Chapter-6

Mechanical & Electrical Properties of CNT- Thermoplastic Composites
6.1 Introduction

In the previous chapters we have discussed the processing and properties of MWCNTs reinforced composites with epoxy and phenol (novalac) resins which are thermosetting polymers. These are non recyclable and need compounding with addition of reinforcing agents, stabilizers or cure systems. These limitations are absent in thermoplastic polymers and hence batch to batch variations in terms of weighing and material components are absent, leading to improve consistency in both raw material and fabrication techniques.

Recently, several studies have been reported on MWCNT reinforced thermoplastics as effective and lightweight materials for structural, electrical and EMI shielding and other applications. This includes poly (methyl methacrylate) (PMMA) [38, 168, 189], polystyrene (PS) [38, 190], polypyrrole (PPY) [190]), polyurethane (PU) [167], polypropylene (PP) [191], polyethylene [192-193] and many more [194-195]. In the present chapter we will discuss low density polyethylene (LDPE), a thermoplastic resin reinforced with MWCNTs. Main emphasis has been given on the electrical conductivity and EMI SE of the composites. There is no study on the CNT-LDPE polymer system for EMI shielding effectiveness primarily because of the lower electrical conductivity of the polymer (~10^{-20} \text{ S/cm}^{-1}) [193] compared to other polymer systems e.g. PMMA (10^{-16}\text{ Scm}^{-1}) [196], PU (10^{-14} \text{ Scm}^{-1}) [167], PS (10^{-17} \text{ Scm}^{-1}) [38] etc. However, LDPE is the most common low cost polymer used for different purposes and could be an interesting material for such applications if large improvement in the electrical conductivity is achieved with CNT reinforcement.
Polyethylene is a semicrystalline polymer consisting of long chains produced by polymerization of the ingredient monomer ethylene (C$_2$H$_4$, structure shown in Fig. 6.1) and is the most widely used plastic polymer. It can be classified into a variety of categories based on density and branching including low density polyethylene (LDPE), high density polyethylene (HDPE), crosslinked polyethylene (XPE), linear low density polyethylene (LLDPE) etc. With respect to sold volume, the most important polyethylene grades are LDPE. It has high degree of branching with long chains gives molten LDPE unique and desirable flow properties with density of 0.91-0.94 g/cm$^3$.

![Fig. 6.1 Ethylene polymerize to form polyethylene](image)

Although this chapter not includes the effect of MWCNT loading on mechanical properties of LDPE composites but certainly it get enhanced by MWCNT incorporation and widely investigated in the past decade with varying reinforcements. Xiao et al [197] carried out the studies on mechanical properties of LDPE- MWCNTs composites and found an increment of 89 % in Young’s Modulus and 56 % increment in tensile strength with 10 wt% MWCNT loading. Several other studies have been carried out on the enhancement of mechanical properties of LDPE with the reinforcement of MWCNTs [198-199].

Studies on the improvement of electrical conductivity for MWCNTs reinforced LDPE composites have been considered by Olga Valentino et al [200] who dispersed MWCNTs by melt mixing and reported six orders of magnitude increase in electrical conductivity with 1 to 2.5 wt% MWCNT concentrations. The final electrical conductivity was $10^{-3}$ S/cm at 7wt% MWCNT loading. In another study by McNally et al. [201], MWCNT-PE composites with weight fractions ranging from 0.1 to 10 wt% of MWCNT were prepared by melt blending using a mini-twin screw extruder. They reported an
almost 16 orders of magnitude increase in conductivity and finally reached to $10^{-4}$ S/cm at 10 wt% MWCNT loading. In one of the most recent study by Fu et al. [192] composites were prepared by solvent casting technique and reported electrical conductivity upto $10^{-4}$ S/cm at 7 vol%. Though these results are encouraging but the overall improvement in the electrical conductivity is still too low for effective EMI shielding. The processing conditions affect the interaction between the CNTs and polymer and hence directly influence the final electrical and mechanical properties of the composite [202]. The present chapter undertakes primarily the further improvement in electrical conductivity of CNT-LDPE composites by using high aspect ratio MWCNT (> 5000, observed in chapter 3) and using solvent casting followed by compression molding techniques different than the one used so far. Moreover, much of the experimental and theoretical research focused on the electrical properties of MWCNTs/polyethylene composites but there are still no reports on the EMI SE of these composites. Thus an important application for electrical conductive composite is still uncovered. In this study the electrical conductivity and EMI shielding effectiveness (SE) of the composites with varying MWCNTs % was measured and found that these can be used as very light weight EMI shielding and antistatic material. EMI SE of these composites was investigated in the frequency range of 12.4-18 GHz (Ku band) for the first time.

