Twin-Screw compounding extrusion of Polystyrene (PS)/Multi walled carbon nanotube (MWCNT) nanocomposites with varying process parameters: Comprehensive investigation of morphology, interfacial behavior, thermal stability, rheology and electrical resistivity

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Abstract

PS was compounded with MWCNT loadings of 1, 2, 3, 5 and 7.5 wt.% at varying speeds, throughputs and extruder barrel temperatures. High SME inputs at enhanced processing speeds seem to have had the single largest effect in enhancing dispersion. Relative evaluations of PS-MWCNT interaction indicate an interphasial layer growth of 24% for 2 wt.% MWCNT additions at 1100 rpm compared to 18% growth at 500 rpm. Raman analysis does not show MWCNT peak shift when incorporated into PS but a constant increase in FWHM is observed irrespective of the MWCNT content. Significant enhancement in thermal stability occurs up to 2 wt.% MWCNT loading while 1-2 wt.% shows the rheological threshold. A drop in 10 orders of magnitude of volume resistivity is achieved on a 2 wt.% sample processed at 1100 rpm compared to those processed at 500 rpm and these do not differ by much to those achieved with higher MWCNT contents.

Introduction

Carbon nanotube (CNT) based polymer composites have been a significant area of research in the last couple of decades owing to CNTs high aspect ratios with nanometric dimensions, low mass density and intrinsically superior electrical,\(^\text{[1-4]}\) mechanical,\(^\text{[4-7]}\) and thermal properties.\(^\text{[4,8,9]}\) Continuously lowering costs of CNTs with increase in demand and production capabilities augments favorably for a huge polymer-CNT nanocomposite market. Interesting observations on MWCNT based composites have been plenty starting from different ways of MWCNT synthesis to its application in electromagnetic shielding (EMI),\(^\text{[10-13]}\) sensors,\(^\text{[14-16]}\) electrostatic charge dissipation (ESD),\(^\text{[17]}\) flame retardancy,\(^\text{[18]}\) wind turbine blades,\(^\text{[19]}\) photovoltaic packaging,\(^\text{[20]}\) electrically conducting cables\(^\text{[21]}\) etc. A critical advantage of MWCNT based composites over other conductive fillers like such as carbon black is their ability to form percolative conductive pathways at low loadings with increase or without significant drop in mechanical behavior. However, the fact that commercially viable CNTs are only available as entangled agglomerates makes it difficult to realize the complete potential of CNT based polymer nanocomposites. The rate at which nanomaterials are developed outweighs the rate of nanoscale analysis owing to the difficulties associated with its characterization and inability to track interaction mechanisms at nanoscale. This may be one major reason for not being able to achieve a deep insight and consensus on a global scale in this research domain.

Several processing methodologies such as solution casting,\(^\text{[22-25]}\) melt mixing,\(^\text{[26-31]}\) solution mixing,\(^\text{[22,23,32-35]}\) different methods of in-situ polymerization of the monomer in the presence of CNTs,\(^\text{[36-38]}\) coagulation spinning,\(^\text{[39]}\) mechano-chemical pulverization,\(^\text{[40]}\) solid-state shear pulverization,\(^\text{[41,42]}\) electro spinning\(^\text{[43-45]}\) to mention a few have been adopted for the synthesis of polymer-MWCNT composites over the past decade. However, owing to its simplicity and adaptability for a commercial scale up melt mixing seems to be the most
commonly employed approach for thermoplastic polymer-MWCNT nanocomposites. For a compounding process to give optimum dispersion quality optimization of all the participating process parameters like the screw configuration, screw speed, throughput/residence time and temperatures is imperative. Higher shear forces are considered ideal for achieving better dispersion qualities as reported for several systems\[^{29,31,46-49}\] as they play a key role in individualization of the MWCNTs.\[^{50}\] High shear processing of Polyvinylidene fluoride (PVDF)-CNT composites resulted in a conductive percolation threshold of 1.5 wt.% CNT while low shear intensity required 2.5 wt.% CNT content in the work of Chen et al.\[^{51}\] Better mechanical properties were observed with high speed processing of Poly (styrene-butadiene-co-butadiene-b-styrene) (SBBS)-MWCNT composite system by virtue of enhanced dispersion qualities at high shear rates.\[^{52}\] Andrews et al. report enhanced dispersion qualities with increasing energy inputs while melt mixing Polystyrene(PS) with MWCNT, but with a tradeoff of shortening the MWCNTs to one-third of their original length.\[^{26}\] The increase in speeds from 100 rpm to 500 rpm gave better macro dispersion irrespective of the screw configuration on Polycaprolactone (PCL)-MWCNT composites according to Villmow et al. owing to the tripled energy input at this condition.\[^{53}\] Another attempt to investigate the effect of extrusion parameters on masterbatch dilution to produce poly (lactic acid) (PLA)-MWCNT composites on a twin-screw extruder by Villmow et al. showed similar observations.\[^{50}\] Several other factors like having specific functional moieties on the CNTs,\[^{54}\] varying polymer molecular weights,\[^{55}\] type of feeding,\[^{56}\] specific orientation setups at the extruder die,\[^{57}\] compatibility of CNTs with one polymer in a blend\[^{58}\] etc. also help in achieving optimum dispersion levels and low percolation thresholds.

The phenomenon of wetting, melt infiltration, rupture and erosion of agglomerates and distribution is common in compounding of a thermoplastic-CNT composite. Shear stresses which are principal driving factors for CNT dispersion are derived primarily from the
nature of the processing conditions. High speeds promote rupture of agglomerates while enhanced shear dominates agglomerate erosion leading to individualized tubes. The work explaining the kinetics of polycarbonate (PC)-MWCNT dispersion in a melt mixing chamber quantifies the extent of dispersion by erosion and rupture according to the extent of shear stresses supplied by the process parameters.[59] To quantitatively describe dispersion qualities is complex, but attempts have been made to assess dispersion indices by the image analysis of optical micrographs.[60,61] These quantifications assume a density factor for CNTs, but it is difficult to assess the porosity of a combination of agglomerates after dispersion in a matrix.

