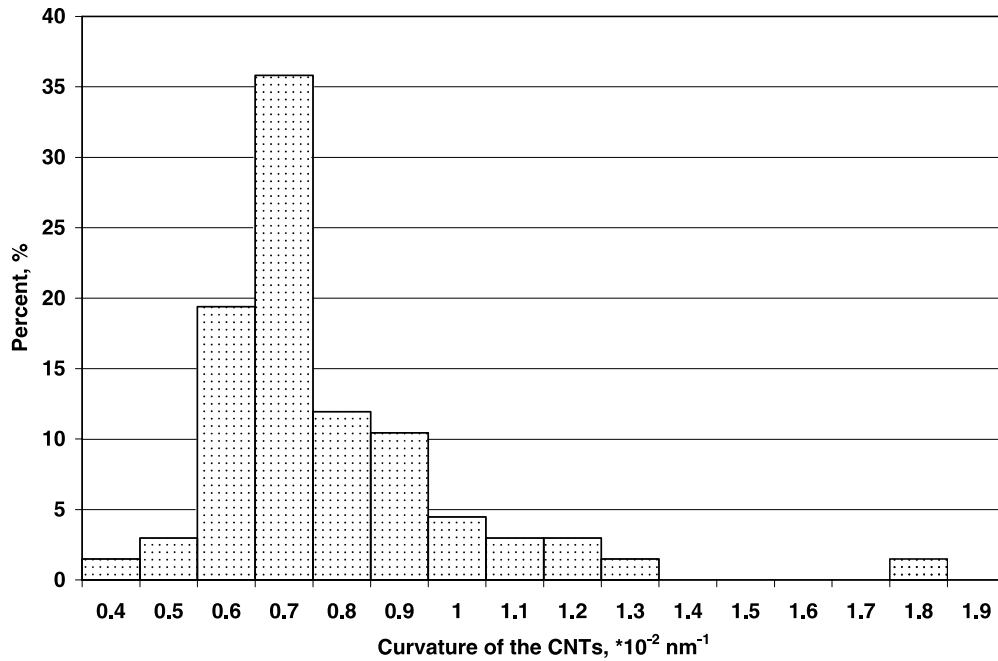Fig. 3. A TEM micrograph of the composite with 3 wt% MWNTs.

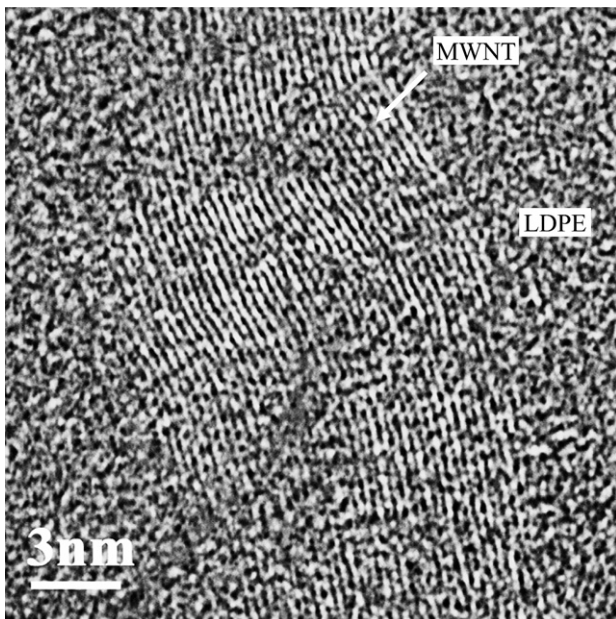Fig. 4. The curvature distribution of the CNTs in the composite.

Fig. 5. A HRTEM image of a MWNT embedded in LDPE.

the stress was below the critical bucking threshold of the CNTs.

3.2. Property during processing

The steady shear viscosity is important to the processing of a composite and is often estimated from the composite's complex viscosity using the Cox-Merx rule. This rule, which is based on empirical observation, states that the steady shear rate viscosity and complex viscosity are closely super-imposable for numerically equivalent values of shear rate and frequency. There are no steady shear measurements reported in polymer matrix composites. However, Kinloch et al. [42] investigated steady shear properties of aqueous MWNT dispersions and found that the Cox-Merz rule is no longer valid for these aqueous MWNT dispersions and the steady shear viscosity is a few orders of magnitude lower than the complex one. A similar phenomenon was also reported in other composite systems [43].

Fig. 6 presents a comparison of the two viscosities of the present CNT composites. It is clear that the Cox-Merz rule holds when the CNT content is low, but becomes inaccurate when it gets higher at which the composite is more solid-like. The composite with 10 wt% CNTs shows a rapid
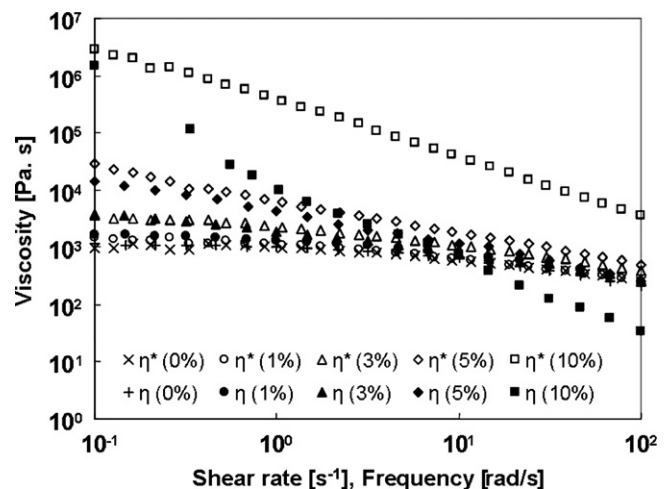

Fig. 6. A comparison of complex and steady shear viscosities.

decrease in steady shear viscosity when the shear rate increases.