MWCNTs have also been shown to alter the crystallization kinetics of semi crystalline polymers like LDPE [77]. Recently Sandler et al [203] highlighted that the intrinsic crystalline quality of the nanocomposite and orientation of the embedded CNTs are major factors controlling the reinforcing capability of CNTs. Li and coworkers [204] in their studies found that the matrix crystallinity affects the percolation threshold and dielectric properties of composites. Also the study of Abbasi et al [205] revealed that the crystallinity of composites also depends on the aspect ratio of the MWCNTs used and found that higher aspect ratio of MWCNTs yields higher crystallinity to the composites. This chapter discusses the change in crystallinity of LDPE- MWCNT composite with variation in MWCNT loading using X-ray diffraction (XRD) and Differential scanning
Calorimetry (DSC). The effect of MWCNT loading on the thermal stability of the LDPE composites has also been discussed.

6.2 Experimental

6.2.1 Materials

Reliance Industries Ltd. India supplies the LDPE used in study in pellet form. The characteristics of the LDPE are: density = 0.925 g/cm$^3$, melting temperature $T_m = 107^0C$ and molecular weight 200000. The synthesis process of MWCNT used is discussed in detail in chapter 2.

6.2.2 Fabrication of MWCNT-LDPE composites

MWCNT reinforced LDPE composites were prepared by the combination of solvent casting followed by compression moulding technique as detailed below.

6.2.2.1 Preparation of nanocomposites film by solvent casting

As-synthesized MWCNT were ultrasonically dispersed in benzene for 5h to obtain a stable suspension of CNT in benzene. The suspensions were then mixed with solutions of LDPE formed by stirring LDPE pellets for 5hr at $70^0C$ in benzene to obtain a series of mixtures of CNT/LDPE containing 2,3,5,7 and 10 wt. % of CNT and designated as PECNT2, PECNT3 PECNT5, PECNT7 and PECNT10 respectively. The mixtures were then stirred on a magnetic stirrer for 24h to obtain a uniform dispersion of CNT in LDPE. Thin CNT reinforced LDPE nanocomposite films were casted from this solution by pouring the solutions into a waxpol coated petri dish (diameter 4 inch) and allowing the solvent to evaporate over 24 hrs followed by drying in oven at $80^0C$. The resulting films had a thickness of about 0.25-0.3mm. Blank LDPE films were also casted by the same technique and designated as PECNT0.
6.2.2.2 Fabrication of MWCNT-LDPE composite blocks by compression molding

In this method solvent casted films from the aforementioned method were cut into pieces and stacked in a die mold (60mm x 20mm x 1.65mm). This stack was then compression molded at 100°C.

6.3 Results and Discussion

6.3.1 Morphology of the MWCNT-LDPE composites

The morphology and degree of dispersion of the MWCNTs in the PE matrix at different length scales was investigated using scanning electron microscopy (SEM). The examination of SEM images confers that the MWCNTs are well dispersed and distributed
in LDPE matrix. Both individual and few agglomerations of different dimensions of MWCNTs were evident.

Fig. 6.2 shows the dispersion of CNT in the LDPE matrix. As evident from the figure that the tubes are wetted good with polymer. As shown in figure that with 2-5wt. % CNT the dispersion is much better as compared to 10wt. % CNT. The tube-to-tube connectivity is very much evident because of long length of CNT marked by arrow.

6.3.2 Crystallinity and thermal stability of the composites
6.3.2.1 XRD Studies

The XRD pattern for MWCNTs (PECNT100), shown in Fig. 6.3 exhibits a sharp peak to (002) plane at about $2\theta=26^0$ and is derived from the ordered arrangement of the concentric cylinders of graphitic carbon [206]. The peaks around $43^0$ are due to the (1 1 0) and (1 0 0) graphitic planes plus small amount of catalyst particle encapsulated inside the walls of the MWCNTs [165]. LDPE shows two characteristic peaks at $21.2^0$ and $23.8^0$ due to crystalline phase. With the addition of CNT the characteristic peak for LDPE at $2\theta=23.8^0$ shows increase in the sharpness. The full width at half maximum (FWHM) [147]
gradually shrinks with the incorporation of MWCNT and changes from 0.924 for PECNT0 to 0.55 for PECNT5 showing increase in the degree of crystallinity of the polymer with addition of CNT as shown in Fig. 6.4. The increase in the crystalline contents could be the result of the strong interactions between CNT and the polymer interface. DSC has also confirmed this as shown later in the text.

