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Observations of a novel strengthening mechanism in HDPE nanocomposites

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ABSTRACT

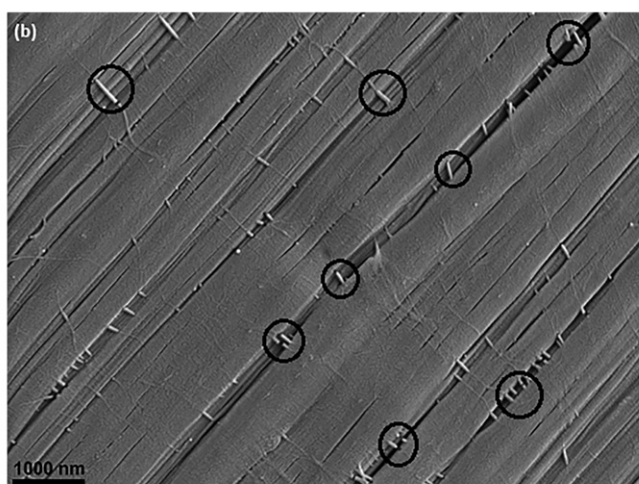
Previous strengthening mechanisms described in literature for high density polyethylene (HDPE) carbon nanotubes composites are typical of those observed in fibre reinforced polymeric micro composites. Here, we present a new molecular level strengthening mechanism based on HDPE carbon nanotubes composite, which has not been reported before to the best of authors' knowledge. The HDPE nanocomposite was produced by melt intercalation technique via twin-screw extrusion. Thereafter, the samples were subjected to mechanical tensile tests and scanning electron microscope (SEM) examination. Carbon nanotubes (CNTs) were found to be disentangled from the polymer molecules after yielding and prior to breaking. SEM and optical microscopic observations revealed visible black agglomerate bands at 45° appeared after yielding and prior to the breaking of the ductile HDPE. It was observed that CNTs were pushed out from the intricate mechanical interlocking with the thermoplastic polymeric chains of HDPE during strain hardening.

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Multi-wall carbon nanotubes (MWCNT); high density polyethylene (HDPE); strengthening mechanism; nanocomposites; orientation; tensile strength; modulus; extrusion



Introduction

Multiwall carbon nanotubes, which are usually in the form of a few to a few tens of concentric cylindrical walls, have been the subject of research since they were discovered [1]. Since then, a significant number of research have investigated their multifunctionalities when added to polymer matrices to prepare polymer nanocomposites. In such form, these materials possess a combination of outstanding mechanical, thermal and electrical properties

attributed to them [2–5]. In a research work, small concentrations of graphene in Nylon 12 significantly increased the flexural and tensile strength of the composite [4]. The tensile strength of liner low-density polyethylene was improved by the addition of 4 wt% graphene to the polymer matrix. The increase was attributed to the optimization of extruder screw speeds to break-up and distribute the graphene nanoplatelets [5]. Despite their potential for proposed functional applications, polymer

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nanocomposites still display mechanical properties that are far below theoretical predictions because of a number and variety of reasons. One of the major causes for the observed discrepancy from experimental studies is the limitation of stress transfer between the matrix and the fillers which has been linked to the slippage of shells in multi-walled nanotubes [2]. Another challenge involves the processing of nanocomposites to achieve a balance of dispersion and distribution with improved properties. In addition, their large surface generally favors the strong influence of intermolecular forces such as Van der Waals forces and dipole-dipole interactions between them, hence making it difficult to disperse them in polymers [3,6]. In general, poor dispersion, which may be identified by the presence of agglomerates in the matrix may lead to reduced interfacial adhesion between the nanotube and the matrix and thus a reduction in the bulk mechanical properties of the nanocomposite [5].