Compared with the neat LDPE, It is clear from Fig. 6 that the composites, in particular those with high nanotube contents, have much greater viscosities. A Newtonian plateau at low frequencies is clearly visible for CNT composites with up to 3 wt% nanotubes. At a higher MWNT content, the plateau vanishes and the composites show a strong shear thinning effect. The viscosity almost decreases linearly with increasing the frequency, but the reduction gradient becomes greater when the MWNT content increases. As a result, viscosity difference of the composites from the pure LDPE at the high frequency region becomes small.

$\tan \delta$, where δ is the phase angle, is very sensitive to the structural change of the materials and decreases with increasing CNT content, as shown in Fig. 7. A viscoelastic peak occurs at the frequency of about 1 rad/s and disappears with increasing the CNT content, showing that the material becomes more elastic. This is also a characteristic when a viscoelastic fluid experiences a fluid–solid transition. Gelation as an example for such a fluid–solid transition has been extensively described by Winter at al. [44]. At the transition point, $\tan \delta$ is expected to be independent of frequency. With the present composites, a similar fluid–solid transition is observed, which occurs at a CNT content between 3 and 5 wt%. After the transition, $\tan \delta$ increases with frequency, indicating a dominating elastic response of the material. The CNT content at the transition point can be estimated more accurately from a multifrequency plot, as shown in Fig. 8. All curves intersect at nearly a single point where $\tan \delta$ becomes frequency-independent. Thus the fluid–solid transition composition of the present composites, C_t, is estimated to be 4.8 wt%. Electrical conductivity measurements [45] demonstrated that a continuous CNT network formed throughout the matrix when nanotube content exceeded the transition composition.
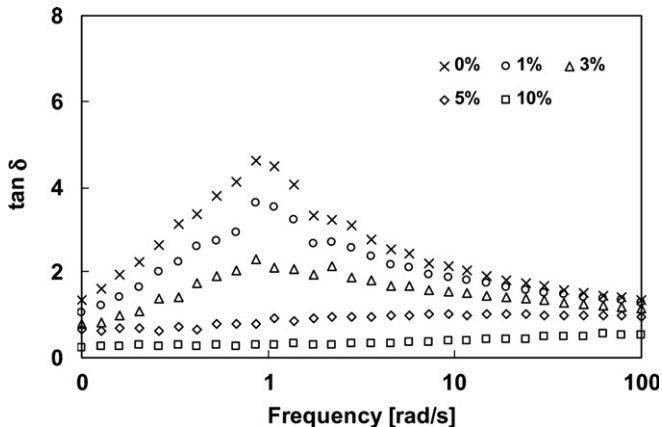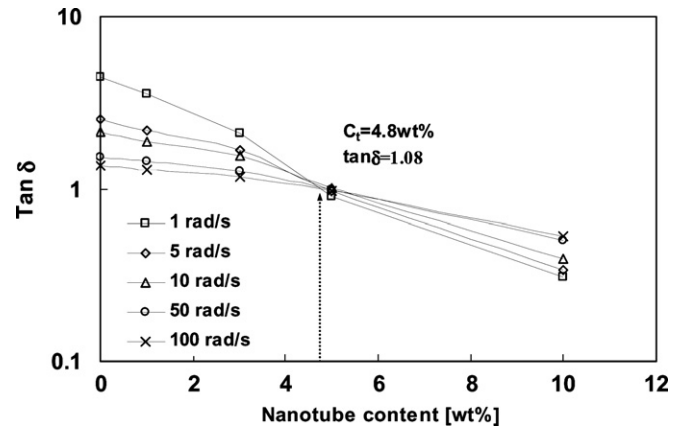

Fig. 8. $\tan \delta$ versus nanotube content at different frequencies.

4. Conclusions

Some important properties of MWNT-reinforced LDPE composites have been studied. The investigation concludes that the mixing and the Cox-Merz rules cannot be applied directly to MWNT composites and a further development is necessary. The study found that the Young's modulus and tensile strength of the composites increase by 85% and 46%, respectively, when 10 wt% MWNTs was added. However, the superior property of high tensile modulus of MWNTs has not been fully utilized in the composites because of the curving and coiling nature of the nanotubes. It was also found that composites experience a fluid–solid transition at a transition composition of $C_t = 4.8$ wt%, at which a continuous MWNT network forms.

Acknowledgments

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Fig. 7. $\tan \delta$ of the composites as a function of sweep frequencies.

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