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Journal Pre-proof

Crystallisation behaviour of composites of HDPE and MWCNTs: the effect of nanotube dispersion, orientation and polymer deformation

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Abstract

Multi-walled carbon nanotubes (MWCNTs) were readily dispersed and distributed in the high density polyethylene (HDPE) matrix and a very low (< 0.3 wt%, 0.17 vol%) rheological percolation threshold obtained. The polymer is seen to coat the MWCNTs, which act as a nucleating agent and induce an oriented nanohybrid shish-kebab (NHSK) crystalline structure, in part an artefact of the injection moulding process. The elastic modulus and yield stress of HDPE increased on addition, but the polymer strain at break increased sharply below percolation before decreasing again above percolation. Addition of MWCNTs, above the percolation threshold, hindered orientation of the polymer chains such that failure occurred before necking during tensile testing, the inclusion of MWCNTs altered the uniaxial deformation behaviour of HDPE. SAXS/WAXS studies on samples post uniaxial drawing revealed that the HDPE and composites of HDPE and MWCNTs developed a highly oriented sheared herringbone lamellar structure. The drawing process also caused surface cavitation and voiding in the composites.

Keywords: Multi-walled carbon nanotubes (MWCNT); high density polyethylene (HDPE); dispersion; orientation, polymer deformation

1. Introduction

The addition of multi-walled carbon nanotubes (MWCNTs) to polymeric matrices continues to gain significant attention within both industrial and academic research communities, due to the prospect of translating their outstanding properties into polymers to form functional composite materials [1]. Carbon nanotubes (CNTs) have an impressive list of properties including, an elastic modulus in the order of 1 TPa [2-6], high mechanical tensile strength [7, 8], extremely large aspect ratio (1,000 - 10,000) [9-11] and surface area per unit volume [8], as well as high thermal and electrical conductivities, e.g. 3000 W/m-K [12] and 10^5 - 10^7 S/m [13], respectively. Reinforcing fillers are widely employed to confer superior properties to polymer matrices [14] and CNTs are ideal functional fillers for such a purpose [2, 15-20].

Composites of polyethylene (PE) and CNTs are considered attractive materials given the low cost of PEs and the enhancement in mechanical and/or electrical properties possible [21-26]. High-density polyethylene (HDPE), in particular, is widely used in industry due to its superior physical and mechanical properties [14, 27, 28]. While HDPE has good wear resistance (fatigue and abrasion properties), a low friction coefficient, high impact strength and moderate stiffness and rigidity [12], the addition of CNTs to HDPE can further enhance rigidity and stiffness along with other properties, at relatively low filler content [29-32]. Various methods have been employed to add CNTs to a polymer matrix, including sonication, solution mixing and *in-situ* polymerization [12], but melt processing remains the most industrially relevant method [20, 33].

The morphology and structure of these composites are determined by the extent of CNT dispersion, distribution and orientation, which in turn influences the composites mechanical properties [11, 20, 34]. Good dispersion and alignment of high aspect ratio CNTs, as well as interfacial stress transfer between the CNT and polymer chains are required for mechanical reinforcement [35, 36]. Despite poor dispersion of pristine CNTs in many poly(olefin)s (due to strong van der Waals interaction between CNTs and weak interaction between PE chains and CNTs [21]), the use of extruder screw speeds between 100 and 500 rpm were found to improve the level of CNT dispersion [37]. Zou et al. [38] found that, at a fixed MWCNT concentration, higher screw speeds increased the dispersion of CNTs in HDPE. More uniform dispersion of MWCNTs in polymers can be achieved at high rotation speeds (involving shorter residence times), as the shear stress applied can reduce the number and CNT agglomerate size. Morcom et al. [39] were able to achieve a high level of MWCNT dispersion in HDPE even at 5 wt% loading, being assessed using SEM and TEM imaging alone.

Typically, electron microscopy (EM) techniques (SEM, TEM) are used to examine the state of CNT dispersion in polymer matrices and, in most instances, only qualitative observations are reported. Unless exhaustive imaging is performed across the length scales then assessment of CNT dispersion using EM is at best representative and at worst misleading [40]. Other techniques should be employed to evaluate CNT dispersion in bulk polymers, such as HDPE. Studies on the melt rheology of composites of HDPE and CNTs are few, despite the relationship between the viscoelastic properties and CNT dispersion in such composites [41]. In particular, the changes in melt viscosity of the composite material can be directly correlated with the CNT dispersion in the matrix [40]. Dynamic oscillation frequency sweep tests can assess the extent of CNT network formation, since at low frequencies, any change in the viscoelastic behaviour of the polymer on addition of CNTs can be readily

detected [42]. The power law index of the viscosity at low frequencies is thus used as a quantitative measure since the steeper this slope, the better the dispersion [37]. It has also been established that the melt rheology will be affected by the level of interactions between CNTs and polymer chains in the melt state [43]. CNTs can form an interconnected network at very low loadings. The lowest CNT concentration at which such networks are formed is known as the percolation threshold [9]. The low percolation thresholds obtainable with CNTs make them superior to other conductive fillers such as carbon black. With the addition of very small amounts of CNTs, it is possible to dramatically change the rheological and electrical properties of the polymer of interest [44]. McNally et al. [24] investigated percolation by studying the melt state oscillatory rheology properties of composites of HDPE and MWCNTs prepared using twin-screw compounding and reported a percolation threshold of 7.5 wt%. El Achaby and Qaiss [45] found a lower rheological percolation threshold, between 1 and 3 wt% MWCNT loading, for composites of HDPE and MWCNTs. Other studies using dynamic rheology measurements on similar composite systems reported the formation of a MWCNT network at loadings of > 2.0 wt% [46].