Thus, overcoming these Van der Waals forces to achieve affinity and thus good interface between the matrix and the nanoparticle is crucial to obtaining improved mechanical properties. A large number of research studies have focused on various functionalization techniques to enhance the dispersion and improve affinity between the polymer matrix and the nanofiller [7–9]. Non-functionalized nanofillers have some drawbacks in that they may encourage the formation stable agglomerates or bundles in the polymer matrix. Functionalization may involve the grafting of appropriate functional units to the frame of the polymer matrix, thus encouraging good filler-matrix interaction [10]. Hence, functionalization may be crucial in taking advantage of the excellent properties of nanofiller and the matrix. Currently, all functionalization methods may be categorized as covalent and non-covalent functionalization. Mohammadzadeh and co-workers demonstrated the tensile strength and modulus of a carbon nanotube reinforced epoxy system improved by 32% and 25%, respectively. The improvement at 2 wt% carbon nanotube (CNT) concentration was attributed to use of surfactants to aid better interaction and stable bonding of the nanotubes in the epoxy matrix [11]. Notwithstanding, it is possible to obtain improvement in mechanical properties of polymer composites without surface treatment of the fillers [12,13]. Other well-known techniques used to promote interaction with the matrix include ionic and non-ionic surface functionalization and polymer wrapping [14–18].

Main processing techniques used to incorporate nanofillers such as carbon nanomaterials in polymer matrices include solution mixing, in situ polymerization, melt intercalation, sol-gel process, direct mixture of polymer and particulates, template

synthesis etc. [4,19]. Intercalation by melt extrusion is an important processing technique as it has been proven to be the most economical in terms of its feasibility in upscaling to industrial scale [20]. Melt extrusion is the most widely adopted method to disperse carbon nanotubes in polymers such as HDPE for commercial applications [21–23]. Song and co-workers reported that the addition of nanofillers with different dimensional characteristics influenced the melt extrusion behavior of HDPE [21]. In this work, we prepared samples via melt mixing process with a view to upscaling the production process. In melt extrusion, the extruder applies shear force to enhance the breakdown of any aggregates and agglomerates of the carbon nanotubes enabling dispersion in the polymer matrix [20]. However, the intermeshing of co-rotating or counter-rotating screws in twin-screw extruders and the polymer viscosity may lead to the degradation of the nanotube length. A significant number of research studies have reported the observed mechanical improvements of polymer nanocomposite samples prepared via melt intercalation using the twin-screw extrusion. In other cases, very little number of studies have demonstrated that single screw extrusion may be employed for production of a polymer nanocomposite. For instance, Liu et al. demonstrated that homogeneous dispersion of carbon nanotubes in a polypropylene matrix could be prepared with single screw extrusion method [24]. Based on the study, 1 wt% CNT concentration in Polypropylene achieved about 16% and 36% increase in the Young's Modulus and Tensile strength, respectively [24]. This route can be used as a complementary process for further processing of polymer nanocomposite prepared via master-batch method with twin-screw extrusion.

In engineering applications, the exceptionally high aspect ratio of carbon nanotubes in combination with the stiffness and low density makes them of interest in the (48) strengthening of thermoplastic materials applications. During tensile testing of these nanocomposites, the energy required to fracture these materials come from the shear yielding of the nanofillers [25,26].

Mokashi et al. found improvements in the tensile strength and elastic stiffness of polyethylene and carbon nanotube composites [27]. Thus, understanding the mechanism behind the strengthening of polymers for structural applications could increase the performance envelope of the polymer material and increase potential for use in many structural applications [25,28].

Here, we present a new strengthening mechanism in HDPE composite based on carbon nanotubes, which has not been reported before to the best of authors' knowledge. High density Polyethylene

(HDPE) with CNTs were prepared via melt mixing and the samples of the resulting nanocomposites were subjected to tension forces. CNTs were found to be dis-entangled from the polymer molecules after yielding and prior to the fracture of the test material. The study also examined the effect of a two-step processing route on the dispersion of the resulting nanocomposite.

