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Self-sensing performance of MWCNT-low density polyethylene nanocomposites

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Abstract
Carbon nanotubes (CNTs) based polymer nanocomposites offer a range of remarkable properties. Here, we demonstrate self-sensing performance of low density polyethylene (LDPE)-multiwalled carbon nanotubes (MWCNTs) nanocomposites for the first time. The dispersion of the CNTs and the morphology of the nanocomposites was investigated using scanning electron microscopy, x-ray diffraction and Raman spectroscopic techniques. The thermal properties were measured using thermal gravimetric analysis and differential scanning calorimetry and were found to increase with increasing wt% of MWCNTs in LDPE matrix. An overall improvement in ultimate tensile strength, yield strength and Young’s modulus was found to be 59.6%, 48.5% and 129.3%, respectively for 5.0 wt% loading of MWCNTs. The electrical percolation threshold was observed at 1.0 wt% of MWCNTs and the highest electrical conductivity of 2.8 × 10⁻² S cm⁻¹ was observed at 5.0 wt% loading of MWCNTs. These piezo-resistive nanocomposites offer tunable self-sensing capabilities with gauge factors in the ranges of 17–52 and 42–530 in linear elastic (strain ∼3%) and inelastic regimes (strain ∼15%) respectively. Our demonstration would provide guidelines for the fabrication of low cost, self-sensing MWCNT-LDPE nanocomposites for potential use as civil water pipelines and landfill membranes.

1. Introduction

Major advances in water and gas pipeline technology have been made in recent years but with the aging water and gas distribution systems the problems of cracks and damage are steadily increasing. It is important to have a good knowledge of these materials in order to monitor any changes in the properties that may occur, which may in turn influence their structural behaviour. Pipes made from polymeric materials such as polyvinyl chloride and both low density polyethylene (LDPE) and high density polyethylene are the most widely used piping materials in civil industries [1, 2]. With their unique combination of properties, PE pipes have revolutionised low pressure pipe system design and they have largely replaced traditional pipe materials, such as metal and concrete [2, 3]. PE pipes are used extensively in gas and water distribution systems. PE has several advantageous properties in pipe design, such as light weight, design flexibility, low cost, ease of transport and handling, corrosion and chemical resistance, long term durability and recyclability [3, 4]. These pipes are not affected by corrosion but often fail in a brittle manner. Failures are often associated with mechanical damage, manufacturing defects, and the generation of micro-cracks which lead to the formation of macro-cracks, fitting problems or under pressure tapping operations. Improper temperature conditions in the water and gas industries can also initiate cracks and damage in polymer pipes.
Damage in such structures is likely to impact the structural performance, operation reliability and human safety and the early detection of such damage or micro-cracks and their proper maintenance can protect the systems from sudden accidents, greatly enhancing their service life [5]. Damage appears in different terms, levels and locations in composite structural components and can have different effects on the life of the structural component. Therefore, proper monitoring of the location and extent of damage of the structural component is necessary.

The process of monitoring deformation and damage in the structural materials is known as structural health monitoring (SHM). SHM is important for civil structures, such as nuclear power plants, buildings and the aerospace industry. An active monitoring system can recognise different defects and monitor damage, strain and temperature, so that timely maintenance of the structure can be undertaken to provide sufficient safety and life span. Visual inspection, tapping and ultrasonic waves are the most widely used methods for damage assessment. However, the sensitivity of visual inspection is very low and it cannot detect the sub-surface flaws that are smaller than what the human eye can see. Tapping can detect sub-surface flaws but only at a macroscopic level. The ultrasonic wave method is more sensitive than visual and tapping methods, but it is limited to flaws that are several millimetres in size. Different types of piezo-resistive, piezoelectric and magnetostrictive composite materials have capabilities to sense various physical and chemical parameters to monitor the health of structural components [6, 7].

Currently, electrically-conductive polymer nanocomposites comprising multifunctional nanofillers represent the promising candidates for the development of the next generation of smart materials, due to their multifunctional capabilities. These conductive polymer nanocomposites, based on epoxy [8, 9], polypropylene [10], polyisoprene [11], polydimethylsiloxane [12], PVDF [13] and polycarbonate [14] matrices, are usually prepared by mixing electrically-conductive fillers such as carbon nanotubes (CNTs) [15], graphene, carbon black, carbon fibre, hybrid fillers [16–18] and other nanomaterials. These nanocomposites have been widely investigated in many fields, such as strain-sensing [19–26], gas-sensing [27, 28] electromagnetic interference shielding [29–32], supercapacitors [33, 34] and damage and self-sensing for SHM [1, 5, 33–37].

Damage and self-sensing nanocomposites are becoming highly attractive materials for civil engineering and defence applications since they can lead to improvement in the safety and performance of the structures. Self-sensing is the property of a material to sense its intrinsic deformation response, such as stress, strain, damage, temperature etc and this ability makes them an excellent material for SHM. Self-sensing nanocomposites function based on the piezoresistivity principle i.e. to detect the change in electrical resistance with respect to strain and/or damage. The advantages of using self-sensing materials compared with the use of embedded or attached devices/sensors are their low cost, durability, large sensing area and they suffer no loss in mechanical properties. Embedded sensors are also difficult to repair. Associated with these advantages, there are several scientific challenges to developing self-sensing structural materials with excellent mechanical properties, durability and good piezo-resistive properties.