It is now understood that MWCNTs can have a strong nucleating effect on semi-crystalline polymers, including poly(olefin)s, inducing different crystal polymorphs, increasing the crystallisation temperature (T_c), altering the kinetics of crystallisation and crystalline content [47-51]. This phenomenon has been studied widely for composites of MWCNTs and polypropylene, but much less so when the matrix is HDPE, no doubt due to very fast crystallisation rate of HDPE. Ultimately, such changes in the crystallisation behaviour of HDPE are directly related to the extent of MWCNT dispersion and orientation in the matrix. Yang *et al.* showed that injection moulded bars of composites of HDPE and MWCNTs had a range of crystalline morphologies through the bar thickness, determined from X-ray and SEM techniques [52]. The injection moulding process orients the MWCNTs

in the shear flow direction at the surface of the bar and leads to a nanohybrid shish-kebab (NHSK) morphology, where the MWCNTs act as shish and the HDPE chains crystallize outwards epitaxially perpendicular to the MWCNT as the lamellar kebabs. However, there have been few systematic studies which directly correlate MWCNT dispersion in HDPE when measured in bulk, that is, using oscillatory rheology measurements and X-ray scattering techniques to investigate the crystallisation behaviour in such composites. In this paper, we report on the use of rheological and microscopy techniques to determine the MWCNT dispersion and rheological percolation in HDPE. Furthermore, we have correlated the crystalline structure development and molecular orientation as a consequence of the initial injection moulding process and then during solid state uniaxial deformation in the composites. Ultimately, the crystalline morphology and molecular orientation of the HDPE-MWCNT composites influence the rheological properties and processability of the polymer. Hence, understanding the relationship between the rheological behaviour and crystalline morphology will allow optimisation of these properties, leading to greater application of these materials.

2. Experimental

2.1 Materials

High-density polyethylene resin (HDPE), grade HMA 025, with a melting point of 135 °C, density of 0.964 g cm⁻³ and a melt flow index (MFI) of 8 g/10 min at 190 °C/2.16 kg was purchased from ExxonMobil in pellet form. Non-functionalised commercially available thin multi-walled carbon nanotubes (MWCNTs) produced by catalytic carbon vapour deposition (CCVD), with an average diameter of 9.5 nm and average length of 1.5 µm (grade NC7000, purity: > 90%) were purchased from Nanocyl S.A., Belgium and used as received. The

density of the MWCNTs was reported as 1.75 g/cm^3 [53], with a surface area of between 250 and $300 \text{ m}^2/\text{g}$ [54].

2.2 Composite preparation

HDPE pellets were first ground to a fine powder (μm size), using a SPEX® SamplePrep Freezer Mill 6870 (Stanmore, UK), and dried in a vacuum oven at 40°C for 12 h to improve dry mixing with the MWCNTs. Care was taken to ensure the cryo-grinding process did not degrade the HDPE and this was monitored using Fourier transform infrared (FTIR) spectroscopy. Composites were prepared by dry blending HDPE and MWCNTs (both in powder form) with MWCNTs loadings of 0.01 wt% ($\sim 0.01 \text{ vol}\%$), 0.1 wt% ($\sim 0.06 \text{ vol}\%$), 0.3 wt% ($\sim 0.17 \text{ vol}\%$), 0.5 wt% ($\sim 0.28 \text{ vol}\%$), 1 wt% ($\sim 0.55 \text{ vol}\%$), 3 wt% ($\sim 1.68 \text{ vol}\%$), and 5 wt% ($\sim 2.82 \text{ vol}\%$). The dry mix was fed in to a 16 mm co-rotating parallel twin-screw extruder, PRISM ThermoFischer Scientific, with a temperature profile along the barrel from 135 to 155°C at the die end and a screw speed of 100 rpm. Neat HDPE was processed using the same conditions as the composite samples as a control. The extruded strands were pelletized using a laboratory pelletizer and the pellets were dried ($\sim 8 \text{ h}$) prior to moulding. The pellets were injection-moulded using a piston injection moulding system, a Thermo-Scientific Haake™ MiniJet Proto to produce standard dumbbell-shaped tensile bars conforming to ASTM D638 V and circular disks of 25 mm diameter and 1.65 mm thickness for oscillatory rheology measurements. The moulding was carried out using an injection temperature of 160°C , injection pressure of 450 bar with a mould temperature of 50°C .

2.3 Characterisation

2.3.1 Oscillatory Rheology

The rheological behaviour of the composites was studied using a Thermo Scientific Haake MARS III rheometer equipped with a 25 mm parallel plate geometry with a 1 mm gap size, in an air atmosphere. Two distinct dynamic mechanical tests were performed. Firstly, oscillatory amplitude stress sweeps were undertaken over a stress range of 0.1 to 100 Pa at a fixed temperature and frequency of 160 °C and 1 Hz, respectively. This test indicated the region in which deformation was small enough for the storage modulus (G') to be independent of deformation. Initially, each moulded disk was allowed to acclimatise between the plates at 160 °C, allowing the sample to melt before being trimmed to size (from a thickness of 1.65 mm to 1 mm) with a sharp blade prior to commencing the test. Second, the 1 mm thick sample was then, subjected to dynamic oscillation frequency sweeps in the range 0.1-100 Hz, under a controlled stress at 100 Pa.

2.3.2 Scanning electron microscopy (SEM)

The extent of MWCNTs dispersion in the HDPE matrix was examined qualitatively using a Zeiss sigma field emission SEM fitted with a Gemini column. For measurements using the InLens detector, a working distance of 2.5 mm was used and an acceleration voltage of 3 kV. Prior to imaging, the sample disks were cryo-fractured after placing them in a liquid nitrogen bath for ~5 hours. The fractured surfaces were mounted on aluminium stubs and sputter coated (~10 nm) using an Au/Pt metal target (Cressington 108 auto) under a weak argon atmosphere. Samples taken from the neck portion of the tensile dumbbells drawn during the tensile testing were also imaged by SEM.