Understanding the mechanism of a polymer-CNT interaction is necessary to effectively tailor CNT based nanocomposites. CNTs being inert materials are not expected to form a strong chemical interface with the polymer unless their surface is modified through either chemical or physical means, but the level of interaction is complex to quantify. This can be attributed to a combination of various factors starting from the significant variations in CNT geometries, intra filler interactions due to electrostatic and Van der Waals forces, nature of CNT agglomerations and porosities, inabilities to produce 100% pure tubes, various types of functional treatments, aftermaths of processing etc. However, interfacial shear strengths and load transfer capabilities on CNT based composites have been reported based on modeling techniques[33,62,63] and experimental analysis.[64-67]

The estimation of the size of the interfacial layer in different nanofillers reinforced composite systems have been demonstrated with NMR measurements on silica filled elastomeric systems,[68,69] calorimetry measurements on PMMA/SiO₂ composites,[70] DMTA measurements of PS/silica nanocomposites,[71,72] combination of dielectric techniques and DSC measurements on poly(dimethylsiloxane)/silica composites[73] etc. These investigations analyse the interface primarily by the variation of glass transition temperature. However there are a lot of contradictions and interpretations vary from author to author. According to Liu
and Wu filler additions are expected to impose restrictions on polymer mobilities and hence glass transition of the system increases.\textsuperscript{[74]} Lowering of glass transitions on filler additions have been described in terms of weak polymer-filler interaction\textsuperscript{[75]} or as increase in the free volume for increased polymer chain mobility.\textsuperscript{[76]} Simultaneous effects of increase and decrease in polymer mobilities due to filler addition creates a dynamic balance in the system causing neither increase nor decrease of glass transition temperatures.\textsuperscript{[77]} Measurements of glass transitions have been made on thin polymer films and their variations have been correlated with the nature of the interactions between the films and the substrates.\textsuperscript{[78,79]} Long and Lequex show that these shifts can be interpreted as interface induced gradients in glass transition temperatures.\textsuperscript{[80]} The nature of this interfacial layer plays a significant role in determining the strength of the composite or even completely dominates the properties of the composite. Calorimetric analysis was also used for the quantification of the interfacial layer in Polyamide 6 (PA6)/CNT composites\textsuperscript{[81]} and on poly(methyl methacrylate)(PMMA)/CNT composites.\textsuperscript{[82]} CNT additions of up to 10 wt.% in PA6 resulted in the lowering of glass transition temperatures while further additions reversed the trend whereas the immobilized portion of polymer increased with increase in CNT loadings in the former while there were no variations on glass transition temperatures in the latter.

Well dispersed tubes with a shorter tunneling distance of less than 1.8 nm\textsuperscript{[48]} in a specified free volume in the matrix leads to low electrical percolation thresholds; while agglomerates in the matrix free volume containing CNT agglomerates within them join to form a conductive network at higher CNT loadings. Distribution of CNTs in the matrix is highly necessary but it is quite complex to imagine how this can be controlled. Independent of how we achieve dispersion and distribution, it is important to optimize process parameters to achieve electrical conductivities at the lowest possible CNT loading with increasing/ not significantly diminishing the mechanical behavior.
The indirect determination of CNT dispersion in a polymeric matrix by evaluation of nanocomposite mechanical and electrical properties is commonplace, but mechanisms governing the property enhancements at nanometric dimensions are complex to investigate. Any analysis on a large scale compounding of thermoplastic-MWCNT composites is a step closer to reality in analyzing the properties of the composite to analyse optimum requirements for an industrial component. This work deals with a PS-MWCNT system processed on a large scale twin screw compounding equipment with varying processing parameters and a comprehensive analysis of the process on the interfacial, thermal, rheological and conductivity behaviors of the composite.
Experimental

Materials

Extrusion grade Polystyrene PS 158K with a specific gravity of 1.04 (ASTM D792) and a Melt Mass-Flow rate (MFR) of 3 g/10min (ASTM D1238) was purchased from BASF SE (Ludwigshafen, Germany). Baytubes C150P used as MWCNTs in this work were purchased from Bayer Material Science AG (Leverkusen, Germany). These tubes had a carbon purity of 95 %, bulk density of 140-160 kg/m$^3$, outer and inner mean diameters of 13-16 nm and 4 nm respectively and 3-15 walls. The materials were used as-received.

Processing

PS-MWCNT composites were compounded on a Leistritz ZSE 27HP-52D extruder (Nürnberg, Germany) having an L/D ratio of 52. Composites with 1, 2, 3, 5 and 7.5 wt.% MWCNT loadings were compounded with varying processing conditions with a screw configuration with kneading, and transportation elements with varying geometry arranged along the barrel length. The extrusion parameters are listed in Table 1. Extrudate strands collected after passing through a cooling bath were used for microscopic investigations. Granulates from extruded strands were used for all other analyses.

Table 1: Compounding parameters for PS-MWCNT composites

<table>
<thead>
<tr>
<th>Temperature, $T$ (°C)</th>
<th>210</th>
<th>Profile (P)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed, $N$ (rpm)</td>
<td>500</td>
<td>1100</td>
</tr>
<tr>
<td>Throughput, $M$ (kg/h)</td>
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<td>10</td>
</tr>
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</table>

Profile (P)*

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<th>Zone</th>
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<th>9</th>
<th>10</th>
<th>11</th>
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<tr>
<td>T °C</td>
<td>230</td>
<td>230</td>
<td>190</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>190</td>
<td>210</td>
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SME inputs were evaluated in kWh/kg using expression (1)

\[
SME = \frac{2 \times M_{\text{max}} \times I \times N}{9550 \times E \times M}
\] (1)

Where \( M_{\text{max}} \), \( I \), \( N \), \( E \) and \( M \) are maximum torque for one screw shaft (in Nm), motor current (in %), screw speed (in rpm), gear drive efficiency, and throughput (in kg/h) respectively.

The extruded granules were compression molded on a Collin Compression Press (Ebersberg, Germany) into bars of (60*10*2) mm. The molding parameters are listed in Table 2. Quenching in cold water was preferred as better sample surface quality and conductivity values were obtained compared to mold cooling.