![Graph showing variation of FWHM with MWCNT loading](image)

**Fig. 6.4 Variation of FWHM with MWCNT loading**

### 6.3.2.2 DSC Studies

The detail theory of DSC to calculate $T_m$ and crystallinity is discussed in chapter 2. DSC curve of LDPE and MWCNT reinforced LDPE nanocomposites is shown in Fig. 6.5 and characteristics are tabulated in Table. 6.1. It shows that addition of MWCNT to LDPE has very little effect on melting temperature ($T_m$) of LDPE. $T_m$ has been increased to $\approx 20^\circ$C for the PECNT5 sample. The similar trend has been observed by McNally et al [201].

The crystalline fraction of polymer within the nanocomposite $F_c$, was calculated from

$$F_c = \frac{4N}{293} \frac{\Delta H}{f}$$  \hspace{1cm} (1)
where $\Delta H$ is the enthalpy of fusion (J/g), 293 is the enthalpy of fusion for a theoretically 100% crystalline PE \{201\} and $f$ is the weight fraction of polymer.

The maximum change in the crystalline content of LDPE is seen upto addition of 5 wt% MWCNT (improvement is around 37%) only. Further addition of the tubes result into agglomeration and does not help in CNT-polymer interactions to cause enhancement in the crystallinity of the LDPE, the phenomena evident in the SEM micrograph for the sample PECNT10 (Fig. 6.2(c)) and XRD data (Fig. 6.3 & 6.4).

![Fig. 6.5 DSC curve of LDPE and MWCNT-LDPE nanocomposites](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$F_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PECNT0</td>
<td>107.30</td>
<td>46.45</td>
<td>15.85</td>
</tr>
<tr>
<td>PECNT2</td>
<td>108.67</td>
<td>60.48</td>
<td>21.06</td>
</tr>
<tr>
<td>PECNT5</td>
<td>109.26</td>
<td>61.03</td>
<td>21.73</td>
</tr>
<tr>
<td>PECNT10</td>
<td>107.26</td>
<td>51.77</td>
<td>19.63</td>
</tr>
</tbody>
</table>

Table 6.1 DSC characteristics of LDPE and LDPE/MWCNT nanocomposites
6.3.2.3 TGA Studies

Fig. 6.6 shows the thermo gravimetric (TG) traces of pure LDPE and its composites with incorporation of MWCNT. As shown in the figure pure LDPE has excellent thermal stability upto 375°C after which it has a single stage decomposition profile and the material suddenly loses 90 % weight. This may be attributed to the complete breakdown of the polymeric backbone. However, on addition of MWCNT the weight loss initiation temperature shifts to higher temperature i.e. 415°C for PECNT5, showing better thermal stability after incorporation of MWCNT. Similarly the onset of degradation of LDPE was enhanced by 30°C and 40°C for 2 wt % and 10 wt % loading of MWCNT respectively. This may be attributed to the increase in crystallization of LDPE as observed by XRD and DSC.

![TGA of LDPE and MWCNT-LDPE nanocomposites](image)

**Fig.6.6 TGA of LDPE and MWCNT-LDPE nanocomposites**

6.3.3 Electrical conductivity

Fig. 6.7 shows variation of room temperature electrical conductivity with change in MWCNTs level. It is observed that there is a sharp increase in the conductivity with increasing wt % of MWCNT loading due to formation of conducting links and increase in the charge transport paths. The conductivity reaches a value of 0.63 S/cm at a loading
level of 10 wt%. This value is much higher than the previous reported value as shown in Table 6.2. The electrical conductivity composites prepared with 10 wt% MWCNTs loading improved by 20 orders of magnitude as compare to pure LDPE. This is the maximum improvement reported so far with LDPE polymer with MWCNTs loading and almost an order of magnitude higher as compared to the closest value reported by Gorassi et al [193]. There could be two reasons for such improvement, first is the long length of the MWCNTs (discussed in chapter 4) and second is the proper dispersion method. It is well known and also discussed in detail in chapter 4 that the length or the aspect ratio of the filler component greatly influences the electrical conductivity of the composite as long length of MWCNTs helps in making conductive networks with composites. Previous studies as shown in Table 6.2 are mainly related to melt mixing where the

![Graph showing variation of electrical conductivity with MWCNT loading](image)

**Fig. 6.7 Variation of electrical conductivity with MWCNT loading**

possibility of opening the bundles into individual tubes was very less. Whereas the present study used solvent to disperse MWCNTs followed by ultrasonication and
magnetic stirring for mixing it with LDPE which ensures better dispersion as compared to previous studies. The present study aimed to achieve high EMI shielding materials which can be obtained with highly conducting materials, so only high loaded MWCNTs composites are discussed.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Wt% and Type of CNT</th>
<th>Processing Technique</th>
<th>$\sigma$ (S/cm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 wt% MWCNT (CVD) aspect ratio &lt;1000 treated with HCL/HNO$_3$</td>
<td>Ball milled and hot pressed</td>
<td>$3 \times 10^2$</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>5wt% MWCNT aspect ratio~1000-3000</td>
<td>Solvent casting</td>
<td>$5 \times 10^{-3}$</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>30 wt% MWCNT aspect ratio~100</td>
<td>Sonicated and melt mixed</td>
<td>$5 \times 10^{-8}$</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>7wt% MWCNT aspect ratio&gt; 2000</td>
<td>Melt mixing in a micro-twin screw extruder</td>
<td>$10^{-3}$</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>10wt% MWCNT Length - &gt;200 µm Diameter-10-60 nm</td>
<td>Solvent casting+ compression molding</td>
<td>0.63</td>
<td>In this study</td>
</tr>
</tbody>
</table>

Table. 6.2 Electrical conductivity of MWCNT-LDPE composites reported by several author

6.3.4 EMI Shielding

The theory of EMI SE of MWCNTs polymer are discussed in previous chapters. SE measurements were carried out in the 12.4–18 GHz microwave range and keeping the input power level at -5dBm.

In two port network analysis, the scattering ($S$) parameter i.e. $S_{11}$ (or $S_{22}$), $S_{21}$ (or $S_{12}$) can be correlated to reflection coefficient (R) and the transmission coefficient (T) as:

$$ T = |S_{12}|^2 = |S_{21}|^2 $$  \hspace{1cm} (2)

$$ R = |S_{11}|^2 = |S_{22}|^2 $$  \hspace{1cm} (3)

The absorbance can then be calculated as

$$ A = 1 - R - T $$  \hspace{1cm} (4)
It is observed that $SE_T$ increases with increase in MWCNT (Fig. 6.8) due to increase in DC electrical conductivity. However, to explore further total shielding effectiveness is separated into two components i.e. $SE_A$ and $SE_R$ (Fig. 6.9(a) & Fig. 6.9(b)).

The $SE_A$ (Fig. 6.9(a)) exhibits rapid enhancement from $-10$ to $-16$ dB with the increased CNT loading. This may be explained in terms of increase in conductivity as well as capacitive coupling effects. The plot of $SE_A$ (dB) versus $(\sigma)^{1/2}$ (Fig. 6.10(a)) shows linear dependence confirming the validity of equation 9 of chapter 4. The increased conductivity may manifest itself as increase in both long range charge transport as well as number of possible relaxation modes, leading to enhanced ohmic losses [207] in the proposed electromagnetic shielding material. The total shielding effectiveness of $-22.4$ dB indicates that these materials could be utilized effectively for the shielding purposes in the Ku-band (12.4–18.0 GHz).

Fig. 6.9(b) shows that $SE_R$ (at 15.2 GHz) increases slightly from $-2.8$ to $-4.8$ dB with the increase in MWCNT content which may be ascribed to increase in the
6.4 Conclusion

CNT with high aspect ratio play a key role in imparting high electrical conductivity to most insulating polymer like LDPE. The electrical conductivity of LDPE was increased by 20 orders of magnitude (from $10^{-20}$ to 0.6 S/cm) on addition of 10 wt% MWCNT. This is perhaps the highest value reported so far for the MWCNT-LDPE composites. The thermal stability of these composites also improved with the improvement in the crystallinity of the MWCNT reinforced LDPE matrix (37% over the pristine LDPE). The total shielding effectiveness of 22.4 dB indicates that these materials could be utilized effectively in the Ku8 band (12.4–18.0 GHz) even though the electrical
conductivity of the pristine LDPE is several orders of magnitude less than the conventional and costlier polymers used for EMI shielding devices.