2.3.3 Differential scanning calorimetry (DSC)

The thermal behaviour of HDPE and the composites of HDPE and MWCNTs was studied using a Mettler Toledo (DSC1, model 700, 400W) equipped with FRS5 thermocouple sensor, robotic sample changer and evaluated using a STARe Version 15.01 software package. Non-

isothermal scans were performed under nitrogen ($20 \text{ cm}^3 \text{ min}^{-1}$). Samples $5 \pm 1 \text{ mg}$ were inserted into aluminium pans with pierced lids, heated from $25 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$ at a heating rate of 10 K/min (first heating), and held at this temperature for 60 s to eliminate any thermal history. Samples were then cooled to $25 \text{ }^\circ\text{C}$ at 10 K/min (first cooling), held at $25 \text{ }^\circ\text{C}$ for 60 s , before being re-heated (second heating) and cooled using the same protocol as the first cycle. Each measurement was repeated in triplicate. The crystallinity $X_{c(\text{DSC})}$ was determined by dividing the enthalpy of melting ΔH_m for the sample by the enthalpy of melting for a theoretically 100% crystalline HDPE [55], as shown in Equation 1:

$$X_{c(\text{DSC})} = \left(\frac{\Delta H_m}{(1 - W_f) \Delta H_{100}} \right) \times 100 \quad (1)$$

where, W_f is the weight fraction of MWCNTs and ΔH_{100} is the melting enthalpy of a theoretically 100% crystalline HDPE (293.6 J/g).

2.3.4 Tensile Testing

Tensile testing at room temperature of neat HDPE and all composites was performed on a Shimadzu Autograph AGS-X fitted with a 10 kN load cell, equipped with a twin TRViewX non-contact digital video extensometer (500 and 120 mm field of view), using a Trapezium X Version 1.4 software package. The standard dumbbell-shaped test samples (ASTM D638 V) with a gauge length of 7.62 mm were deformed using a constant crosshead speed of 10 mm min^{-1} , to determine the modulus, with an extensometer fitted using a 25.4 mm gauge length (i.e. distance between the grips). The tensile modulus was reported as the secant of the initial linear part of the stress-strain curve. A linear regression technique was utilised to define the slope of the stress-strain curve in the initial region before yield, taken to be a strain range of 0.05% to 0.25% determined from BS EN ISO 527-1:2012. A minimum of seven replicates of each sample were tested and the average values reported with error bars where appropriate.

2.3.5 Small- and Wide-Angle X-ray scattering (SAXS/WAXS) measurements

The SAXS/WAXS data was collected using a Xenocs Xeuss 2.0 X-ray instrument operating with a Cu-K α source ($\lambda = 1.54 \text{ \AA}$). Simultaneous 2D SAXS/WAXS data were collected on Pilatus 300K and Pilatus 100K detector systems, respectively, calibrated with silver behenate. The SAXS detector was positioned at a distance of 2.48 m from the sample. An evacuated chamber was placed between the sample and SAXS detector to reduce air scattering and absorption. The WAXS detector was positioned in the evacuated sample chamber at a distance of 162 mm. The undrawn samples were positioned vertically in the instrument's evacuated sample chamber and static 2D SAXS/WAXS data was taken at an acquisition time of 120s ($\lambda = 1.54 \text{ \AA}$). 2D SAXS/WAXS data of the drawn samples were taken at the neck section of the sample at an acquisition time of 60 s.

X-ray diffraction (XRD) data were collected using a PANalytical Empyrean diffractometer with a Co-K α source ($\lambda = 1.79 \text{ \AA}$) operating at 40 kV and 40 mA. The samples were mounted in flat circular holders and rotated during measurement (0.5 s^{-1}). Data was collected on a PIXcel detector system (1D mode) with a continuous scanning mode over a scattering angle range of $2\theta = 5^\circ - 60^\circ$.

2.3.5 SAXS/WAXS data analysis

All SAXS/WAXS data were normalised for sample thickness, transmission and background scattering. X-ray data reduction and analysis was performed using the Xeuss 2.0 instrument data processing and analysis software. 2D SAXS/WAXS data were reduced to 1D scattering profiles of intensity (I) versus scattering vector (q) for SAXS and 2θ for WAXS (where $q = (4\pi/\lambda) \sin(\theta)$, 2θ is the scattering angle and λ is the X-ray wavelength), by sector averaging around the beam stop by a fixed angle and radius, q . To estimate the relative orientation azimuthal 1D profiles were obtained from the 2D SAXS data, where the angular variation in intensity, $I(q, \varphi)$, was obtained at a fixed radius q , over an azimuthal angle, φ ,

range of 0-360°. The two peaks from the 1D azimuthal profiles were then fitted using Lorentzian functions to obtain the average full-width half-maximum (FWHM). Correlation functions were computed on the 1D SAXS profiles using the Corfunc software [56] incorporated into the SasView SAXS analysis package [57]. The 1D correlation function, $\gamma(R)$, is expressed as:

$$\gamma(R) = \frac{1}{Q_s} \int_0^\infty I(q) q^2 \cos(qR) dq \quad (2)$$

where, $I(q)$ is the scattering intensity and Q_s is the experimental invariant obtained from the 1D SAXS profile between the experimental limits of q_1 (first data point) and q_2 (region where $I(q)$ is constant). The scattering invariant is expressed as:

$$Q_s(t) = \int_0^\infty q^2 I(q) dq \approx \int_{q_1}^{q_2} q^2 I(q) dq \quad (3)$$

The 1D correlation functions were obtained from the extrapolation of the 1D SAXS data ($q \rightarrow \infty$) according to Porod's law [58] and a Guinier model back extrapolation ($q \rightarrow 0$) [59]. The correlation function analysis assumes an ideal two-phase lamellar morphology [59, 60] where various parameters including the long period, L_p , crystalline layer thickness H_b , and estimated local percent crystallinity X_c [61] can be extracted.

3. Results and Discussion

3.1 Rheological measurements

In the first instance, the linear viscoelastic behaviour of the composites was investigated, and the oscillatory rheology measurements performed were used to assess the extent of MWCNT dispersion in the HDPE matrix and to determine if a rheological percolation was obtained. The formation of a percolated system can be detected by examining the changes in complex viscosity ($|\eta^*|$), storage modulus (G') and loss modulus (G'') as a function of frequency [24, 62-64]. The change in rheological behaviour of the MWCNT filled HDPE and

formation of a percolated filler network results in the composites displaying ‘pseudo-solid’-like behaviour, manifested by an increase of several orders of magnitude in $|\eta^*|$ and G' as a function of angular frequency.