Table 2: Compression molding parameters for PS-MWCNT composites

<table>
<thead>
<tr>
<th>Stage</th>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<td>T (°C)</td>
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<td>220</td>
<td>Quenched in water</td>
</tr>
<tr>
<td>Time (min)</td>
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<td>1</td>
<td>1</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>15</td>
<td>35</td>
<td>145</td>
<td>210</td>
<td></td>
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</tbody>
</table>

**Nanocomposite Characterization**

Differential Scanning Calorimetry (DSC) measurements were carried out on 8-10 mg samples in nitrogen atmosphere (50 ml/min) on DSC Q1000 (TA Instruments, USA). Samples were placed in hermetic aluminum pans. First heating cycle involved heating of the sample from room temperature to 170 °C and held at isothermal conditions for 5 minutes to remove any thermal history due to processing. The sample was cooled down to room temperature after which second heating was carried out similar to the first heating regime. Heating and cooling rates were 10 °C/min. Glass transition temperature (\( T_g \)) and the heat capacity jump at glass transition (\( \Delta C_p \)) were measured.

Thermo Gravimetric Analysis (TGA) was performed in air atmosphere (25 ml/min) on TGA Q5000 (TA Instruments, USA). Samples (10-12 mg for composites and 4 mg for...
MWCNTs (Multi-Wall Carbon Nanotubes) were placed in platinum pans and heated from room temperature to 120 °C at 20 °C/min, kept under isothermal conditions for 10 minutes and thereafter heated at 10 °C/min to 700 °C. The residue at 700 °C was weighed. The onset of decomposition (T<sub>o</sub>) (temperature at 5 % weight loss) and temperature of maximum weight loss (T<sub>d</sub>) (temperature peak from dw/dT) are estimated.

Melt rheology measurements were carried out under nitrogen atmosphere on Anton Paar Rheometer MCR 501 (Graz, Austria) equipped with a conventional temperature device CTD 450 in a parallel plate configuration. The upper measuring plate had a 10 mm diameter and the measuring gap was maintained between 1-2 mm. Increasing frequency sweeps from 0.1 to 100 rad/s were carried out at 210 °C after equilibration. The strains were always checked to be within the linear viscoelastic limit.

Raman spectra were collected between 800 cm<sup>-1</sup> and 3000 cm<sup>-1</sup> using a Dispersive Raman RXN1 spectrometer from Kaiser Optical Systems Inc., USA. A 785 nm wavelength laser source was employed and the maximum laser power was limited to 100 mW to avoid sample burnouts. 10 accumulations were collected for an integration time of 10 seconds each and results were averaged. Baseline corrections were made with RAMalyze software (LabCognition, Analytical Software GmbH & Co. KG, Germany).

The morphology of the extrudate strands was investigated using optical microscopy. Thin slices of 5 µm thickness were cut perpendicular to the direction of extrusion on at least 6 different strands at room temperature on an R.Jung Microtome, Heidelberg, Germany with a diamond knife. Imaging was done using 10x magnification objective lens of a BRESSER Science TRM-301 Transmission microscope (Meade Instruments Europe GmbH & Co.KG, Germany) fitted with a BRESSER Microcam. A minimum of 6 mm<sup>2</sup> micrograph area was investigated for every sample. Image analysis was performed using macros developed in house with Image J software. The area fraction of undispersed MWCNT agglomerates (A<sub>f</sub>)...
defined as the area of the undispersed MWCNT to the overall micrograph area was quantified. Agglomerates having an area of less than 20 µm² were ignored in the analysis according to ISO 18553 standards.

Field Emission Scanning Electron Microscopy (FESEM) were carried out on the extruded strand and compression molded bar using Zeiss SUPRA 55 VP microscope, Carl Zeiss GmbH, Germany. Samples were cryofractured and sputter coated with Gold-Palladium for 120 s at 0.05 mbar and 40 mA on a Cressington 208HR Sputter Coater, Cressington Scientific Instruments Ltd., United Kingdom. As-received tubes without any sputter coating were examined additionally with an Energy Dispersive Spectrometer (EDS), EDAX, Germany built in with the FESEM setup.

Transmission electron microscopy (TEM) investigation was carried out on a Philips CM20 transmission electron microscope fitted with a tungsten electron gun and operated at 200 kV. 70-100 nm thin sections were cut at room temperature from the cross section of compression molded bars.

Electrical Resistivity measurements of the PS-MWCNT composites were made on compression molded bars (at least 5 specimens) at 40 % relative humidity and 24 °C. As there was a limitation of the measuring equipment to measure the entire range of volume resistivities, two different measuring sources were employed. Low resistivity measurements (< 10⁶ Ω.cm) were carried as a 4-probe measurement on a FLUKE 8846A Digital Multimeter (Glottertal, Germany) while higher volume resistivities (> 10⁶ Ω.cm) were measured using Agilent Technologies’ 4339B High Resistance Meter (Waldbonn, Germany) as 2-probe measurements. Contact points were created using RS Silver Conductive Paint (Northants, United Kingdom) and were allowed to dry for 24 hours before measurements.
Results and Discussion

Processing and Morphology

Figure 1 shows the variation of area fraction of undispersed MWCNT agglomerates as a function of process parameters for 2 wt.%, 3 wt.% and 5 wt.% MWCNT loadings along with their respective specific mechanical energy inputs (SME) in kWh/kg.

From Figure 1 it is evident that $A_f$ of all the MWCNT weight fractions lowered significantly when the composites are processed at 1100 rpm. This effect is supported by the
higher SME inputs at this speed. For example, a PS-3 wt.% MWCNT composite processed at 10 kg/h, 210 °C and 500 rpm shows an A_f of 7.54% while the sample processed at 1100 rpm shows 3.92%. Their respective SME’s were 0.63 kWh/kg and 1.15 kWh/kg. Employing a temperature profile on the extruder with an aim to increase the shear rates contributing to dispersion by tube erosion due to the increase in viscosity in the mixing zones does not seem to have a greater impact as was theoretically envisioned. The effect of throughput variations is not significantly felt at lower processing speeds. On the other hand, 2 wt.% and 3 wt.% MWCNT filled samples processed at 7.5 kg/h, 210°C and 1100 rpm show a 1 % lower A_f compared to those processed at a higher throughput of 10 kg/h. It would be logical to consider the reduction in A_f in terms of increasing the content of active MWCNT (smaller agglomerates and individualized tubes beyond the resolution of an optical microscope) which is critical for tailoring a nanocomposite for good mechanical and electrical properties.