Experimental procedure

Materials

A commercial grade, PLASTICYL™ HDPE1501, was utilised for this study. The material consisted of a two-part system (Multi-wall carbon nanotubes in HDPE matrix) supplied by Nanocyl SA, Belgium. As per supplier, MWCNT (9.5 nm average diameter, 1.5 mm average length, purity 90% by TGA, NC700 series) was synthesized by the Catalytic Carbon Vapour Deposition method (CVD). The polymer matrix used is a High-Density Polyethylene commercial grade, Borpure MB7541.

Composite fabrication

The composite fabrication was performed in two stages: compounding of nanotubes in HDPE with twin-screw extrusion and test sample production via single screw extruder. At the start, Multiwall Carbon Nanotubes were compounded with the HDPE matrix in a twin-screw extruder to produce a polymer nanocomposite (rod shaped) with specific CNT concentration—1 wt% (HDPE-1CNT) and 2 wt% (HDPE-2CNT). The extruded strands were pelletized into smaller granules.

Melt intercalation was performed with Brabender PL-19 single screw extruder (Brabender Measuring Extruder 19/25D) at screw speed of 90 rpm and temperatures between 150 °C and 180 °C. The materials were dried in vacuum at 80 °C for at least 5 h and fed as a granular mixture into the extruder via the hopper. In order to promote orientation of the nanotubes, a rectangular shaped die, with a unique funnel design and area was used in the formation of the extrudate. The extrudate was received as rectangular strip samples from which standard dumbbell test samples were collected.

During the sample fabrication, the extruder variables (screw speed and temperature) were gradually tailored to suit the extrudate geometry. The size of the rectangular die head with a funnel shaped mould—100 × 3 mm. Two sample sets with different percentage concentrations—HDPE-1CNT and HDPE-2CNT were produced.

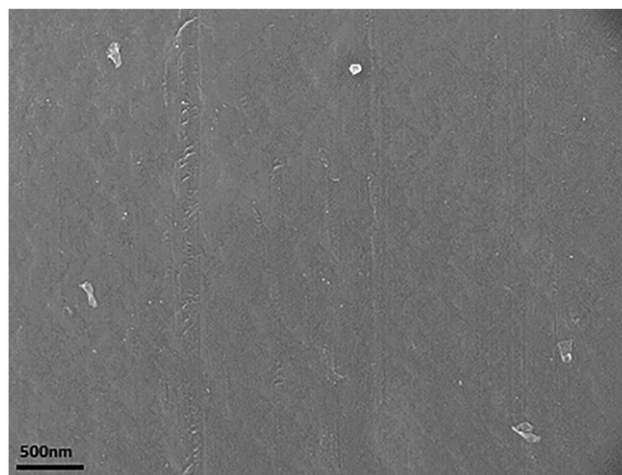


Figure 1. Representative FE-SEM images showing neat polymer HDPE (a) and polymer nanocomposite—HDPE-1CNT (b).

Characterization

Mechanical tests (Tensile tests)

Tensile samples were prepared by mechanically cutting out standard dumbbells with die cutter sized-ISO 527-2 5 A with specimen thickness 4 mm. For each composition, five specimen were tested.

Field emission scanning electron microscope (FESEM)

Fractured surfaces were obtained from the tensile samples and the morphology was examined via FESEM (TESCAN MIRA 3; Voltage -5 KV). The surfaces were sputter coated (Q150T Turbo-Pumped Sputter Coater) with platinum thickness of 3 nm.

Results and discussion

Morphological characterization

The extruded strands produced via twin-screw extrusion were subjected to morphological examination via FESEM. Figure 1(a) and 1(b) shows the micrograph of neat HDPE and HDPE-1CNT produced with a twin-screw extruder.

From the micrograph (Figure 1b), individual carbon nanotubes are clearly seen (highlighted with dark circles) in the polymer microstructure. The shear mixing generated by the counter rotation of the twin-screw extruder, detached the individual carbon nanotubes from the bundles. In addition, the high viscosity of the polymer melt promoted the separation nanotubes from their stable aggregate form thus contributing to the homogeneous dispersion observed in the composite's microstructure (Figure 1b).