Figures 1(A) and 1(B) clearly show a dramatic increase in both $|\eta^*|$ and G' with increasing MWCNTs loading at low frequencies.

Figure 1. Variation in (A) complex viscosity $|\eta^*|$ and (B) storage modulus (G') as a function of frequency for unfilled HDPE and MWCNT filled HDPE and, (C) Cole-Cole plot (G' versus G'') and (D) Van-Gurp Palmen plot (phase angle (δ) versus complex modulus).

From the complex viscosity ($|\eta^*|$) versus frequency (ω) plot (Figure 1(A)), the complex viscosity increases slightly as the concentration of MWCNTs increases up to 0.3 wt%, over the frequency range investigated. However, in the low-frequency range (i.e. $<10 \text{ rad s}^{-1}$), at MWCNT concentrations between 0.3 wt% ($\sim 0.17 \text{ vol\%}$) and 0.5 wt% ($\sim 0.28 \text{ vol\%}$), $|\eta^*|$

increases by over two orders of magnitude and by almost three orders for 5 wt% (~ 2.82 vol%) MWCNTs. As expected for MWCNT loadings above 0.3 wt% there was also a monotonic increase in G' at low frequencies, Figure 1 (B). At 0.1 rad s^{-1} the change in G' was over four orders of magnitude indicating the formation of a MWCNT percolated network [41]. At higher frequencies ($>10 \text{ rad s}^{-1}$), the curves tended to plateau, again indicative that the MWCNTs had formed a percolated network in the HDPE matrix restricting polymer chain mobility; the composite now displaying 'pseudo-solid-like' behaviour [24, 62, 65-67]. Furthermore, G' becomes almost independent of angular frequency (non-terminal low frequency behaviour) as MWCNT loading increases at low frequencies, again indicative of the transition from 'liquid-like' to 'solid-like' viscoelastic behaviour in composites and attributable to the interconnected MWCNT network restraining the long-range motion of the polymer chains [41, 43]. In contrast, at high frequencies ($>10 \text{ rad s}^{-1}$), the effect of the MWCNTs on the rheological behaviour is relatively weak, suggesting they do not significantly influence the short-range dynamics of the HDPE chains, especially on length scales comparable to the entanglement length.

It is more appropriate to assess if a rheological percolation has been attained by constructing Cole-Cole and Van-Gurp Palmen plots, see Figure 1(C) and 1(D). From the Cole-Cole plot, the effect of MWCNT addition on the viscoelastic behaviour is shown from a divergence from the linear relationship between $\log G''$ and $\log G'$. It can be clearly seen there is a significant divergence which first occurs for MWCNT loadings between 0.3 wt% (~ 0.17 vol%) and 0.5 wt% (~ 0.28 vol%). This observation is confirmed from the Van-Gurp Palmen plot (δ versus $|G^*|$), Figure 1(D), where a significant decrease in phase angle (δ) is obtained for MWCNT loadings ≥ 0.5 wt% (~ 0.28 vol%) MWCNTs; a consequence of the network structure relaxing differently and with varying relaxation times. Interestingly, despite numerous replicate measurements and from different batches, δ increased again going from 3

wt% to 5 wt% MWCNT loading, presumably due to the greater difficulty uniformly dispersing MWCNTs in the polymer melt at higher loadings.

3.2 SEM analysis of MWCNT dispersion in HDPE

Qualitatively, the extent of MWCNT dispersion was examined using scanning electron microscopy (SEM) at different magnifications on cryo-fractured surfaces of specimens. Representative SEM images of the composites at different filler content are shown in Figure 2.

Figure 2. Representative high magnification SEM images of the fractured surfaces of composites of HDPE with (A-B) 3 wt% and (C-D) 5 wt% MWCNTs.

From the SEM micrographs, homogeneous dispersion of the MWCNTs in HDPE was obvious and no large MWCNT agglomerations observed. From Figure 2, examination of the

fractured surface also revealed the HDPE had coated many of the MWCNTs protruding from the surface. A thin layer of polymer appears to coat or wrap around the MWCNTs creating a polymer sheath surrounding the MWCNTs (as highlighted by the red circle in Figure 2(A)), a similar morphology has been observed previously from etched injection moulded or drawn composites of HDPE and MWCNTs [68]. Such morphology should provide a route for effective load transfer to the MWCNT network and result in a more uniform stress distribution [35]. Critically, the inclusion of MWCNTs in HDPE and the formation of a trans-crystalline polymer layer on the surface of the MWCNTs will alter the crystallisation behaviour of the HDPE and consequently mechanical properties of the composite. Therefore, the crystallisation behaviour of the composites of HDPE and MWCNTs was studied using a combination of thermal (DSC), X-ray diffraction (XRD) and X-ray scattering (WAXS/SAXS) techniques.

3.3 Thermal analysis

Thermal analysis was carried out using DSC to determine the melting temperature T_m , crystallisation temperature T_c , melting enthalpy ΔH_m and bulk crystallinity $X_{c(DSC)}$ of neat HDPE and composites of HDPE and MWCNT, see Table 1.

Table 1. Thermal parameters determined from DSC measurements for neat HDPE and composites of HDPE and MWCNTs.