In the present study, a linear LDPE polymer is investigated because of its usefulness as a water piping material in the civil and gas industries and landfill membranes. Electrically conductive fillers, such as CNTs, graphene, graphite, carbon black and metal powders, are generally introduced to fabricate electrically-conductive polymer nanocomposites. As the loading of the conductive filler is increased, the percolation threshold is reached where the conductivity starts to increase rapidly. The level of electrical conductivity depends upon the concentration, geometry, orientation and distribution of the filler. In this regard, multi-walled carbon nanotube (MWCNT) is an ideal filler for the fabrication of polymer nanocomposites, due to their excellent mechanical [38–40], thermal [40–42] and electrical properties [40, 43, 44]. The high aspect ratio of MWCNT makes it the perfect choice to improve electrical, thermal and mechanical properties of polymer nanocomposites. The coefficient of thermal expansion of neat LDPE is very high. CNT has a negative coefficient of thermal expansion; therefore, CNTs can reduce the overall coefficient of thermal expansion and also improve the mechanical properties of LDPE and likelihood of failure by stress cracking.

Few studies have been reported on the electrical, mechanical and thermal properties of LDPE nanocomposites with addition of different wt% of MWCNTs. Gorrasi et al [45] prepared MWCNT-LDPE nanocomposites using a ball milling method and they found a 43% improvement in elastic modulus at 10.0 wt% loading of MWCNTs. Xiao et al [46] used a mechanical mixing method to fabricate MWCNT-LDPE nanocomposites. They observed improvements of 56% and 89% in the tensile strength and elastic modulus, respectively at 10.0 wt% loading of MWCNTs. Aalaie et al [47] fabricated MWCNT-LDPE nanocomposites using a melt blending technique and reported 10% improvement in the elastic modulus at 5.0 wt% loading of MWCNTs. Few studies have been conducted on the electrical conductivity of MWCNT-LDPE nanocomposites, however, Valentino et al [48] reported electrical conductivity values of $10^{-3}$ Scm$^{-1}$ at 7.0 wt% of MWCNT concentration. McNally et al [49] reported an electrical conductivity of $10^{-4}$ Scm$^{-1}$ at 10.0 wt% of MWCNT loading. They used a melt blending technique to fabricate these MWCNT-LDPE nanocomposites. Fu et al [50] in the recent study prepared MWCNT-LDPE nanocomposites using a solvent mixing technique where an
electrical conductivity of $10^{-4}$ S cm$^{-1}$ at 7.0 vol% of MWCNT loading was reported. However, no studies were found on the piezo-resistive behaviour of MWCNT-LDPE nanocomposites.

The aim of this paper is to investigate the electrical, thermal and piezo-resistive properties of LDPE nanocomposites, comprising different wt% of high aspect ratio MWCNTs. Solution mixing, followed by compression moulding techniques, was used to fabricate MWCNT-LDPE nanocomposites. The main focus is on piezo-resistive response of MWCNT-LDPE nanocomposites both in elastic and inelastic regimes. It is believed that this study can provide a guideline for the fabrication of low cost MWCNT-LDPE self-sensing nanocomposites useful for civil water pipelines, SHM and landfill membranes.

2. Experimental section

2.1. Materials

The linear LDPE used in this study was an extrusion grade polymer (melt flow index 0.70 g/10 min) with a density of 0.92 g/cc obtained from the Borouge Polymer Company, Abu Dhabi, UAE. The pre-aligned carbon nanostructures (CNS) used in this work was supplied by Applied Nanostructured Solutions, LLC and consisted of aligned bundles of MWCNTs in which the number of walls varied from 2 to 9 with outer diameters of 10 to 20 nm and lengths of 30–50 μm.

2.2. Fabrication of MWCNT-LDPE nanocomposites

LDPE nanocomposites with different wt% of MWCNTs (0.0, 0.1, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0) were fabricated via solution mixing, followed by a compression moulding technique. In this method, as shown in figure 1, LDPE pellets were first dissolved in toluene using magnetic stirring and MWCNTs were dispersed separately in ethanol using a horn sonicator at an amplitude of 20% to obtain a stable suspension of CNT in ethanol. The suspension of MWCNTs was mixed with a solution of LDPE by magnetic stirring and then transferred onto a flat petri dish and finally placed in an oven at 80 °C for 12 h to evaporate the solvent. The mixed powder of MWCNT-LDPE nanocomposites was compression moulded at 140 °C for 5 min using a hydraulic press and the resulting sheets of 1 mm thickness were cut to the desired size and shape according to the standards for mechanical, electrical, thermal and piezoresistivity tests. The same procedure was used to prepare all of the LDPE nanocomposites from 0.1 to 5.0 wt% loading of MWCNTs and the samples were designated as PECNT0, PECNT0.1, PECNT0.5, PECNT1, PECNT2, PECNT3 and PECNT5, respectively. The pristine MWCNT is designated as PECNT100 i.e. without a polymer matrix.
2.3. Characterisations