Mechanical characterization

The samples produced via single screw extrusion were subjected to mechanical characterization

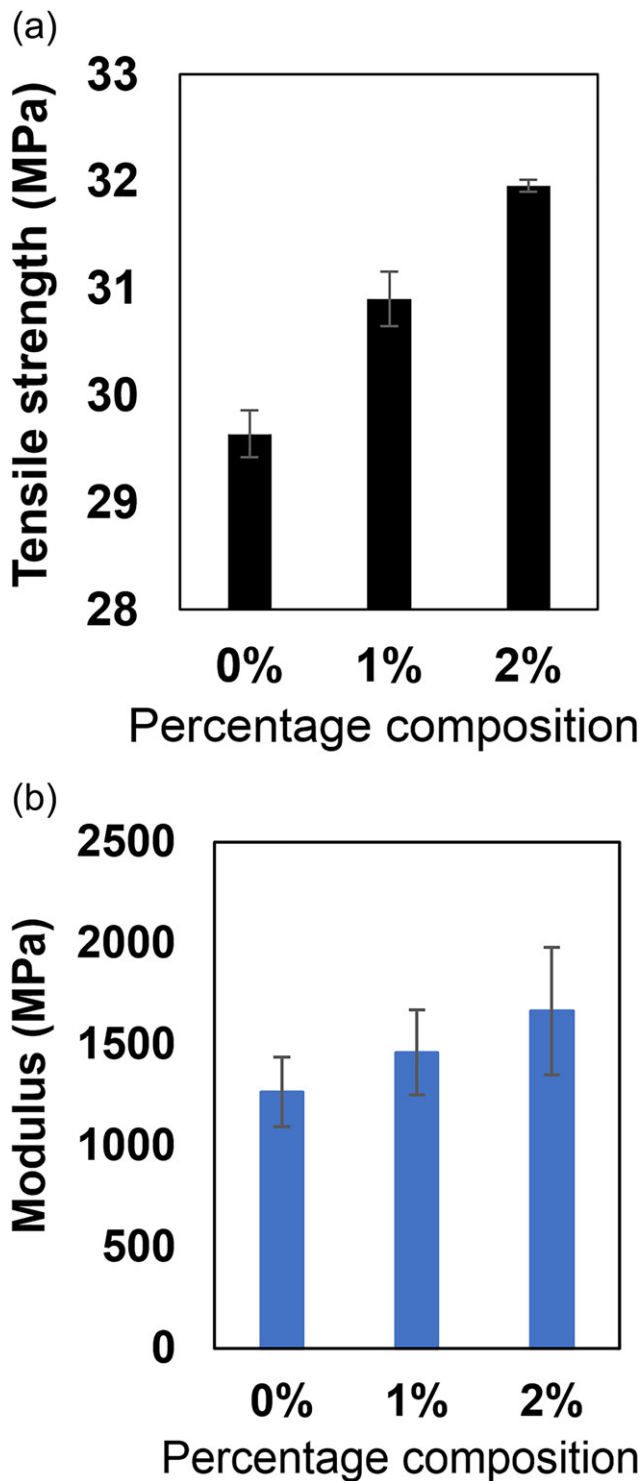


Figure 2. Mechanical properties of various HDPE nanocomposite compositions: (a) tensile strength; and (b) modulus.

(tensile testing). **Figure 2(a)** and **2(b)** reveal the improvements in the tensile strength and modulus with the addition of CNTs. Based on a study conducted by Li C. and co-workers, the degree of dispersion may be correlated to the mechanical performance of the polymer nanocomposite based on carbon nanotubes [24]. The elastic modulus of HDPE, HDPE-1CNT, and HDPE-2CNT was calculated to be 1200, 1500, and 1660 MPa, which represents a gradual improvement of 25% and 38% with

the addition of 1 wt% and 2 wt% CNT, respectively. The same gradual increasing trend was observed for the tensile strength behavior. A maximum improvement of 32 MPa was achieved at 2 wt% CNT content as compared to 29.5 MPa in HDPE while tensile strength at 1 wt% CNT content was 30.8 MPa representing a 4% increase. It can be observed that the mechanical improvement might not be significantly high as theoretical composite prediction due to imperfect mechanical interlocking with the polymer matrix. Similar gradual increments in the tensile strength and young's modulus were observed with coated MWCNTs in Polypropylene matrix to improve mechanical strengthening [29]. The improved properties indicate that nanotubes were dispersed in the polymer during the second stage processing of samples with single-screw extrusion.