MWCNT loading /wt%	$T_m/^{\circ}\text{C}$	$T_c/^{\circ}\text{C}$	$\Delta H_m/\text{J g}^{-1}$	$X_{c(DSC)}/\%$
0	134.8	120.0	221.6	75.5
0.01	135.4	121.1	216.4	73.7
0.1	135.3	121.0	222.5	75.9
0.3	135.9	122.0	218.6	74.7

0.5	136.3	123.3	218.8	74.9
1	136.7	121.5	216.4	74.4
3	139.1	118.7	215.2	75.6
5	140.2	117.8	210.4	75.4

Figure 3 shows the thermograms of the first cooling and second heating cycles. In Figure 3(A), for neat HDPE, $T_c = 120^\circ\text{C}$, indicated by the vertical line in the figure. With the addition of MWCNTs T_c tends to shift to a slightly higher temperature with up to ~0.5 wt% loading but, for higher loadings, T_c begins to decrease (allowing for instrument error) compared to that of neat HDPE. The increase in T_c is indicative of the heterogeneous nucleating effect of the MWCNTs [69-73] at low loading in the HDPE matrix. However, as the MWCNT loading increases T_c tends to decrease, which is due to the confinement effect of the formation of a MWCNT network [71, 72], which inhibits nucleation of the polymer. The formation of a percolated MWCNT network in the HDPE matrix at loadings approaching 0.5 wt% was confirmed from oscillatory rheology measurements. Similarly, in Figure 3(B), T_m is seen to increase slightly on the addition of MWCNTs, again up to ~0.5 wt% loading, and then begins to decrease, to lower than that of neat HDPE (120°C). The initial increase in T_m is indicative of the increased nucleation of HDPE at low MWCNT loadings. This increase in T_m , can be attributed to the well dispersed MWCNTs in the HDPE matrix resisting the conduction of heat to the crystallites until the heat flow is enough to melt the crystallites at higher temperatures [74, 75]. As the MWCNT loading is increased, the network formation will allow the conduction of heat to melt the crystallites at lower temperature.

Figure 3. DSC thermograms for neat HDPE and composites of HDPE and MWCNTs; (A) cooling cycle, (B) heating cycle.

The T_c and T_m peaks in Figure 3, show significant broadening with increasing MWCNT content, this behaviour can be related to the size distribution of the crystallites. The broader peaks indicate a wider distribution of crystallite sizes, which melt over a wider range of temperatures compared to the narrower peak for neat HDPE, indicating a narrower range of crystallite sizes [70, 71]. Finally, from Table 1, the bulk crystallinity $X_{c(DSC)}$, determined from the second heating cycle, generally decreases very slightly on addition of MWCNTs. The unexpected reduction in crystallinity observed (an increase of polymer crystallinity is typically claimed in literature with addition of CNTs [55]), can be attributed to the fact that

the MWCNT network hinders crystal growth, by breaking the continuity of the polymer matrix while preventing formation of large and uniform crystallites. Here, the MWCNTs act as heterogeneous nucleating agents for HDPE crystallization, but the reduction in crystallinity observed here may be related to the formation of smaller and less perfect crystallites [76].

Hence, to investigate the effect of adding MWCNTs on the crystallite size and crystalline content of HDPE, X-ray scattering methods were employed with, the specific aim of giving further insight into the morphology and crystalline structure of the HDPE matrix and the nucleating effects of MWCNTs.

3.4 Small- and wide-angle scattering (SAXS/WAXS) analysis

Figure 4 shows the 2D SAXS/WAXS patterns of the undrawn HDPE and composites of HDPE and MWCNTs (columns two and three) and column four gives a physical interpretation of the lamellar macro-morphology structure from the SAXS/WAXS patterns. The SAXS pattern for neat HDPE shows an isotropic ring of intensity which is indicative of a randomly oriented crystalline lamellar structure [77]. Similarly, the WAXS pattern shows several rings, the two strongest are the (110) and (200) reflections of the orthorhombic unit cell of HDPE [78]. The WAXS pattern indexing also shows other strong reflections attributed to the (210) and (020) basal planes. The SAXS patterns of the composites of HDPE and MWCNTs are quite different from the unfilled HDPE homopolymer. At MWCNT loadings between 0.01 wt% and 0.5 wt% the SAXS patterns show two features; an isotropic ring of scattering and concentrated spots and arcs of intensity as well, superimposed on the ring. The isotropic ring again indicates the randomly oriented crystalline lamellar structure of the HDPE, but the concentrated spots and arcing suggest some orientation of the lamellar structure, leading to a fibril or 'shish-kebab' type of structure [77], which is usually seen in polymers having undergone deformation [79, 80]. Here, the CNTs can act as the shish

offering heterogeneous nucleation sites for the HDPE polymer chains to wrap around, and crystallites (kebabs), grow epitaxially outwards. This structure is often termed a nanohybrid shish-kebab (NHSK) morphology and is often seen during solution crystallization of the polymer on to the surface of the CNT [81].

Figure 4. 2D SAXS/WAXS patterns for undrawn HDPE and composites of HDPE and MWCNTs, including crystalline lamellar structure interpretation.

However, we have also observed this NHSK structure in melt-processed composites of PET and MWCNTs [80, 82, 83] where the MWCNTs have been aligned in the polymer during extrusion, and act as oriented nucleation sites for the crystallization of the polymer [84]. Here, for the composites of HDPE and MWCNTs the MWCNTs have some residual orientation from the initial injection moulding process of the samples, where they act as stiff

rod-like structures in the polymer melt and do not relax in the mould once aligned in the polymer matrix, even on cooling. The HDPE chains in close proximity of the oriented MWCNTs can then crystallize epitaxially out from the CNT surface. The HDPE matrix not in near contact with a MWCNT will crystallize as an un-oriented lamellar structure.

To investigate the orientation of the shish-kebab/lamellar stack structure in the composites of HDPE and MWCNTs, 1D azimuthal profiles were obtained from the 2D SAXS patterns and the FWHM obtained from the averaged fits of the peaks in the 1D azimuthal profiles.

Figure 5. (A) 1D Azimuthal profiles from SAXS of undrawn HDPE and composites of HDPE and MWCNTs and, (B) change in FWHM from 1D azimuthal scans of the HDPE-MWCNT composites.