The morphologies of the MWCNT and the fracture surfaces of MWCNT-LDPE nanocomposites (following mechanical testing) were analysed by scanning electron microscopy (SEM) (Quanta 250, UK). A high resolution transmission microscopy (HRTEM) study of CNS was carried out using a Tecnai TF20, 200 kV instrument. Samples of MWCNT-LDPE nanocomposites were coated with a thin layer of gold for improved imaging. X-ray diffraction (XRD) measurements of the MWCNTs and MWCNT-LDPE nanocomposites were carried out using a PANALYTICAL RAYONS-X XRD spectrometer equipped with a Cu tube and scanned from 5° to 70°. A Raman spectroscopic study of MWCNTs and MWCNT-LDPE nanocomposites was carried out using a Witec confocal Raman spectrometer with an excitation source of 532 nm.

The thermal stability of MWCNT-LDPE nanocomposites was examined using a thermogravimetric analyser (NETZSCH High Temperature thermal gravimetric analysis (TGA)). The tests were performed at temperatures between 50 °C and 500 °C, at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere with a flow rate of 50 ml min⁻¹. In order to investigate the change in the crystallisation temperature, specific heat and crystallinity, differential scanning Calorimeter (DSC) measurements were conducted using a NETZSCH High Temperature DSC from 0 °C to 250 °C with a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere, with flow rate of 20 ml min⁻¹.

Electrical conductivity of MWCNT-LDPE nanocomposite was measured using an Ecopia four point probe system according to the Van der Pauw method. The electrical contact was made by placing the contact needles onto the four corners of the 10 mm × 10 mm size of the sample. To facilitate the electrical contact, conductive silver ink was manually painted onto the four corners of the sample. The electrical conductivity (σ) was computed as σ = 1/ρ, where, ρ is the electrical resistivity of the sample. Rectangular samples with dimensions of 60 mm × 6 mm were cut from nanocomposite films of 1.0 mm thick as per the ISO 527-3 standard for tensile tests. For the piezo-resistive measurements, a Tektronix DMM4050 6-1/2 digital precision multimeter was used and the samples were clamped with aluminium electrodes over a gauge length of 20 mm. A Zwick–Roell universal testing machine was used to stretch the sample connected to the multimeter to record the changes in resistance with increasing load at room temperature. Both the mechanical and piezo-resistive properties were measured at a loading rate of 5 mm min⁻¹ and three repeats of each sample were tested.

3. Results and discussions

3.1. Characteristics of MWCNTs

Surface morphology and structure characterisations were carried out using SEM, TEM and Raman spectroscopic techniques and these are discussed in the supplementary information (figures S1 and S2 are available online at stacks.iop.org/MRX/5/015703/mmedia).

3.2. Raman spectroscopic studies of MWCNTs, neat LDPE and MWCNT-LDPE nanocomposites

The microstructure of the neat LDPE and MWCNT-LDPE nanocomposites was investigated using Raman spectroscopic technique. A series of Raman spectra of the neat LDPE, MWCNTs and MWCNT-LDPE nanocomposites are presented in figure 2. The MWCNT shows two main peaks; the D-band and G-band. The D-band at 1344 cm⁻¹ is due to the presence of defects and disorder in the CNTs that break the sp² symmetry of the CNTs. The G-band at 1574 cm⁻¹ corresponds to in-plane vibrations of the sp² hybridised carbon atoms on the surface.

The Raman spectrum of the neat LDPE shows a number of peaks in the skeletal optical modes, CH₂ twisting modes, bending and stretching modes of crystalline and the amorphous phase as shown in figures 3(a)–(d). The Raman bands at 1064 cm⁻¹ and 1132 cm⁻¹ are due to the antisymmetric and symmetric C–C stretching vibrations of skeletal chains parallel and perpendicular to the chain axis, respectively [51, 52] as shown in figure 3(a). In addition to these peaks, LDPE also has a very weak band at 1082 cm⁻¹ which is assigned to the C–C stretching mode of the amorphous region. The low intensity Raman band at 1169 cm⁻¹ is assigned to the rocking vibrations of C–C bond in CH₂. The Raman band at 1296 cm⁻¹ is due to the C–C twisting mode of the crystalline chains, as shown in figure 3(b). The three different peaks around 1411 cm⁻¹, 1441 cm⁻¹ and 1460 cm⁻¹ as shown in figure 3(c) are assigned to the C–C bending mode of vibration in LDPE [51–53]. The peak at 1411 cm⁻¹ is used to determine the orientation of the crystalline chains and also the crystallinity of LDPE [54].

The peaks at 1441 cm⁻¹ and 1460 cm⁻¹ are assigned to the CH₂ bending modes of the amorphous trans chains and the melt like amorphous chains, respectively [54, 55]. The intensity of the bands in the high frequency region of CH₂ stretching depends upon chain conformation, environment and mobility. Figure 3(d) displays three bands at 2850 cm⁻¹, 2887 cm⁻¹ and a shoulder at 2940 cm⁻¹, respectively. The band at 2850 cm⁻¹ is the antisymmetric C–H stretching vibration, the bands at 2887 cm⁻¹ and the shoulder at 2940 cm⁻¹ arise from a
Fermi resonance interaction between overtones of the CH$_2$ bending with the symmetric C–H stretching vibrations [51, 53]. All assignments of Raman spectrum of the LDPE are shown in figures 2 and 3 and are also listed in table 1 [51–53].