Individualization of tubes would be the ideal scenario if the intrinsic properties of the CNT are to be effectively translated to the composite. This primarily depends on the extent to which the CNT could be dispersed in the composite. Effective CNT dispersion is hindered by the intrinsic agglomerate strength due to Van der Waals and electrostatic forces of attraction. The application of shear forces in the extruder to effectively break the agglomerates would depend on the agglomerate strength. For example, Baytubes C150 P agglomerates have a deformational stress of 0.64 MPa at 25% deformation and require five times the energy input as Nanocyl NC7000 which has a deformational stress value of 0.39 MPa. The application of high shear has a two-fold effect on the nature of dispersion. The probability of formation of individual tubes is directly proportional to the extent of shear applied. Higher shear rates, on the other hand facilitate the migration of dispersed tubes or the remaining agglomerates towards each other. When the distance between the tubes or the agglomerates is within the range of intra-CNT attractive forces, re-agglomeration of the
dispersed tubes cannot be ruled out. Hence, an optimal amount of shear stress (i.e. a balance between individualization of tubes and their re-agglomeration) must be applied to the CNT to achieve required dispersion levels. It is to be kept in mind that increased shear stresses would result in tube breakage and polymer degradation. Figure 2 shows the optical micrographs of a PS-3 wt.% MWCNT and PS-5 wt.% MWCNT composite strand processed with variations in speed.

Figure 2: Optical micrographs of PS-MWCNT composite samples processed at 210 °C, 10 kg/h. Top: PS-3wt.% MWCNT Samples 500 rpm (left), 1100 rpm (right) Bottom: PS-5wt.% MWCNT Samples 500 rpm (left), 1100 rpm (right) – Images are representative of the analyzed lot.
The number of agglomerates per mm$^2$ of the optical micrographs is counted and is plotted as a function of MWCNT content for varying process parameters in Figure 3. The only visible difference is found in the decrease in the number of particles as a function of speed for all the MWCNT contents. Composites with 5 wt.% MWCNT content showed lesser number of particles than its 3 wt.% counterpart when processed with 7.5 kg/h, 1100 rpm at both the temperature conditions. This is significant considering the fact that the 5 wt.% MWCNT loaded composite had twice the $A_f$ of a 3 wt.% composite as shown in Figure 1. Inspite of reducing the number of agglomerates, the size contribution of individual agglomerates at their respective volume fraction is significant.

![Figure 3: Illustration of number of visible MWCNT agglomerates in the optical micrographs for different processing conditions. MWCNT loadings in wt.% are listed on top of the bars.](image)

The authors resorted to a morphological analysis on a microscopic scale owing to the limitations of SEM and TEM equipments to provide sufficient data over a larger picture.

dimension to statistically evaluate dispersions. However, a few TEM pictures at a lower magnification is presented in Figure 4 for qualitative visuals on the effect of varying CNT loadings and speeds on the morphology of the nanocomposites.

Theoretically envisioning the quality of dispersion is practically impossible due to a restriction in completely individualizing CNT irrespective of melt energy input and inability to create a situation where every nanotube is wetted by the polymer melt. It must be remembered that a very short processing window is available for the wetting, infiltration, dispersion, and distribution of CNT in a polymer melt in the extruder.

Figure 4: TEM micrographs of PS-MWCNT composite samples processed at 210 °C, 10 kg/h
Probing PS-MWCNT Interaction

a. Interfacial investigation with Differential Scanning Calorimetry (DSC)

The interfacial layer (IL) surrounding the filler particle can be approximately deduced by equation (2)

$$IL \ (%) = \left(1 - \frac{\Delta C_{p}^{*}}{\Delta C_{PS}}\right) \times 100$$  (2)

where $\Delta C_{p}^{*}$ refers to the specific heat jump normalized to the pure polymer content in the nanocomposite and $\Delta C_{PS}$ refers to the heat capacity of pure PS. $\Delta C_{p}^{*}$ is given by

$$\Delta C_{p}^{*} = \left(\frac{\Delta C_{p}}{1 - w}\right)$$  (3)

where $w$ refers to the MWCNT loading by weight.

As seen from Figure 5, $T_g$ of pure PS processed at 1100 rpm increases from 106 °C to 115 °C when 2 wt.% MWCNT are added to it. Correspondingly there is a formation of interfacial layer fraction (quantified with respect to the pure polymer) of 24% around the filler surface. On addition of 3 wt.% MWCNT, no significant change in $T_g$ is observed but further additions result in decrease of the $T_g$. On the other hand the IL fraction grows at a significant rate up to MWCNT loadings of 3 wt.% after which the curve approaches a plateau. Though trends observed with varying MWCNT contents are the same for both $T_g$ and IL, higher values are obtained for samples which have been processed with high speeds.
Herein, glass transition and interfacial layer observations are discussed hand in hand in an attempt to uncover the nature of polymer-MWCNT interaction.

An interfacial layer is idealized to have a defined thickness strongly dependent on the nature of interaction between the polymer and the filler. The polymer chains which come in the interfacial domain would be tethered onto the surface of the filler, whether physical or chemical is difficult to predict. The part of the polymer which is in close proximity to the filler will have properties much different than the bulk matrix owing to the restrictions imposed on its mobility due to the alterations of the conformational entropy and chain kinetics. This contributes to the increase in the glass transition temperature. The presence of an interfacial layer hinders the mobility of the polymer molecules by causing an increase...
energy barrier for chain mobility. The variation of glass transition and hence the interface is strongly dependent on the CNT type, content and the nature of dispersion. When the MWCNT are well dispersed there is an increased contact surface presented by the CNT for interactions with the polymer resulting in a strong interface. With increased CNT loadings above optimum, the distance between the neighboring filler particles decreases. When this spacing is in the order of the molecular size of the matrix, the fillers interact through short range interactions by overlapping with the interfacial layers of neighboring fillers and the distance between the tube walls is at its minimum. This overlapping enhances filler-filler interaction or the formation of an intra filler network within the interphasial layer. The instance when the adjacent foreign layers overlap due to enhanced CNT volume fraction would be more appropriate if referred to as an “interphase” than an “interface”. Theoretically, the regions of the polymer in the interphase would now begin to behave as those in the bulk resulting in further variation in conformational kinetics. As a result, the packing density of the polymer molecules decrease and chains are presented with increased free volume for mobility which would lower the glass transition temperature.