Figure 5(A), shows the 1D azimuthal profiles of the samples and the averaged widths of the two peaks for each sample are, shown in Figure 5(B). Lower values of FWHM indicates a higher relative orientation of the lamellar stacks. The unfilled HDPE did not show any preferred orientation so the azimuthal 1D profile is flat. However, for the composites of HDPE and MWCNTs there is preferred orientation as shown by the development of the peaks in the 1D azimuthal profiles. The orientation of lamellar/shish-kebab stacks are greatest for the lowest MWCNT loading, up to 0.1 wt%. Stack orientation decreases as the content of MWCNTs increase up to 1 wt%. As the morphology changes to a lamellar structure at $\text{MWCNT} > 1 \text{ wt\%}$, the orientation starts to increase slightly again and then plateaus. At low MWCNT loadings of between 0.01 - 0.1 wt% the MWCNTs being more isolated from each other [71], can easily be oriented in the polymer matrix during melt processing (moulding) and do not relax on cooling, so an oriented nanohybrid shish-kebab (NHSK) structure is formed; confirmed by the 2D SAXS patterns (Figure 4). As the MWCNT loading increases the nanotubes entangle more and agglomerate and, are more difficult to orient during the moulding process, so the shish-kebab morphology is less oriented. This structure then develops into an interconnected lamellar structure [69, 71] with increasing MWCNT loading $> 1 \text{ wt\%}$.

To investigate the crystallite lattice structure of the composites, 1D WAXS profiles were obtained from the 2D WAXS patterns (in Figure 4), along with the XRD profiles. Figure 6(A), shows the 1D WAXS profiles of the moulded HDPE and composites of HDPE and MWCNTs. The 1D WAXS profiles of all samples show two intense peaks which correspond to the (110) and (200) orthorhombic unit cell peaks of polyethylene [85] (as indexed in Figure 6A). There is no significant difference in the position of these peaks with increasing MWCNT loading thus it can be, concluded that the MWCNTs do not influence or modify the orthorhombic unit cell of HDPE. Furthermore, there is no real evidence of the

(002) peak at 26° , which corresponds to the d -spacing between graphene sheets of $3.42 \text{ \AA}$ [86, 87]. Other MWCNTs peaks are in similar positions to the HDPE peaks so cannot be confirmed as extinct or not, i.e. (100) at 43° and (101) at 44° corresponding to the in-plane graphitic structure and lateral spacing of graphite layers [87]).

Figure 6. (A) 1D WAXS profiles of moulded HDPE and composites of HDPE and MWCNTs and (B) XRD profiles of neat HDPE and a composite of HDPE and 5 wt% MWCNTs.

In Figure 6(B), the XRD profiles of neat HDPE and the 5 wt% composite are shown. From the XRD profiles there is some evidence of the (010) monoclinic polyethylene peak (labelled as (010)m) therefore, there is some mixture of unit cells in the samples, but other monoclinic peaks are absent, so this phase is only a very minor component [88] and is not influenced by

the addition of MWCNTs to the polymer matrix. There is a very broad shoulder at $\sim 30^\circ$, which can possibly be assigned to the (002) graphitic sheet spacing [87, 89], but again this is very weak. The lack of distinct strong MWCNT peaks in both the WAXS and XRD data for the composites is attributed to the good dispersion of the MWCNTs in the polymer matrix [89, 90].

To investigate the shish-kebab and lamellar macrostructure of the moulded HDPE and composites, 1D SAXS profiles were obtained from the 2D SAXS patterns and are shown in Figure 7. All samples show a main SAXS peak at $q \sim 0.027 \text{ \AA}^{-1}$ which represents the average length of the crystalline and amorphous regions of the lamellar stacks in the polymer, or long period (L_p). As the weight fraction of MWCNTs is increased in the composites, the low angle scattering intensity ($q < 0.02 \text{ \AA}^{-1}$) increases which is attributed to scattering from the MWCNTs [69, 91].

Figure 7. 1D SAXS profiles of neat HDPE and composites of HDPE and MWCNTs with up to 5 wt% MWCNTs. Vertical dashed line indicates the peak maximum at $0.027 \text{ \AA}^{-1}$.

From the 1D SAXS profiles, correlation functions were obtained to investigate the crystalline morphology development in the samples. Several parameters were extracted from the correlation functions, such as long period (L_p), crystalline layer thickness (H_b) and local crystallinity (X_c) and the data is collated in Table 2. The L_p , tends to increase from a MWCNT loading of > 0.5 wt%, which is confirmed by the shift to low q in the 1D scattering profile (Figure 7). Similarly, H_b , tends to increase slightly and then decreases with MWCNT loadings of > 0.3 wt%. As the L_p is the average length scale of the crystalline layer plus amorphous layer, the increase (and as such decrease in H_b), indicates that the amorphous layer increases with increasing MWCNT loading. This is mirrored with the decrease in X_c , where a reduction in the local crystallite size follows a decrease in crystallinity. Hence, from these results the MWCNTs at low loadings (up to 0.1 wt%) can have a nucleating effect on HDPE increasing the crystallite size and crystallinity slightly. However, at MWCNTs loadings > 0.3 wt% and above, there tends to be a reduction in the crystallite size and local crystallinity, indicating that the MWCNTs when more concentrated in the matrix, hinder nucleation and growth of crystallites [80]. This is also seen in the DSC data, where the bulk crystallinity ($X_{c(DSC)}$), is reduced at higher MWCNTs loadings due to the confinement effect of the MWCNTs.

Table 2: Correlation function parameters extracted from the 1D SAXS profiles of neat HDPE and composites of HDPE and MWCNTs.

Sample	$L_p/\text{\AA}$	$H_b/\text{\AA}$	$X_c/\%$
HDPE	203	53	26
MWCNT 0.01 wt%	204	54	27
MWCNT 0.1 wt%	201	54	27
MWCNT 0.3 wt%	205	51	25
MWCNT 0.5 wt%	207	49	24

MWCNT 1.0 wt%	204	41	20
MWCNT 3.0 wt%	224	38	17
MWCNT 5.0 wt%	215	35	16

3.5 Mechanical analysis

The change in crystallization behaviour of HDPE on inclusion of MWCNTs is expected to alter the mechanical properties of the HDPE matrix. The variation in the tensile mechanical properties of HDPE as a function of MWCNT loading was studied under static mechanical tensile loading, representative stress-strain curves are shown in Figure S1. Additionally, the average values (from 7 replicates), for the elastic modulus (Young's modulus), tensile strength (yield stress, σ), strain at tensile strength (elongation at yield) and tensile strain at break (elongation at break, ϵ) for the composites are listed in Table 3.