Mixing of different wt% of MWCNTs in LDPE matrix, the Raman bands of neat LDPE weaken up to 0.5 wt% of MWCNT loading and finally disappear at higher loadings. The presence of D-band and G-band clearly indicate the effect of MWCNT dispersion in the LDPE matrix and the LDPE chains penetrate between the MWCNTs during hot pressing. This systematic increment in the peak intensities of D- and G-band depend upon the wt% of MWCNTs.
3.3. XRD analysis of MWCNT, neat LDPE and MWCNT-LDPE nanocomposites

An XRD analysis of the neat LDPE, MWCNT and MWCNT-LDPE nanocomposites is shown in figure 4. The XRD pattern of the as procured MWCNTs exhibits a diffraction peak of \((002)\) reflection at 26.5° corresponding to the d-spacing between the graphene sheets in the radial direction i.e. the ordered arrangement of the concentric cylinders of graphitic carbon \([56]\). The peak around 43° for the \((100)\) and \((100)\) planes is due to the in-plane graphitic structure and the small amount of catalyst particles present in the MWCNTs. Neat LDPE shows two characteristic peaks at 21.2° and 23.8° for the crystalline phase of \((110)\) and \((200)\) planes.

With the addition of different wt% of MWCNTs in the LDPE matrix, the peak of MWCNT at 26.5° for \((002)\) does not have much effect on LDPE peak, because the effect of LDPE is more on the surface of MWCNTs which may be attributed to homogeneous dispersion of the MWCNTs in LDPE matrix. Small effect of \((002)\) plane of CNTs is seen at higher wt% of MWCNTs in LDPE matrix which may be due to the excess amount of CNTs in LDPE matrix.

3.4. Mechanical properties of MWCNT-LDPE nanocomposites

Figure 5(a) shows the representative stress–strain curves for the LDPE and its nanocomposites with different wt% loading of MWCNTs. It is evident from figure 5 that the mechanical properties were enhanced significantly by adding MWCNTs as compared to neat LDPE. The mechanical properties, such as Young’s modulus, ultimate tensile strength (UTS), yield strength and toughness of MWCNT-LDPE nanocomposites are calculated from stress–strain curve and the results are compared with those of neat LDPE as shown in figures 5(b)–(e) and are also summarised in table 2. From figure 5(b), the UTS with 0.1 wt% MWCNT loading is improved by about 15.40% (from 8.93 to 10.31 MPa) as compared to the neat LDPE. This enhancement is attributed to the efficient stress transfer from the LDPE matrix to the CNTs due to the homogeneous dispersion of the MWCNTs in LDPE matrix.
However, the UTS for the PECNT0.5 and PECNT1.0 are slightly lower than that of PECNT0.1 but still higher than PECNT0. With further increase in the wt% of MWCNTs in the LDPE matrix, the UTS increases continuously and reaches a maximum value of 14.25 MPa for PECNT5 (overall improvement $\sim 59.57\%$). The Young’s modulus is also increased upon the addition of different wt% of MWCNTs in the LDPE matrix because of the significant increase in stiffness of nanocomposites. It can be seen from the figure 5(c) that the Young’s modulus increased by about 11.72% for PECNT0.1 and maximum up to 129.33% for PECNT5 nanocomposites. This enhancement in Young’s modulus has also increased the yield strength about 10.26%–48.54% from PECNT0.1 to PECNT5 nanocomposites (figure 5(d)).

Figure 5. Representative stress–strain curves (a), ultimate tensile strength (b), yield strength (c), Young’s modulus (d) and toughness (e) of MWCNT-LDPE nanocomposites as a function of MWCNT wt% with error bar. (f) Surface strain field images obtained from DIC during tensile loading for monitoring the strain distribution over the sensor area at stress of 4.5 MPa for different wt% of MWCNT loading.

This unexpected enhancement in the toughness may be due to uniform dispersion of CNTs in polymer matrix and efficient stress transfer between two components. However,
Table 2. Mechanical properties of MWCNT-LDPE nanocomposites. Changes (shown in brackets) are calculated versus the neat LDPE, and only statistically significant increases are shown.

<table>
<thead>
<tr>
<th>MWCNT wt%</th>
<th>Young’s modulus (MPa) (% change)</th>
<th>Poisson’s ratio</th>
<th>Yield strength (MPa) (% change)</th>
<th>UTS (MPa) (% change)</th>
<th>Toughness ($\times 10^6$ J m$^{-3}$) (% change)</th>
<th>Yield strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PECNT0</td>
<td>298.68 ± 32.70</td>
<td>0.4</td>
<td>8.57 ± 0.23</td>
<td>8.93 ± 0.04</td>
<td>11.49 ± 1.51</td>
<td>2.87</td>
</tr>
<tr>
<td>PECNT0.1</td>
<td>333.70 ± 23.32 (+11.72%)</td>
<td>0.41</td>
<td>9.45 ± 0.15 (+10.26%)</td>
<td>10.31 ± 0.19 (+15.40%)</td>
<td>36.25 ± 2.92 (+215.5%)</td>
<td>2.83</td>
</tr>
<tr>
<td>PECNT0.5</td>
<td>396.20 ± 21.00 (+32.65%)</td>
<td>0.49</td>
<td>9.76 ± 0.53 (+13.88%)</td>
<td>9.54 ± 0.60 (+6.83%)</td>
<td>10.41 ± 2.75 (−9.4%)</td>
<td>2.46</td>
</tr>
<tr>
<td>PECNT1</td>
<td>447.23 ± 53.64 (+49.73%)</td>
<td>0.44</td>
<td>10.32 ± 0.17 (+20.42%)</td>
<td>9.79 ± 0.34 (+9.63%)</td>
<td>8.01 ± 0.92 (−30.3%)</td>
<td>2.30</td>
</tr>
<tr>
<td>PECNT2</td>
<td>582.70 ± 29.34 (+95.09%)</td>
<td>0.47</td>
<td>11.08 ± 0.44 (+29.28%)</td>
<td>11.49 ± 0.48 (+28.67%)</td>
<td>3.84 ± 0.56 (−66.6%)</td>
<td>1.90</td>
</tr>
<tr>
<td>PECNT3</td>
<td>608.94 ± 9.00 (+103.87%)</td>
<td>0.45</td>
<td>11.29 ± 0.94 (+31.74%)</td>
<td>12.27 ± 0.88 (+37.40%)</td>
<td>2.64 ± 0.53 (−77.0%)</td>
<td>1.85</td>
</tr>
<tr>
<td>PECNT5</td>
<td>684.99 ± 55.23 (+129.33%)</td>
<td>0.45</td>
<td>12.73 ± 0.98 (+48.54%)</td>
<td>14.25 ± 1.21 (+59.57%)</td>
<td>(2.32 ± 0.53) (−79.8%)</td>
<td>1.86</td>
</tr>
</tbody>
</table>
the toughness decreased sharply at higher loading and reached a value of $2.32 \times 10^6$ J m$^{-3}$ for PECNT5 which falls below the toughness of neat LDPE. The reason of decrease in toughness is that the deformation of LDPE molecular chains under loading was limited at higher CNT loading, causing the reduction in fracture strain \[58\].

In order to measure the surface strain fields over the surface of specimen during deformation, in situ optical strain mapping, usually referred to as digital image correlation (DIC) was used. In the present experiments, white dot spots were artificially produced by spraying black and white paints on the surface of composite specimens. A single CCD camera was used to record images during deformation. Using, VIC-2D DIC software, the displacement of each surface point is evaluated by comparing the digital images captured at different instants during the deformation process. Figure 5(f) shows the distribution of strain over the entire rectangular surface of all the composite specimens in the linear elastic regime at a stress of 4.5 MPa. It was found that, in the case of PECNT0.1, the strain is higher and the distribution is less uniform. With the addition of different wt% of MWCNTs; the stiffness increases as shown in the stress–strain curve in figure 5(a) and the strain decreases which is shown in figure 5(f) in the different colour mapping.

3.5. Thermal analysis of MWCNT-LDPE nanocomposites

The LDPE is an attractive option as pressure pipe materials due to its high flow but the pressure resistance and mechanical properties are affected at high temperature because of the degradation of the LDPE. Therefore, thermal properties of the MWCNT-LDPE nanocomposites were studied in order to determine the thermal stability and the crystallisation of polymer nanocomposites. TGA was employed to evaluate the effect of MWCNT loading upon their thermal stability. The weight loss in LDPE and MWCNT-LDPE nanocomposites with different wt% of MWCNT loadings, along with neat MWCNTs was evaluated as a function of temperature in a nitrogen gas atmosphere, as shown in figure 6(a). The weight loss up to 76% in the case of MWCNTs clearly indicates the presence of 24% impurities in the form of metal catalysts which is further confirmed by SEM, HRTEM and Raman spectroscopy, as discussed in supplementary information (figures S1 and S2).

Next LDPE is thermally stable up to 360.8 °C beyond which point the material suddenly loses weight up to 90%, perhaps due to the complete breakdown of the polymeric chains. However, with the addition of 0.1 wt% MWCNTs in the LDPE matrix, the thermal stability was increased to 390.6 °C which was higher than that of the neat LDPE matrix. With further increases in the MWCNT loading, the degradation performance was improved to 415.2 °C for the LDPE nanocomposite filled with 5.0 wt% of MWCNT and this change in decomposition temperature with respect to MWCNT loading is also shown in figure 6(b). This improvement in the degradation performance is attributed to the good thermal properties of MWCNTs and the increase in crystallisation in the MWCNT-LDPE nanocomposites, which is also observed in DSC study as shown in figure 7.

Figures 7(a) and (b) shows exothermic and endothermic curves for LDPE and MWCNT-LDPE nanocomposites. These scans are used to evaluate the melting and crystalline behaviour of MWCNT-LDPE nanocomposites with varying wt% of MWCNTs. It was observed that the addition of different wt% of MWCNT in LDPE matrix has no effect on melting temperature ($T_m$) of LDPE. However, the crystallisation temperature ($T_c$) of neat LDPE was 98.3 °C and the $T_c$ was increased by about 2 °C in the nanocomposite with 5.0 wt% of MWCNT loading, which indicates that the presence of MWCNTs in nanocomposites promotes the crystallisation of LDPE by serving as a nucleating agent \[59\]. The addition of MWCNT provides more surface area for the nucleation process.
The enthalpy of crystallisation ($H_c$) is calculated from area under the curve in figure 7(a) and a value of 58.82 J g$^{-1}$, was found for PECNT0 sample. On addition of different wt% of MWCNT in LDPE matrix, $H_c$ increased from 74.36 J g$^{-1}$ to 82.25 J g$^{-1}$ for PECNT0.1 to PECNT5 nanocomposites, respectively. The nucleation and growth of individual crystallites are so rapid that a very large number of crystallites are formed simultaneously and thus the large amount of heat is liberated during the crystallisation of LDPE by adding MWCNTs [60].

The crystalline fraction of polymer within the nanocomposites is $F_{H_293}$, where, $H_D$ is the enthalpy of fusion (J g$^{-1}$) and 293 J g$^{-1}$ is the enthalpy of fusion for a theoretically 100% crystalline LDPE [31]. The maximum change in the crystalline content of LDPE was seen up to 30.40% on addition of 5.0 wt% of MWCNTs.

An appreciable enhancement in crystallinity of MWCNT-LDPE nanocomposites suggests that CNT surface has a crystalline polymer coating which is clearly seen in the SEM micrographs of the fractured surface of MWCNT-LDPE nanocomposites in figure 8. CNTs not only nucleate polymer crystallisation, but can also be used to propagate the crystallisation for a large distance. The SEM micrographs in figures 8(a) and (b) for 1.0 wt% of MWCNT loading clearly show the coating of polymer on CNT surface and few pull-outs of CNTs are also seen but at higher loading of MWCNTs up to 5.0 wt% in LDPE matrix (figures 8(c) and (d)), more CNTs are pull-out from the matrix because of more concentration of CNTs and few small aggregates are also seen (inset of figure 8(d)). This confirms that CNTs interact at the interface of the crystalline polymer surface and an ordered interface can maximise the total stress transfer and can participate in the enhancement of the mechanical properties.

All the parameters such as crystallisation temperature ($T_c$), melting temperature ($T_m$), enthalpy ($\Delta H$) and % crystallinity ($F_c$) of these nanocomposites obtained from DSC curve are summarised in table 3.

### 3.6. Electrical properties of the MWCNT-LDPE nanocomposites

The electrical conductivity of polymer nanocomposites as a function of nanofiller content can be described using a simple percolation theory,

$$\sigma = \sigma_0 (\phi - \phi_c)^t; \quad \phi > \phi_c,$$  \hspace{1cm} (1)

where, $\sigma$ and $\sigma_0$ are the electrical conductivity of conductive polymer nanocomposites at different wt% of CNTs and the proportionality constant that is related to the intrinsic conductivity of the CNTs, respectively. $\phi$ is the weight fraction of the CNTs and $\phi_c$ is the percolation threshold. $t$ is the critical exponent, which reflects the dimensionality of the conductive network formed in the conductive polymer nanocomposites. The values of $\phi_c$ and $t$ for the MWCNT-LDPE nanocomposites were determined by fitting of the experimental data. The bulk electrical conductivity of the LDPE nanocomposites reinforced with different wt% of MWCNTs is shown in figure 9. Initially, the electrical conductivity was very low ($10^{-9}$ Scm$^{-1}$) and was close to that of neat LDPE matrix since wt% of CNTs was very less (i.e. 0.1 wt%). This may be due to the fact that only a small numbers of long CNTs are connected to each other and form a weak conductive network. Another reason is that some CNTs are close enough to each other and form a conductive network by the tunnelling effect, although there is no complete conductive path formed by contacting CNTs. The electrical conductivity was further improved from $10^{-11}$ Scm$^{-1}$ (theoretical value of neat LDPE) to $5.0 \times 10^{-6}$ Scm$^{-1}$ i.e. by 7 orders of magnitude, when the MWCNTs loading was increased from 0 to 1.0 wt%. This enhancement in electrical conductivity is strongly linked to the dispersion of MWCNTs in the LDPE matrix and the formation of electrically conductive path. This

![Figure 7. DSC exothermic (a) and endothermic (b) curves for MWCNT-LDPE nanocomposites.](image)
remarkable increase in electrical conductivity of 1.0 wt% CNT loaded LDPE nanocomposite is referred to as its percolation and the wt% of CNT at this stage is called the percolation threshold \( (\phi_c) \).

The electrical conductivity increased continuously and reached a value of \( 2.38 \times 10^{-2} \text{ Scm}^{-1} \) with increasing wt% of MWCNTs up to 5.0 wt% which is 11 orders of magnitude higher than that of neat LDPE. At this stage, the CNT concentration was large enough to form electrical conductive network easily. Low percolation threshold of 1.0 wt% (see figure 9) may be due to high aspect ratio (>3000) and uniform dispersion of MWCNTs, which allow them to form a good electrical path more easily in the LDPE matrix. The critical exponent \( t \) is expected to depend on the system dimensionality and was estimated to be 2.0 for three-dimensional systems [61]. Generally, the value of \( t \) for two-dimensional systems is around 1.5 and greater than 2 for three-dimensional systems.

### 3.7. Piezo-resistive performance of MWCNT-LDPE nanocomposites

Four different samples of MWCNT-LDPE nanocomposites (i.e. PECNT1, PECNT2, PECNT3 and PECNT5) were tested to investigate the relationship between change in electrical resistance and the applied mechanical
strain, since the percolation threshold was 1.0 wt%. Two aluminium wires were bonded to the specimen in a back-to-back configuration and the sample was set in a tensile testing machine as shown in figure 10(a). $l_0$ is the distance between the electrodes under no load. The piezo-resistive response was measured under monotonic tensile loading at a loading rate of 5 mm min$^{-1}$. These nanocomposite samples exhibited a change in electrical resistance up to a strain level of 16% as shown in figure 10(b). During stretching, the length, cross section and the electrical resistivity of the nanocomposite samples changed with strain causing change of resistance with increasing strain. Figures 10(c) and (d) show piezo-resistive response of these nanocomposites in linear elastic

Figure 9. Electrical conductivity of MWCNT-LDPE nanocomposite films with different wt% of MWCNTs loading and inset shows log $\sigma$ versus log ($\phi - \phi_c$), where, $\phi$ is the CNT wt% and $\phi_c$ is the percolation threshold.

Figure 10. (a) Schematic of specimen and test setup used for piezo-resistive measurements, (b)–(d) piezo-resistive behaviour of MWCNT-LDPE nanocomposites at linear elastic and inelastic regimes.
(up to 2.3% strain) and inelastic (2.3%–15% strain level) regimes, respectively. Note that the uni-axial yield strain \( \varepsilon_y = \frac{\sigma_y}{E} \) for the composites tested here is \( \sim 1.8\%–2.3\% \) (see figure 5(a) and table 2).

Initially, the composite film with dense CNT network (lower initial resistance, \( R_0 \)) under no load, has more number of electrical paths as many CNTs are in contact with each other. This happens when the inter-CNT distance \( d \ll D \), where \( D \) is the diameter of CNT. As we used high aspect ratio CNTs in this study, one CNT might be connected to several other neighbouring CNTs, resulting in more number of electrical paths. CNT geometry, orientation, position and entanglement of the CNTs, type and content of CNTs have strong influence on piezoresistivity. During early stages of loading, disturbance in the conductive network cause electrical resistance change in a gradual manner due to reducing number of electrical paths, ultimately leading to disconnection between CNTs. Once disconnected network of CNTs is formed, current flow due to direct contact between CNTs ceases. At this stage, further changes in the piezo-resistive behaviour can be well explained via electron tunnelling and hopping mechanisms in the polymer nanocomposites [62, 63]. Tunnelling current flows when \( D < d \ll C \), where \( C \) is the cut-off distance (distance at which the resistance between two neighbouring CNTs is 30 times higher than the resistance of single CNT) such that the electrons can tunnel through the LDPE matrix and can form a quantum conductive junction [64]. With increase in load, the inter-CNT distance (\( d \)) between the conductive path increases further predominantly due to rigid body rotation and translation of CNTs in the LDPE causing topological changes of CNT network but the tunnelling mechanism remains active as long as \( D < d \ll C \). When the load is increased further, micro-cracks are generated and these cracks grow in size and numbers, leading to separation of conducting paths. This contributes to the large irreversible change in resistance.

For applied strain \( \varepsilon < 2.3\% \) (within elastic regime), regardless of the wt% of CNTs, the relative change in resistance with strain is linear for all cases, albeit a slight non-monotonic change is observed for the one with 2.0 wt% (figure 10(c)). The piezo-resistive response becomes nonlinear (see figure 10(d)) only for \( \varepsilon > 10\% \) (inelastic regime). For low wt% of MWCNTs in LDPE matrix, CNTs are well dispersed. During tensile loading of such composites, inter-particle distance increased; therefore, electron tunnelling and hopping mechanisms were dominant, causing increase in resistance. At higher wt% of MWCNTs in LDPE matrix, changes in resistance was very low during early stages of loading, which may be due to the fact that CNTs are entangled together at high filler concentration. The sensitivity of the nanocomposite to strain and/or damage state can be assessed by the gauge factor (\( k \)). Gauge factor at any instant of stretching can be defined as

\[
k \overset{\text{def}}{=} \frac{1}{R_0} \frac{dR}{d\varepsilon},\tag{2}
\]

where, \( R_0 \) is the resistance at no load and \( \frac{dR}{d\varepsilon} \) is the rate of change of resistance with strain. Therefore, gauge factor was calculated for all of the nanocomposite samples in different regimes of strain i.e., in the linear-elastic and inelastic regimes to determine the sensitivity of these nanocomposites to strain and/or damage (figures 11(a) and (b)). The value of gauge factor was found to be 17.75, 52.82, 4.88 and 9.92 for the PECNT1, PECNT2, PECNT3 and PECNT5 nanocomposites, respectively in the linear-elastic regime. With these high values of sensitivity coupled with linear piezo-resistive response, our nanocomposites can be used for self-sensing at low strain up to 2.3%. As shown in figure 10(c), the maximum change in electrical resistance was about 40% for the MWCNT-LDPE nanocomposites at 2.3% of strain (linear elastic regime).
We could derive the following expression for the gauge factor considering linear-elastic, isotropic behaviour of the nanocomposite specimens undergoing simple extension, at any instant of loading such that \( 0 < \varepsilon < \varepsilon_{\gamma} \) and \( |\varepsilon| \ll 1 \). For brevity, details of derivation are not included here.

\[
k = (1 + 2\nu) + \frac{1}{\rho_0} \frac{d\rho}{d\varepsilon} + \frac{(\nu - \rho_0)}{\rho_0} (1 + 2\nu).
\]  

(3)

Here, \( \nu \) is the Poisson’s ratio of the composite film and we assume that \( \nu \) remains constant during elastic deformation. For the composite films tested here, \( \frac{1}{2} < \nu < \frac{1}{2} \). Taking \( \nu \sim \frac{1}{2} \), we could simplify the above expression to the following

\[
k = 1.9 + \frac{1}{\rho_0} \frac{d\rho}{d\varepsilon} + 1.5\frac{(\nu - \rho_0)}{\rho_0},
\]  

(4)

where, \( \rho_0 \) is the average resistivity of the film at no load (i.e., at \( \varepsilon = 0 \)), \( \rho \) is the resistivity at any \( \varepsilon \) and \( \frac{d\rho}{d\varepsilon} \) is the resistivity gradient at \( \varepsilon \). The values of \( k \) obtained from the experiments for all of the composites tested here vary from 4.88 to 52.8 in the linear elastic regime. Therefore, it can be inferred from the above equation clearly that the resistivity gradient (second term) and the coupling between the deformation and relative resistivity change (third term) contribute to overall resistance change significantly even at small strain, although these effects are usually omitted in the calculation of gauge factor.

In first inelastic linear regime (2.3%–11% strain range), the average gauge factor for in figure 11(b), the values of gauge factor were found to be 2.85, 20.38, 5.73 and 42.63 for the PECNT1, PECNT2, PECNT3 and PECNT5, respectively.

Similarly, in second inelastic regime (11%–15% strain range), the gauge factor values were calculated and were found to be 259.72, 530.74, 13.94 and 292.94 for the PECNT1, PECNT2, PECNT3 and PECNT5, respectively. At higher strain level, nanocomposites showed a strong nonlinear trend in piezoresistivity. This large change in gauge factor from the linear elastic regime to the inelastic regime may be due to the fact that with increasing load, the distance between the CNT networks starts to increase, leading to a sudden raise in resistance. In these cases, electron tunnelling and hoping mechanisms are dominant giving raise to non-linear piezoresistive behaviour of these nanocomposites.

Therefore, LDPE with low wt% of CNTs (high initial resistance) can be used for strain sensing if expected level of loading on the composite is less than the yield limit (\( \varepsilon \sim 3\% \)). On the other hand, composite with higher wt% of CNTs (low initial resistance) can be used for sensing the damage state and its evolution when the composite is loaded beyond the yield limit (\( \varepsilon \sim 3\%–16\% \)). Interestingly, the sensitivity, linearity of piezoresistive behaviour, and stretchability of the nanocomposite can be tuned by adjusting the concentration of the CNTs and process parameters.

4. Conclusions

In summary, MWCNT-LDPE nanocomposites were prepared by solvent mixing followed by a compression moulding technique and their mechanical, thermal, electrical and piezo-resistive performances were studied. A significant increase in electrical conductivity from \( 10^{-13} \) Scm\(^{-1} \) for the neat LDPE to \( 2.38 \times 10^{-2} \) Scm\(^{-1} \) for 5.0 wt% loaded MWCNT-LDPE nanocomposites was achieved with a low percolation threshold of 1.0 wt%. The thermal properties highlighted the enhancement in thermal stability as well as crystallinity of these nanocomposites. The overall improvements in UTS, yield strength and Young’s modulus were found to be 59.6%, 48.5% and 129.3%, respectively for 5.0 wt% loading of MWCNTs in LDPE matrix. These nanocomposites also possessed good self-sensing properties with good sensitivity (gauge factor) in the range of 4.88–52.82 for PECNT1 to PECNT5 in the linear elastic regime. Therefore, these nanocomposites can be useful for strain sensing applications in linear elastic regime. In inelastic regimes, these composites provide good sensitivity up to 15% of strain. Therefore, they can also be useful for damage sensing and SHM (at higher strain levels). Such nanocomposites, filled with MWCNTs, will open up opportunities for its novel applications as a self-sensing material such as for civil water pipeline and landfill membranes.

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Conflict of interests

The authors declare no competing financial interest.

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