Figure 3 presents the micrograph of a fractured test specimen of HDPE-1CNT and HDPE-2CNT. The state of dispersion from both nanocomposites produced via single screw extrusion can be seen in the images. CNT strands were covered by the polymer melt appear as white dots in the HDPE matrix. From the micrograph, there were no observed voids or nanotube graves between the HDPE matrix and the nanotubes suggesting that the polymer melt bonded well with the nanotubes. Thus, the state of dispersion in the fractured specimen indicates that good interaction of the nanotubes with the polymer matrix was achieved for both concentration.

As observed from the results in **Figures 2** and **3**, the reinforcing efficiency any composite can be attributed to efficient load transfer at the nanofiller-polymer interface. This efficiency may be influenced by the presence of agglomerates [14,30]. A closer analysis of the mechanical results indicates that the underlying nanoscale strengthening mechanism may be governed by microstructural changes due to embedded CNTs in the microstructure. The strengthening mechanism is discussed in the following section.

Strengthening mechanism

Figure 4 shows the schematic diagram of the behavior of HDPE-1CNT concentration under tension. The black strip is a representative HDPE-1CNT before application of a tensile force. A tension force of 1 kN was applied to the dumbbell sample. As the sample is pulled apart, visible dark agglomerates appearing as bands begin to develop on the strained section of the dumbbell. This suggests that some form of rejection or dis-entanglement of the black CNTs from the polymer molecules occurred during tensile straining. However, this feature was less visible from the HDPE-2CNT samples.

The microstructure of strained tensile samples of HDPE-1CNT were observed via optical microscopy

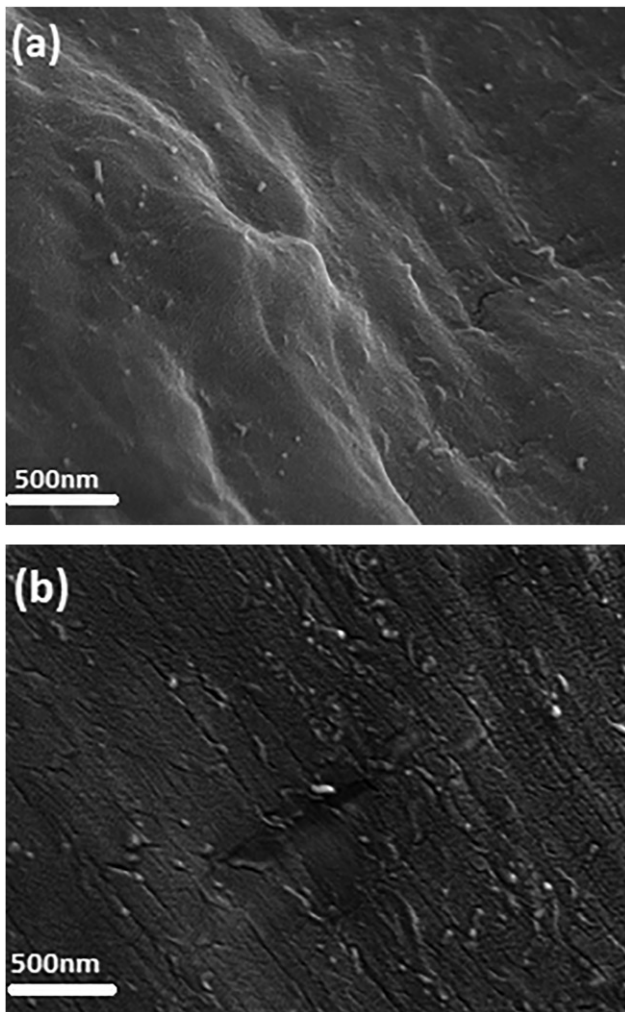


Figure 3. FESEM image showing state of dispersion at HDPE-1CNT (a) and HDPE-2CNT (b).

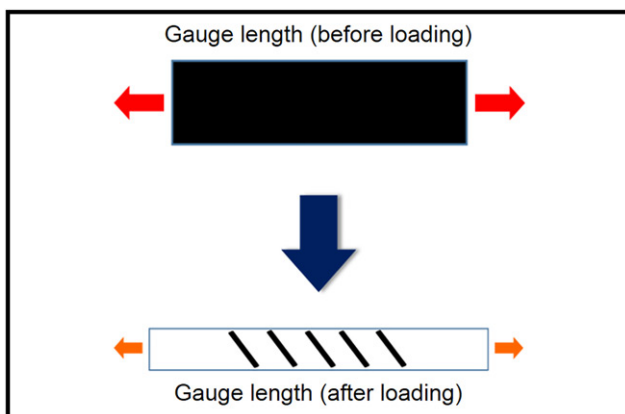


Figure 4. Schematic representation of behavior of strained tensile sample under 1 kN force.

and FESEM shown in Figures 5 and 6, respectively. Clear bright translucent matrix with dark agglomeration in the form of circular patches and oriented in 45° direction were observed in the optical microscopic images. We hypothesize that the appearance of the black bands indicates the presence of bundles of the nanotubes in that region which suggests some

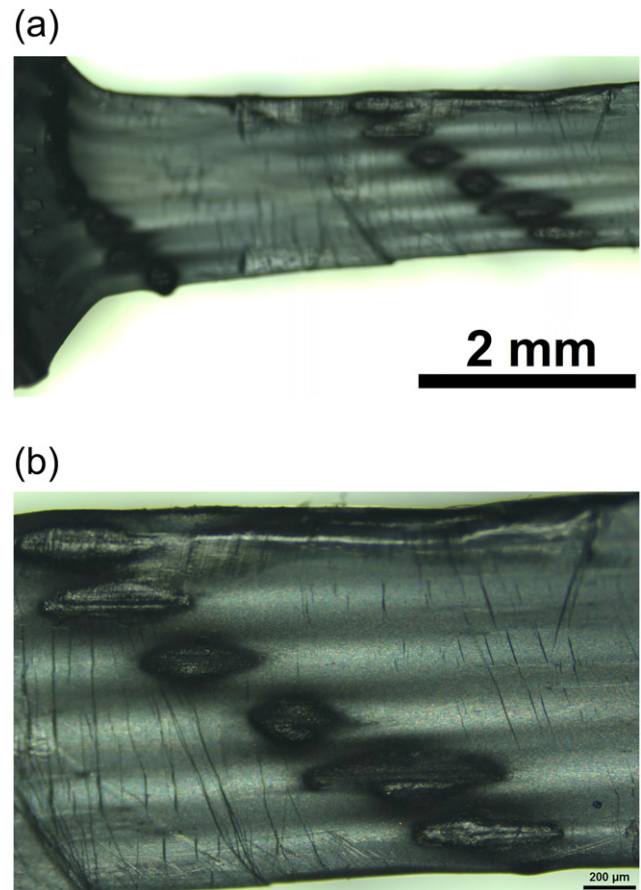


Figure 5. Representative 2D Optical microscopic images for 1wt% HDPE nanocomposites. Clear bright translucent (matrix) and dark (agglomerated nanotubes) bands are visible in both images.

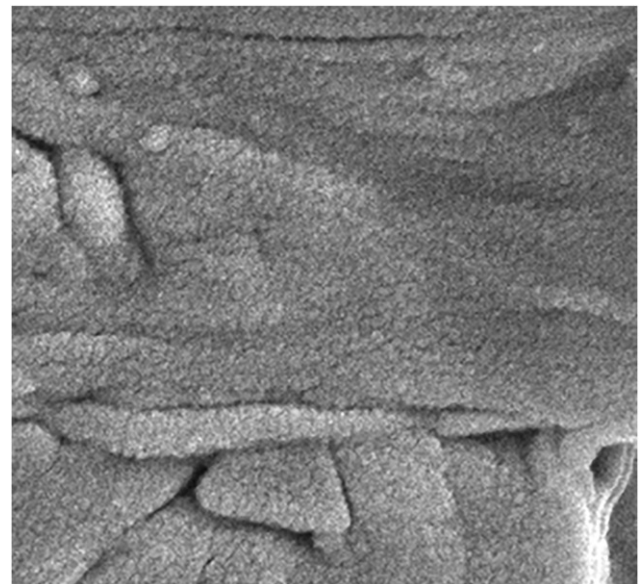


Figure 6. SEM image of fractured surface of neat HDPE.

sort of dis-entanglement of the CNT from the polymer matrix occurred during the load transfer. Figure 6 reveals the fractured microstructure of neat HDPE. In Figure 7(a)–(d), the SEM images of the fractured HDPE-1CNT sample is shown. From the

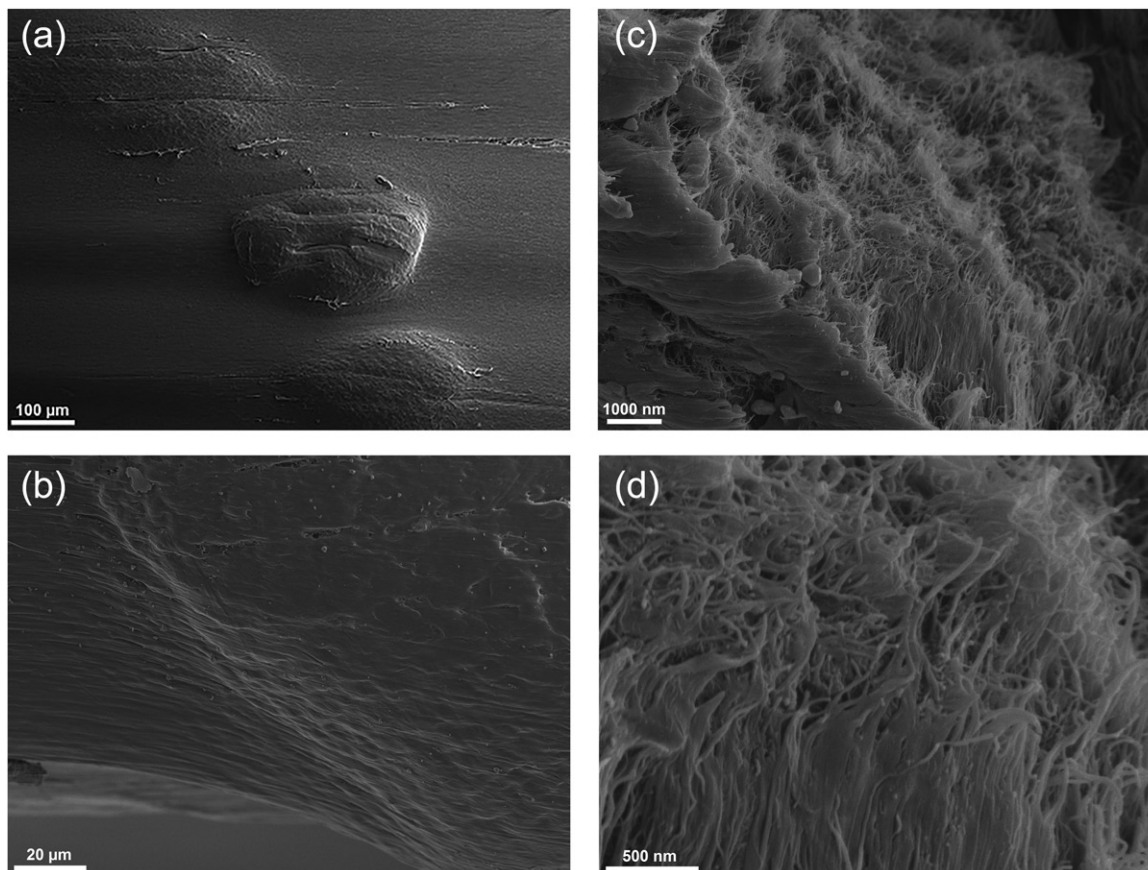


Figure 7. FE-SEM images of fractured surface with appearance of dark bands of agglomerated nanotubes: (a) and (b) elevated regions/bumps at lower magnification; (c) Agglomerates of nanotubes visible beneath the surface of elevated regions; and (d) higher resolution image showing clear agglomerates of nanotubes.

microscopic images, the dark regions appear as bumps or forcefully elevated surfaces aligned in at 45° angle, Figure 7(a). The edge of the elevated regions, Figure 7(b) reveals its contour which suggests a type of load transfer mechanism. Small cracks on the surface of the elevated areas show carbon nanotubes buried underneath the polymeric material swell, Figure 7(c) and (d). In Figure 7(c), the image shows the region where a crack has been formed with buried carbon nanotubes beneath the HDPE matrix. A closer look in Figure 7(d) reveals a grave of buried carbon nanotubes covered by the matrix material. This confirms the ‘dis-entanglement and accumulation of nanotubes during tensile loading. The mechanism was more pronounced in HDPE-1CNT samples than in the HDPE-2CNT samples. It should be noted that this behavior has not been reported in any of the previous reports on nanocomposites strengthening mechanisms based on carbon nanotubes.

It appears that as the samples were stretched under tension, the interfacial strength for effective load transfer became important to restrict distortion of the polymer molecules. As the sample was being pulled apart, the shear force became dynamic along the HDPE–nanotubes interface, thus encouraging

the orientation of some CNTs in directions other than the tensile axis thus restricting deformation. The shear force caused the dis-entanglement of nanotubes resulting in energy dissipation from the composite leading to improved modulus and tensile strength at HDPE-1CNT (see Figure 2).

Agglomerates of nanotubes visible beneath the surface of elevated regions; and d) higher resolution image showing clear agglomerates of nanotubes.

Conclusion

The results presented here demonstrate a novel mechanism for CNTs to be used in strengthening of HDPE. The load transfer mechanism was investigated after CNTs were incorporated into the polymer at different concentrations. CNTs were observed to have been rejected by the polymer molecules and aggregated as black bands. Further investigation showed that CNTs were being rejected as the polymer expended energy during tensile straining. The mechanical properties also showed the CNTs improved the tensile modulus and maximum strength of the neat HDPE material by 30% and 8%, respectively at HDPE-2CNT.

From the foregoing, it was concluded that in addition previous load transfer/toughening mechanisms demonstrated in HDPE–CNT composites. Further work will be carried out in quantifying the interfacial interaction in the composite material.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Notes on contributors

Chinyere Okolo is a research associate at Northumbria University, Newcastle. She received her B. Eng. (Hons.) in Mechanical Engineering in 2009 and MSc in Subsea Engineering from Newcastle University in 2014. Her research interests include the study of carbon nanomaterials for mechanical and thermal enhancement of polymer nanocomposites for industrial applications. Fawad Inam joined the University of East London as the Head of Department, Engineering and Computing in September 2018. His research interest is in the development of advanced materials including nanomaterials filled with fullerenes, carbon nanotubes and graphene. He has worked with numerous aerospace, petroleum, manufacturing, defence and subsea industrial organisations. His expertise includes materials physics and chemistry, processing, characterisation, performance evaluation, applications, materials sustainability and technology commercial exploitation. Prof. Inam has produced several high impact publications and authored more than 75 papers in peer-reviewed scientific journals and proceedings to date. He was the founding editor of journal “Epoxy” and on the editorial boards of various journals.

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