Table 3. Changes in tensile mechanical properties for unfilled HDPE and composites of HDPE and MWCNTs.

MWCNT loading /wt%	Young's Modulus /GPa	Tensile Strength /MPa	Strain at Tensile Strength /%	Tensile strain at break /%
0	1.69 $\pm$ 0.16	30.78 $\pm$ 5.63	9.83 $\pm$ 1.02	109.35 $\pm$ 48.66
0.01	1.15 $\pm$ 0.39	28.70 $\pm$ 0.99	10.12 $\pm$ 2.60	133.25 $\pm$ 35.15
0.1	1.49 $\pm$ 0.22	28.11 $\pm$ 2.63	10.98 $\pm$ 0.62	190.76 $\pm$ 59.66
0.3	1.64 $\pm$ 0.14	29.55 $\pm$ 4.02	11.73 $\pm$ 0.71	157.73 $\pm$ 82.02
0.5	1.53 $\pm$ 0.13	28.10 $\pm$ 0.96	11.13 $\pm$ 0.46	107.85 $\pm$ 22.60
1	1.75 $\pm$ 0.10	30.87 $\pm$ 1.05	10.23 $\pm$ 0.48	78.66 $\pm$ 53.85

3	1.96 ± 0.13	34.97 ± 0.63	9.62 ± 0.34	50.12 ± 5.72
5	1.81 ± 0.09	33.32 ± 0.81	10.33 ± 0.38	72.78 ± 19.03

From the stress versus strain curves for the composites (Figure S1), it can be observed that the composite samples tend to reach the upper yield point (yield stress), drawing through its neck (where the sample extends elastically), and reaches the lower yield point, after which it draws until break. Necking of the composite samples is followed by a plateau region that extends until the breaking point due to strain induced crystallisation of the polymer resulting in the material hardening. Overall, a modest improvement in the mechanical properties of HDPE was obtained on inclusion of MWCNTs. Minor effects of increased stiffness and reduced strength are commonly reported in the mechanical properties of composites after adding reasonably low concentrations of fillers in polymers [92]. Effective reinforcement in composites requires individual nanotubes to be coated with polymer in order to ensure load transfer from matrix to nanotube [39]. The greatest increases in the elastic modulus ($\uparrow 16\%$) and yield stress ($\uparrow 14\%$) were observed for composites containing 3 wt% MWCNTs. The presence of MWCNTs stiffens the polymer matrix, resulting in increased values for elastic modulus relative to the unfilled HDPE [75]. Although less crystalline content in composites support higher elongations [93], the trends of the elongation at yield and even more so the elongation at break versus weight percent of MWCNTs (also reported in Figures S2(C) and S2(D), respectively), showed a rather interesting behaviour. The results revealed a steep increase in elongation at break (i.e. tensile strain at break) moving from neat polymer to composites with filler loadings up to 0.5 wt%, while further increases of MWCNTs negatively affected the ductility of composites.

Generally, addition of rigid particles to a polyolefin matrix reduces the elongation at break [94]. Reductions in elongation at break are reported to be dependent on the segmental

flexibility of the polymer chains [95]. The conformational change of polymer chains restricted by the presence of MWCNTs should induce a decline in elongation at break. Surprisingly, inclusion of MWCNT content between 0.01 and 0.3 wt% increased the amount of deformation achieved by the composites before failure. Stabilisation and growth of a neck occurred in the composites at low MWCNT content up to 0.3 wt%, indicating that polymer chains in the amorphous regions were still able to orientate and stretch in the direction of the applied tensile stress despite the presence of the MWCNTs. Thus overcoming the increase in stress due to the reduced cross-sectional area. However, addition of MWCNTs above the percolation threshold hindered the orientation of the polymer chains to such an extent that failure occurred before this neck could stabilize. The presence of a MWCNT-polymer network formed provides a high resistance to polymer chain orientation as, fundamentally, the rheological percolation threshold is determined by polymer chain immobility [24]. The strain at break (ϵ) of HDPE steadily increases by 22%, 74% and 44% for the composites with MWCNT content of 0.01, 0.1, and 0.3 wt%, respectively. The highest increase in ϵ was achieved for the composite with 0.1 wt% MWCNTs. In contrast, on inclusion of 3 wt% MWCNTs, ϵ is reduced by 54% compared to the neat polymer. Addition of MWCNT to HDPE increased the ductility of the matrix. This was quantified by integrating the area under the stress-strain curves and, determining the ratio of plastic to elastic energy, see Table 4. This ratio increases with increasing MWCNT loading. Several different processes can come into play (e.g. spherulite and/or lamella slip and breakup in crystalline polymers in addition to amorphous chain segment reorientation) [96]. It is clear from the necking behaviour observed during tensile testing that the, inclusion of MWCNTs alters the uniaxial deformation behaviour of HDPE.

Table 4. Estimated values of tensile toughness, resilience and the ratio between tensile toughness and resilience (i.e. ratio of plastic to elastic energy) for neat HDPE and composites of HDPE and MWCNTs.

MWCNT wt%	Tensile Toughness GPa	Resilience GPa	Ratio of Plastic:Elastic Energy
0	2.01	0.16	12.6
0.01	2.31	0.19	12.2
0.1	2.58	0.20	12.9
0.3	2.61	0.19	13.7
0.5	2.63	0.17	15.5
1	2.89	0.20	14.5
3	4.18	0.19	22.0
5	3.59	0.23	15.6

3.6 SAXS/WAXS of uniaxially drawn HDPE and composites of HDPE and MWCNTs

To investigate the effect of the MWCNTs on the crystalline morphology development in HDPE after uniaxial deformation, 2D SAXS/WAXS data was taken at the neck section of a drawn sample. Figure 8 shows selected 2D WAXS/WAXS patterns of the drawn samples, where the draw direction is vertical in all cases.