The restriction in the chain mobilities caused by filler addition does not extend throughout the composite, but extends to a few nanometers in proximity to the filler surface. On the other hand NMR measurements by Litvinov and Speiss support the existence of three types of polymers in the composite namely immobile and strongly bound polymers, chains with restricted mobility, and the other exhibiting a quasi-bulk behavior.

Figure 6 shows the variation of \( T_g \) and IL as a function of different processing parameters in a PS-3 wt.% MWCNT composite. Samples produced at 1100 rpm show higher \( T_g \) (> 115 °C) and IL fractions (> = 26 %) than those produced at 500 rpm. Though the variations are not significant, experimental error was very minimal and hence results could be treated as highly accurate. The used MWCNT were not functionalized and hence the only
possible scope for the indicated variations is the quality of dispersion. Results indicated here have to be correlated with the observations from Figure 1. Throughputs of 7.5 kg/h seem to be effective in increasing the $T_g$ and IL % irrespective of the processing speed.

Figure 6: Variation of glass transition temperature and interfacial layer fraction of a PS-3 wt.% MWCNT composite at different processing conditions.

Heat capacity variation at glass transition of the composites in the calorimetric measurements gives a direct measure of the amount of polymer taking part in the glass transition. Also the degradation of the polymer on processing with the filler will not show up significantly during these measurements unless it heavily affects the molecular weight. Hence, calorimetric measurements could be qualitatively employed for studying the interphases of nanocomposites.

b. Peak variations with Raman Spectroscopy
Zhao and Wagner state that polymer-CNT interactions are reflected as peak shifts or as changes in the peak width in Raman spectra.\cite{86} Raman spectra of Baytubes (Figure 7) show the characteristic D, G and G* peaks positioned at 1311 cm$^{-1}$, 1608 cm$^{-1}$, and 2622 cm$^{-1}$ respectively. No peak shifts are observed when different loadings of MWCNTs are incorporated into PS. The full width at half maximum (FWHM) values of the D, G and G* peak of the Baytubes and the composites are listed in Table 3.

Table 3: FWHM values of the samples presented in Figure 7

<table>
<thead>
<tr>
<th>Baytubes</th>
<th>D</th>
<th>G</th>
<th>G*</th>
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<tbody>
<tr>
<td>PS-1 wt.% MWCNT</td>
<td>73.02</td>
<td>56.89</td>
<td>69.25</td>
</tr>
<tr>
<td>PS-2 wt.% MWCNT</td>
<td>73.42</td>
<td>61.42</td>
<td>69.76</td>
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<tr>
<td>PS-3 wt.% MWCNT</td>
<td>73.21</td>
<td>61.26</td>
<td>69.60</td>
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<td>PS-5 wt.% MWCNT</td>
<td>73.04</td>
<td>62.43</td>
<td>69.14</td>
</tr>
<tr>
<td>PS-7.5 wt.% MWCNT</td>
<td>73.95</td>
<td>62.58</td>
<td>70.30</td>
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The FWHM of the all the MWCNT characteristic peaks undergo a very similar shift of about 3-4 cm$^{-1}$ irrespective of CNT loadings except for the G peak of 1 wt.% MWCNT loaded composite, where a tiny shoulder was observed at 1582 cm$^{-1}$. The inset of Figure 6 illustrates that the reason for a shoulder at 1582 cm$^{-1}$ arises out of the strong aromatic ring stretching vibration of pure PS. This effect diminishes with increasing MWCNT loadings.

The polymers peaks are visible in the composite and their intensity varies inversely with MWCNT loadings.

Figure 8 shows the normalized Raman spectra between 800 and 1200 cm$^{-1}$ of PS incorporated with 3 wt.% MWCNT and processed with different processing parameters. Though the FWHM of the PS peaks at 1002 cm$^{-1}$ (C-H in plane vibration) in these composites were constant, it was observed that the intensity varied from 1.08 to 1.12 by increasing the speed from 500 rpm to 1100 rpm. Temperature profile extrusion on samples with a processing speed of 500 rpm shows a peak intensity of 1.21 compared to 1.12 for the sample processed at 210 °C. This observation qualitatively shows that better dispersions arising out of enhanced SME inputs results in enhanced matrix-filler interaction.
McClory et al. show that the tangential G peak of the Baytubes shifted positively by 24 cm\(^{-1}\) when High Impact Polystyrene (HIPS) was added to the MWCNT.\(^{[87]}\) The shift was independent of the MWCNT loadings and processing parameters. The authors attributed this shift to the compressive strain acting on the MWCNT due to the shrinkage of HIPS on solidification. Lourie et. al have shown that for epoxy filled with SWNTs the G* band shifted to positive wavenumbers by 15 cm\(^{-1}\)\(^{[88]}\) and attributed them to C-C band compression arising out of epoxy resin contraction during polymerization. Raman Spectroscopy on PS-MWCNT composite films show that with increase in MWCNT concentrations the D, G and G* peak of MWCNT shifted to lower wavenumbers. The G peaks of 8 wt.% and 10 wt% CNT loaded composites shifted to lower wavenumbers by 14–18 cm\(^{-1}\) compared to 6 wt.% MWCNT loaded composites. The authors term this as a measure of interfacial interaction.\(^{[89]}\) These literature evidences contradict what has been observed with our work. However, variation in peak widths and polymer peak intensities observed with our composites can be attributed to some interaction between the polymer and the MWCNTs. This could be a result of varying dispersion qualities. Interfacial analysis elaborated earlier through calorimetric
measurements also show evidences of interactions between polymers and MWCNTs and significant variations with the nature of processing. Though changes in MWCNT peak widths in the composite and variation of intensities of polymer peaks with respect to processing parameters have been noticed, there is no concrete evidence to argue Raman measurements on composites can stand alone as a significant proof in evaluating the interfacial interaction in a composite.

The $I_D/I_G$ ratio of as-received Baytubes is estimated to be 1.52. The higher intensity of the D-band shows that as-received MWCNT contain intrinsic defects in the form of graphitic imperfections and amorphous carbon. With increased MWCNT loadings the defect concentration is increased and hence the intensity of the disorder induced D-band at similar processing conditions. With variation in processing conditions the concentration of the defects increases for the same CNT content as seen from Figure 9. For example, composites with 1 wt.% MWCNT loadings show an increase in $I_D/I_G$ from 1.54 to 1.56 by the increase of processing speed from 500 rpm to 1100 rpm. SME variation for this process was from 0.61 kWh/kg to 1.09 kWh/kg. High energy inputs could have resulted in the breakage of the tubes which could have contributed to increased tube defects. The processing of composites in the extruder with heat and high shear rates causes mechano-chemical and thermo-oxidative degradation of Polystyrene resulting in the release of macromolecular free radicals. CNTs being good radical acceptors readily accept these radicals from PS, contributing to the intensity increase of the D band.
Figure 9: Enhancement of $I_D/I_G$ ratio of the composites with varying MWCNT loadings as a function of process conditions. MWCNT loadings in wt.% are marked.

**Thermal Stability of PS-MWCNT composites**

Figure 10 illustrates the variation of the oxidative stability of the PS-MWCNT composites for different nanotube loadings. The onset of degradation and temperature of maximum weight loss for pure PS are 300 °C and 365 °C respectively. On addition of 1 wt.% and 2 wt.% CNTs these values are shifted to 312 °C, 398°C and 337 °C, 407 °C respectively. The incorporation of more than 2 wt.% MWCNTs does not show significant improvements in the thermal stability.
Figure 10: Improvement in thermal stability of the composites and lowering of decomposition temperatures of MWCNT portion of the composites with increasing MWCNT contents.

When the composite is heated, the polymer chains undergo scission due to abstraction of hydrogen from their functional chain. The rate of degradation is lower in this case as the released radicals are intercepted by the CNT present in the composite. CNT belonging to the C_{60} family have high electron affinities of about 2.65 eV\textsuperscript{[91]} thereby enabling them to act as efficient radical scavengers. The strong radical accepting capacities interrupt the radical propagation mechanism and hence decrease the rate of degradation. Restriction to radical propagation would also mean a decrease in the quantity of hydroperoxides formed. The by-products arising as a result of hydrocarbon oxidations are highly reactive and act as inherent impurities during the process contributing to deterioration of polymer properties. With the increase in CNT content there is increase in the surface area available for the
released free radicals which contributes to a enhancing the thermal stability of the nanocomposites. On the other hand the restriction of molecular mobility of the composites as previously mentioned could have also played significant role in regulating the thermal stability. With molecular mobility being the driving force behind transportation of the reactive species during degradation, the reactivity of the nanocomposites could have been lower and hence display a higher thermal stability compared to virgin PS. The analyses of oxidized samples in linear low density polyethylene (LLDPE)-MWCNT nanocomposites by Bocchini et al.\textsuperscript{[92]} show that stabilization is due to a relatively thin surface film (1–2 μm) composed by MWCNT and polyaromatic carbon char which prevents oxygen diffusion towards the underlying polymer matrix and the development of volatiles product from the polymer. At MWCNT loadings above 2 wt.% the net effect of agglomeration prevents enhancement in the thermal stability, the intra filler network builds up instead and dominates. Any further enhancement in thermal stability is attributed to the intrinsically high thermal stabilities of CNT themselves. Hence, it can be said that there exists a threshold limit for CNT loadings above which the radical accepting tendencies of CNT are dwarfed by intra filler networks.

CNT continuously accept the radicals from the polymer chains until the latter undergoes complete degradation. On complete degradation of the polymer, there is a state which is occupied by condensed gases and hydrogen peroxide. When the oxidation temperatures reach a zone where the CNTs are susceptible to degradation, the CNTs begin to degrade progressively. The inset table in the Figure 9 shows that temperature of maximum weight loss decreases from 579°C for pure MWCNTs to 548 °C for composites with 7.5 wt.% MWCNT. This shows that the stability of the MWCNT suffers inspite of increasing the anti-oxidative tendencies of the composite. The inset figure shows the final stages of degradation of as-received Baytubes and p-CNT (Baytubes washed with a mixture of 3 M
HNO₃ for 20 hrs at 60 °C and 5 M HCl for 6 hours at 110 °C). On measuring the weight of the residue of Baytubes it was observed that 2.3 % of the initial weight remained as residue on complete burning while it was less than 0.12% for p-CNT. As-received Baytubes contains Cobalt (1.12 %) and Manganese (1.02%) which was used as a catalyst during their production in a CVD reactor as observed from the EDX-FESEM analysis in Figure 11. Acid washing is effective in the removal of these transitional metal ions. It is reported that transitional metal ions act as catalyst in activating the by-products of thermo-oxidative degradation of the hydrocarbon.[93] Increase in the concentrations of these transitional metals in the composite with increasing CNT loadings plays a significant role in the reduction of the oxidative stability of the CNT. Baytubes also comprises of amorphous carbon whose content has not been specified accurately by the manufacturer. This amorphous carbon tends to burn earlier than the bulk CNT. As a result, they potentially act as an intrinsic heat source contributing to lowering the oxidative stability of CNT with increasing concentrations.[94]

Figure 11: EDX-FESEM combined illustrating the concentration of transition metals present catalyst in Baytubes (FESEM image of the Baytube magnified by 5000 times)

From Figure 12 it is seen that at lower MWCNT loadings of 1 wt.% and 2 wt.% the increase of speed from 500 rpm to 1100 rpm has a drastic influence in increasing the oxidative stability of the polymer. This can be correlated to the high SME inputs and better dispersion levels at 1100 rpm as discussed earlier in the processing section. Higher throughput seems to be effective at lower speeds and 210 °C for enhanced thermal stability. Lower SME plays a significant role in reduced degradation of the polymer chains. No significant variations in the values of thermal stability are evident when the MWCNT content is greater than 3 wt.% inspite of significant changes in SME inputs and dispersion levels with varying processing conditions. Hence, a good CNT dispersion below the threshold limit is critical for attaining enhanced thermal stabilities.

![Figure 12: Effect of processing parameters on the thermal stability of PS-CNT composites](image-url)
Melt rheological behavior of PS-MWCNT composites

Oscillatory melt rheological response of composites is used to assess the regime at which a composite shows its rheological percolation threshold which in turn gives a measure of mechanical percolation. The rheological behavior at lower frequencies is indicative of the contribution of the filler to the composite and to an extent can be used to assess the nature of polymer-CNT interaction.

Figure 13: Melt rheological response of PS-MWCNT composites as a function of MWCNT content. Samples were processed at 500rpm, 210 °C and 10 kg/h. **Top:** Storage Modulus G’
Figure 13 analyses the influence of MWCNT additions on composites prepared with different MWCNT loadings under similar processing conditions of 210 °C, 10 kg/h and 500 rpm. It is generally known that the variations of $G'$ are more pronounced with filler additions than $G''$ and hence only the former is plotted as a function of frequency. The plot of $G'$ vs frequency indicates an increase in the composite elasticity with increase in MWCNT loadings. It was earlier elaborated in the calorimetry discussion that increasing MWCNT contents in the composite resulted in an increase in IL fraction. Lower mobilities of the polymer chains in this region could be a reason for the increase in $G'$. The dependence of frequency diminishes with increase in MWCNT content which is an evidence of a transition from a liquid like to solid like behavior owing to intra-filler interactions. The “elastic behavior” tends to dominate in between 1 wt.% and 2 wt.% MWCNT loadings in the composite indicating a rheological percolation threshold. Herein, a pseudo-like network is expected to be formed by the MWCNT which could potentially arise due to strong polymer-CNT interactions.\[95\] Very little variation is noticed in the $G'$ values of composites with 5 wt.% and 7.5 wt.% CNT loadings as a function of frequency. Rheological properties at high frequencies are dominated by the polymer as increased shear tends to orient the CNTs which lower the effect of CNT interactions. As no relaxation modes faster than the relaxation times of pure polymer exists in the composite, a solid like plateau is noticed at higher frequencies.\[71\]

The variation of complex viscosity $\eta^*$ vs frequency of pure PS reveals a Newtonian plateau at low frequencies and shear thinning effects at higher frequencies which is typical of a viscoelastic material. The complex viscosity increases as a function of frequency at lower
frequencies, while the shear thinning behavior is more prominent compared to pure PS at higher frequencies which is owing to the result of heat generated due to frictional forces in addition to the shearing forces. The Newtonian regime starts to disappear at 2 wt.% MWCNT loadings, however a clear cut evidence of rheological percolation threshold cannot be detected from this plot.

The logarithmic plot of storage modulus $G'$ vs the loss modulus $G''$, known as the modified Cole-Cole plot arises out of an analogy from dielectric measurements made on polymer relaxations by Cole and Cole.\cite{96} It has been used as a comprehensive evidence for rheological percolation thresholds in a filled polymer system.\cite{29,87} When there is no change in the microstructure of homopolymers, blends and block co-polymers, the modified Cole-Cole plot is expected to coincide independent of temperatures. This was observed by investigations performed on compatible blends of two low density Polyethylenes (LDPE) and Poly (methyl methacrylate) PMMA - Poly (vinylidene fluoride) PVDF and an incompatible Poly (methyl methacrylate) PMMA – Polystyrene blend by Chuang and Han.\cite{97} However, the curves in Figure 11 indicate that there is a significant variation in the values of $G'$ with respect to $G''$ which indicates a microstructural change arising out of MWCNT additions to PS. The slope of the curves decreases significantly with MWCNT increments. At MWCNT contents greater than 2 wt.\%, the values of $G'$ is greater than $G''$ at lower frequencies indicating that the rheological percolation threshold occurs in the composite between 1 wt.% and 2 wt.% MWCNT content. A network structure of the tubes should have been formed at 2 wt.% MWCNT content. Any further additions of MWCNT show a similar behavior and at high frequencies the variations are very similar to what was observed earlier with polymer rheology dominance. The behavior of the modified Cole-Cole plot of PS-MWCNT follows the speculative categorization of terminal relaxation patterns made on Polystyrene – clay nanocomposites by Zhao et al.\cite{98}
Tan Delta variations with frequency are sensitive to structural changes. The modified Cole-Cole plots described earlier also confirms change in the structure with CNT loadings. A viscoelastic peak which is a typical characteristic of a polymer material is evident for PS, while the intensity decreases with CNT additions. Exponential decay patterns of tan delta with frequency of lower CNT contents is lost at composites with 2 wt.% MWCNT content which shows a transition from a viscoelastic to a more elastic behavior or in other terms a fluid to solid transition or gelation. At gelation, tangent delta variation with frequency is at its minimum.\textsuperscript{[99,100]} Hence, it can be stated that the PS-MWCNT composites have a rheological percolation threshold between 1 wt.% and 2 wt.% MWCNT loading. For composites with 5 wt.% and 7.5 wt.% MWCNT loadings, Tan Delta increases with frequency in the low frequency domains which is indicative of a dominative elastic behavior of the composite, which potentially arises out of intra-MWCNT interactions.

Figure 14 gives the variation of $G'$ and $\eta^*$ as a function of speed for varying MWCNT loadings. Elasticity of the samples processed at 1100 rpm is slightly higher up to 2 wt.% MWCNT loading after which there is a predominant increase compared to processing at 500 rpm. The increase at lower loadings can only be attributed to enhanced dispersion of CNTs as observed earlier. The better dispersion of MWCNT at high processing speeds is likely to lower the density of agglomeration, thereby resulting in enhanced intra CNT interactions at loadings above the percolation threshold. This is well reflected in the variations of $\eta^*$, wherein the viscosities of composites with greater than 2 wt.% MWCNT loadings was always higher at 1100 rpm processing speeds. The combined observations of these curves indicate enhancements in elasticity above the threshold loading as a measure of intra-MWCNT interactions. They also seem to be valuable indicators to establish maximum permissible MWCNT loading in the matrix.
Figure 14: Effect of processing speed on storage modulus and complex viscosity at varying MWCNT loadings at 0.1 Hz. Samples were processed at 210 °C and 10 kg/h.

Figure 15 shows the variation of storage modulus and complex viscosity for a PS-3 wt.% MWCNT composite with processing parameters. Both of these graphs show that variations in $G'$ and $\eta^*$ exist upon employing different processing conditions, but the change is not very significant. It is observed that samples with 1100 rpm show higher elasticity and increased viscosity at lower frequencies which can only be attributed to the extent of interaction between the polymer and the filler. Lower throughputs and extrusion temperature profiles are effective only at higher speeds. Other key rheological observations noticed (not depicted graphically) are listed below:

- Samples processed with 1100 rpm show rheological percolation thresholds between 0 and 1 wt.% MWCNT content irrespective of throughputs and extruder barrel temperature (Verified with curves of $G'$, Tan delta vs Frequency and Modified Cole-Cole plots).
- Post gelation behavior on tan delta curves is very predominant at 1 wt.% MWCNT loading on samples processed at 1100 rpm, in contrast to a very small variation seen starting from 5 wt.% MWCNT content composite processed at 500 rpm.
• At higher speeds and lower throughputs, samples processed with an extruder temperature profile exhibited higher elasticity while no significant variations were noticed at higher throughputs.

Figure 15: Variation of storage modulus $G'$ (left) and complex viscosity $\eta^\ast$ (right) with processing conditions of a PS-3 wt.% MWCNT composite.

**Measurement of volume resistivity of the composites**

Volume resistivity of pure PS is observed to be $10^{19} \ \Omega\cdot cm$ (Figure 16). Addition of 1 wt.% MWCNT lowers the volume resistivity by three orders of magnitude independent of the processing condition. On incorporating 2 wt.% MWCNT, a percolation threshold is observed with a strong dependence on the processing speed. Composites processed at 1100 rpm showed a volume resistivity drop of ten orders. Volume resistivities of $10^4 \ \Omega\cdot cm$ achieved by processing a 2 wt.% PS-MWCNT composite at 1100 rpm does not differ significantly than those achieved with higher MWCNT loadings. Improvements in the quality of dispersion facilitated by higher energy inputs at higher speeds can be attributed to the variation in resistivities at 2 wt.% MWCNT loadings. An interconnected network of anisometric CNTs
(individual tubes and agglomerates) could have been formed and thus electrical percolation threshold is envisioned at this loading. Lower resistivity at higher MWCNT loadings is a result of a conductive network formed by conglomeration of agglomerates. These results are a potential indicator to hereafter describe CNT percolation thresholds in terms of process parameters at a defined loading rather than describing them in terms of different weight fractions.

Figure 16: Variation of volume resistivities of PS-MWCNT composite with process parameters as a function of different MWCNT loadings.

Compression molded composites always showed lower volume resistivities compared to measurements made on extruded strands. The reduction in the viscosity sans shear during compression molding facilitates the re-agglomeration of previously dispersed tubes. The reason for lower high resistivities of the extruded strands could be the orientation of the

CNTs along the flow direction which potentially prevents a 3-D percolation. Differences in the morphology of PS-2 wt.% MWCNT extruded strand and a compression molded bar are shown in Figure 17. Images have a lower contrast owing to a very low magnification as we are interested in showing the re-agglomeration of dispersed tubes on compression molding.

Figure 17: FESEM morphology of PS-3 wt.% MWCNT nanocomposite Strand (left) and Compression molded bar (right) (Note scale differences)

It was very interesting to note that the electrical percolation occurred between 2 wt.% and 3 wt.% MWCNT loadings when measured on extruded strands (not shown here). Inspite of achieving significantly enhanced dispersion qualities at 1100 rpm processing of 2 wt.% MWCNT composites, resistivities of the order of $10^{12}$ Ω.cm was achieved for all processing conditions. Increased dispersion effectively means an increased thickness of the polymer melt stream between distributed tubes. Recalling quantum mechanics theory, electron tunneling can be idealized as a wave like behavior. When a thicker barrier is presented to the electrons, the wave tapers quickly in that regime resulting in a higher probability of a failure to jump to the neighboring tube and thereby form a conductive pathway. Hence, an optimal amount of dispersion with a defined $A_{f}$ is expected for a good conductive composite.
Conclusion

PS-MWCNT composites with varying MWCNT loadings were processed on a compounding extruder using a combination of varying process parameters. Processing at higher speeds of 1100 rpm almost halved the undispersed MWCNT area fraction in the optical micrographs irrespective of filler loading owing to the doubling of the SME input. Calorimetric observations show an increase in the glass transition temperature up to 2 wt.% MWCNT loading and a drop on incorporating greater than 3 wt.% MWCNT. The amount of immobilized polymer quantified in terms of %IL grows rapidly until 2 wt.% MWCNT loading, similar to the $T_g$. The growth of the interfacial layer correlates very well with enhancement in dispersion quality. FWHM of the composites as observed with Raman spectroscopy indicate a constant increase in the peak widths for the composites compared to the signature peaks of pristine MWCNTs independent of the MWCNT concentration. The absence of peak shifts in these composites however contradicts recent reports in the literature suggesting that peak shifts indicate a favorable polymer-MWCNT interaction. On the other hand, the observed variation in the intensity of C-H in plane vibration peak of PS at 1002 cm$^{-1}$ for a constant MWCNT loading which is inversely proportional to the SME input is a result of varying qualities of dispersion and degree of interaction between the polymer and the tubes. This raises the question as to whether Raman analysis alone is sufficient to explain polymer-MWCNT interactions. Incorporations of 2 wt.% MWCNT into PS increases the maximum temperature of degradation of PS from 365 °C to 407 °C which seems to be the

threshold limit. In contrast, the thermal stability of the MWCNTs themselves in the composites decreases with increasing MWCNT loadings in the composites which has been ascribed to the presence of Co and Mn catalysts by EDX analysis. Although variation in processing parameters show enhanced storage modulus and complex viscosity as a function of improved dispersion quality, rheological percolation threshold occurred between 1 wt.% and 2 wt.% MWCNT loading in all cases. The volume resistivity of the compression molded composites with 2 wt.% MWCNTs was lowered by 10 orders of magnitude from $10^{14}$ $\Omega$.cm to $10^4$ $\Omega$.cm by processing at 1100 rpm instead of 500 rpm. These values were not very different from those obtained with 3 wt.% MWCNT loadings. It was also interesting to observe that the electrical percolation threshold was lower in the compression molded plates compared to those observed in the extruded strands owing to the re-agglomeration of previously dispersed tubes to form a network in the former by extrusion. The observations with volume resistivity measurements on our composites show that it is worthy to hereafter describe electrical percolation thresholds of CNT based nanocomposites in terms of varying process conditions at a defined loading rather than elucidating them as a function of varying weight/volume fraction loadings at a particular processing condition.
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References


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Increasing processing speed from 500 to 1100 rpm lowers resistivity by 10 orders of magnitude with 2 wt.% MWCNT loading in PS. Variation of dispersion levels with compounding parameters correlates nicely with enhancements in thermal stability and rheological behavior. Raman Spectroscopy and Calorimetry are employed to understand PS-MWCNT interactions.