Figure 8. 2D SAXS/WAXS patterns of HDPE and composites of HDPE and MWCNTs post-drawing. (The draw direction is vertical in all patterns.)

All 2D SAXS patterns show intense lozenge shaped scattering in the equatorial direction for all samples. This equatorial scattering is due to cavitation occurring when the samples were deformed, (SEM images in Figure 10). Furthermore, diffuse scattering around the central beam stop is seen due to, the increasing MWCNT content. In the vertical direction the, SAXS patterns for the neat HDPE and the composites show evidence of a 4-point pattern, which indicates an oriented sheared herringbone lamellar structure [77, 80]. Hence, on cold drawing the un-oriented crystalline lamellar structure of the HDPE matrix becomes oriented in the draw direction. This is also confirmed in the 2D WAXS patterns in Figure 8, where in all samples the rings from the orthorhombic crystal structure of HDPE, are now concentrated as spots, indicating highly oriented crystallites are now present.

Figure 9. 1D SAXS profiles of drawn HDPE and composites of HDPE and MWCNTs.

Figure 9 shows the 1D SAXS profiles obtained from the vertical sector integration of the 2D SAXS patterns in Figure 8. The main peak position has shifted to lower q ($\sim 0.037 \text{ \AA}^{-1}$) compared to the undrawn samples. However, this peak is masked at higher MWCNT loadings ($> 0.5 \text{ wt\%}$) from the low angle scattering intensity due to the MWCNTs themselves. 1D correlation functions obtained from the 1D SAXS profiles (where a fit was possible), were obtained and the data collated in Table 5. From this data the, shift in L_p of the peak is confirmed, being reduced compared with the undrawn samples. There is also a reduction in crystallite thickness, which is likely due to the insertion of thinner lamellae in the amorphous regions due to some strain-induced crystallization. The local crystallinity X_c , is seen to increase very slightly, again this can be attributed to the insertion of thin lamellae in the amorphous regions during strain (elongation) induced crystallization. The same trend in crystallinity is seen in the drawn samples compared with the undrawn samples, that is, a nucleating effect occurs on addition of MWCNTs at lower loadings (up to $0.1 \text{ wt\%}$) in the HDPE. At MWCNTs loadings of $> 0.3 \text{ wt\%}$, there is a reduction in local crystallinity,

indicating that the MWCNTs, hinder nucleation and growth of crystallites of the HDPE matrix, irrespective of the rate of HDPE crystallization kinetics.

Table 5. Correlation function parameters extracted from the 1D SAXS profiles of drawn HDPE and composites of HDPE and MWCNTs.

Sample	$L_p/\text{\AA}$	$H_b/\text{\AA}$	$X_c/\%$
HDPE	152	44	29
MWCNT 0.01wt%	145	44	30
MWCNT 0.1wt%	145	40	28
MWCNT 0.3wt%	146	30	21
MWCNT 0.5wt%	144	30	21

During tensile testing of both the HDPE and the composites of HDPE and MWCNTs, a stress-whitening zone developed perpendicular to the draw direction. The surface of the samples in this region were imaged with a SEM and the, micrographs obtained are given in Figure 10.

Figure 10. SEM images of crazed regions in drawn (A) HDPE and composites of HDPE and MWCNTs at loadings of (B) 0.5 wt%, (C) 1 wt% and (D) 5 wt%. Arrows in each image indicates the draw direction (scale bar 200nm).

The SEM images in Figure 10, all show evidence of crazing and voiding occurring perpendicular to the draw direction (indicated by the arrow in the images). This explains the stress whitening occurring in the drawn samples and the intense equatorial scattering observed in the 2D SAXS patterns in Figure 8.

4. Conclusions

A combination of rheological, mechanical, microscopy, thermal and X-ray scattering techniques have been used to determine the extent of MWCNT dispersion and crystalline structure development in composites of HDPE and MWCNTs at loadings up to 5 wt% (2.82 vol%). Oscillatory rheology measurements and SEM imaging confirmed the MWCNTs were highly dispersed in the HDPE matrix and a rheological percolation threshold attained at an MWCNT loading between 0.1 wt% and 0.3 wt%. Adding MWCNTs to HDPE resulted in an increase in elastic modulus ($\uparrow 16\%$), yield stress ($\uparrow 14\%$) and the elongation at break up to loadings of 0.3 wt% MWCNTs. However, addition of MWCNTs above the percolation threshold retarded orientation of the polymer chains to such an extent that failure occurred before necking. Thermal analysis showed that low levels of MWCNTs in the HDPE acted as nucleation sites increasing the crystallisation temperature. This was confirmed from SEM imaging and SAXS data, which showed a nanohybrid shish-kebab morphology (NHSK) developed, whereby MWCNTs act as shish for the epitaxial growth of HDPE crystallites. Furthermore, WAXS data showed again that the MWCNTs were well dispersed in the HDPE and there was no modification of the orthorhombic unit cell of HDPE.

In summary, it is only at very low loadings (< 0.3 wt%) that the MWCNTs are very well dispersed in the HDPE matrix and a rheological percolation attained along with an oriented crystalline morphology. The results here provide a greater understanding of the relationship between the rheological behaviour and crystalline morphology in composites of HDPE and MWCNTs. Thus, modification of the HDPE polymer matrix with very low loadings of MWCNTs can significantly influence the physical properties of the polymer and therefore, its potential in many industrial applications.

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Highlights

- MWCNTs were readily dispersed and distributed in HDPE by melt mixing
- A very low rheological percolation $< 0.3\text{wt}\%$ ($<0.17\text{ vol}\%$) was achieved.
- The MWCNTs act as a nucleating agent for HDPE and induce a NBSK crystalline structure
- Above the percolation threshold, the MWCNTs hinder polymer chain orientation
- Uniaxial deformation results in a highly oriented sheared herringbone lamellar structure.
- The drawing process caused surface cavitation and voiding in the composites

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: