Short Communication

Study on Polystyrene/MWCNT Nanocomposite as a Temperature Sensor

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(Received: 13 April 2020 and Accepted: 16 July 2020)

Abstract

The aim of this research is to fabricate a novel temperature sensor for any calorimetry system. A new mixed solution method was introduced to prepare polystyrene/multiwall carbon nanotube nanocomposite samples with different weight percentages as 0.05, 0.1, 0.28, 1, and 2 of MWCNTs. To demonstrate the dispersion state of the inclusion into the polymer matrix, the SEM analysis was applied. Also, XRD and Raman spectroscopy analyses were carried out. The electrical percolation threshold was investigated and achieved at about 0.28 weight percent of the inclusion. Finally, the electrical resistance of the samples was measured from room temperature up to ~100ºC. Consequently, positive temperature coefficient and negative temperature coefficient effects were observed before and after T_g for the most nanocomposite samples, respectively. The best linear response of the resistance-temperature curve was achieved at 20-50ºC, which using a second-order fitting curve it can be used up to ~70ºC. Results show that the polystyrene/multiwall carbon nanotube nanocomposite near the percolation threshold can be used as a temperature sensor for calorimetric purposes.

Keywords: Temperature sensor, Calorimetry, Electrical percolation threshold, Polystyrene/MWCNT nanocomposite, Electrical resistance.

1. INTRODUCTION

Over the past two decades, polymer materials reinforced with nano-fillers such as carbon nanotubes (CNTs) have attracted much attention from both the scientific and industrial communities as a result of the significant property enhancement. CNTs are ideal reinforcing fillers for a polymer matrix, because of their nano-metric size, high aspect ratio, and more importantly, their excellent mechanical strength, electrical and thermal conductivity [1]. Polymer-CNT nanocomposites have great potential applications in flexible electronics, solar cells, antistatic devices, electromagnetic interference shielding, radiation shielding, and electrode materials for batteries, supercapacitors, piezoelectric sensors, temperature sensors, and radiation sensors [2-11].

Recently, the development of the flexible sensors mainly polymer nanocomposite due to low cost, easy handling, lightweight, and biocompatible has been carried out. Since several electronic, chemical, mechanical, and biological systems are influenced by temperature, the investigations on the temperature sensor materials play an important role in these systems. In fact, temperature sensors prepare inputs to these control systems. In solids, the most important heat transfer mechanism is conduction. The heat flux of a material, \( q(Wm^{-2}) \), is described as \( q = -kVT \) in which \( k(Wm^{-1}K^{-1}) \) is the thermal conductivity of the material and \( VT(Km^{-1}) \) is the temperature gradient [12]. Several investigations have been done on temperature sensors based on
polymer-composites [13-17]. Carbon nanotubes (CNTs) exhibited a resistivity dependent on temperature, therefore, CNT-nanocomposites can be used for the fabrication of miniaturized temperature sensors [16]. The CNTs are categorized into two groups of single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). MWCNTs would have diameters ranging from 2-100 nm and lengths of up to tens of microns, and they exhibited electrical conductivity as high as 10^5-10^7 S/m, and also high values of thermal conductivity as 2000-6000 [18, 19].

Polymer-CNT nanocomposites exhibit a percolation behavior in which the presence of interconnected nanotube networks results in a drastic increase in their electrical conductivity. In percolation systems, there is a critical volume fraction, the lower which the electrical properties are dominated by the insulating component and the higher which the conducting component dominates [19]. At the point of electrical percolation threshold (EPT), spanning cluster is formed [20]. The EPT amount of the CNTs depends on the type, size, shape, specific surface area (SSA), and distribution of the filler particles [21]. It is obvious that when CNTs have a high aspect ratio, the tubes have a higher possibility to connect with each other. Therefore, few nanotubes are required to form the conductive paths [22].

Herein, several investigations on temperature sensors based on polymer-composites are exhibited. Neitzert et al investigated the stability of a negative temperature coefficient (NTC) sensor based on a syndiotactic Polystyrene/MWCNT nanocomposite by applying gradually higher voltages to control the Joule heating but limiting the maximum current [23].

Giuliani et al, introduced MWCNT/PVBC_Et3N nanocomposite for wearable skin temperature sensors at the range of 20-40 °C with a resolution of 0.004 K−1 [13]. Giuliani suggested this nano-composite as a wearable temperature sensor for the monitoring of chronic wounds.

Maiti et al applied PS-MWCNT-GNP nanocomposite with very high electromagnetic interference (EMI) value at an extremely low loading of MWCNTs (2 w%) for shielding the electromagnetic waves [24]. Wang et al investigated the electro-thermal behavior of MWCNT/PMIA nanocomposite under low-voltages of 3-12 V [25]. They found that when the electric current flows through the MWCNT network, the electrical energy transforms to heat energy according to Joule’s law, which gives rise to the temperature of the matrix.

In our experimental research work, the heating process of the samples leads to change the electrical resistance. Therefore, it is possible to use this nanocomposite as a calorimeter system. Thus, the temperature-dependent electrical resistance of the PS-MWCNT nanocomposite as a temperature sensor was investigated.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

The polystyrene 1540 with a density of 1.04 g/cm^3 was supplied from Tabriz Petrochemical Company in Iran, was used in this research.

The MWCNT nano-powder with purity greater than 98 w%, the density of 2.1 g/cm^3, 5-15 nm outside diameter, 3-5 nm inside diameter, the average length 50 μm, specific surface area (SSA) 233 m^2/g, electrical conductivity 10^4 S/m was prepared from the US Nano Inc.

High purity toluene and dichloromethane (DCM) as the solvents were prepared from Merck Company.

2.2. Apparatuses

The used apparatuses were a conventional ultrasonic system UP200H model, operating at 200 W and 24 kHz; digital multi-meter model HIOKI-3804; Behdad oven 50, and SEM system, Zeiss
Company EVO 18 model, and Raman spectroscopy Takram P50C0R10.

2.3. Sample Preparation
MWCNTs with different amount of 1.25, 2.5, 7, 25, and 50 mg were added to DCM and were sonicated for 1 hour. On the other hand, 2.5 g of PS was dissolved in toluene at ~100°C in a separate vessel and the solution was stirred for 40 min. Then, the sonicated MWCNT content solution was added to the PS solution and was mixed with a hot plate magnet stirrer for 40 min to achieve well-dispersed MWCNT in the PS matrix. It was observed that during adding the MWCNTs content solution into the PS solution, due to the evaporation of DCM at lower temperatures of ~40°C, near the boiling point of DCM, some cavities or bubbles appear in the mixed solution. It is probable that breaking or bursting bubbles during the evaporation of DCM from the mixed solution can prevent the re-agglomeration of the MWCNTs in the nanocomposite. To make the PS-MWCNT nanocomposites, the mixed solution was poured into a silicone mold with a diameter of 5 cm and was kept at room temperature for 24 hours to make the thin nanocomposite samples. Finally, the nanocomposites sample with 0.05, 0.1, 0.28, 1, and 2 w% of MWCNT were prepared for our experiments.

2.4. Electrical Conductivity Measurement
The silver paste was chosen as an electrode material and coated on both the surfaces of the samples to fabricate the electrodes.

The electrical resistances of PS-MWCNT nanocomposite samples were measured with a two-probe method using the Fluke 87V Industrial Multi-meter. For each nanocomposite, three measurements were performed and the average values of electrical resistance were obtained. The heating rate process in the samples was ~0.036 °C·s⁻¹ which performed from room temperature to near of glass transition temperature of the PS is (Tg=90°C).

3. RESULTS AND DISCUSSION
3.1. Dispersion of MWCNTs
Figure 1 shows the SEM image of the PS-MWCNT(0.05w%) nanocomposite sample. This figure confirms that the MWCNTs are dispersed in the PS matrix homogeneously.

3.2. XRD Analysis
As can be seen from Figure 2, XRD analysis of 0.05 w% Polystyrene-MWCNT nanocomposite is depicted. The main peak at 2θ=16 is related to Polystyrene with a formula of (C8H8)n. Also, there are two peaks at 31, and 41, in which belong to MWCNT. These positions are in good agreement with the other experimental works [26, 27].

Figure 1. SEM image of fractured surface corresponding to 0.05 w% MWCNT-PS nanocomposite sample.

Figure 2. XRD analysis of 0.05 w% Polystyrene-MWCNT nanocomposite.
3.3. Raman Spectroscopy

Raman spectroscopy (Takram P50C 0R10) with Nd:YAG laser, laser wavelength=532 nm, laser power=100 mW, the spectral resolution of 10 cm$^{-1}$, the optical spatial frequency of 1200 line/mm, an exposure time interval of 15 ms to 10 min, at the range of 100–3600 cm$^{-1}$ was applied to characterize the MWCNT. In Figure 3, Raman spectroscopy analysis of pure MWCNT is exhibited. Two main peaks of D-band at 1344 cm$^{-1}$, G-band at 1574 cm$^{-1}$ and also, G’-band at 2680 cm$^{-1}$ indicating the second mode of vibrations in the carbon atoms can be observed. These bands are in good agreement with the other similar works [28-30].

Figure 3. Raman spectroscopy analysis of MWCNT.

3.4. Electrical Conductivity Measurement

Figure 4 depicts the EPT region in the PS-MWCNT nanocomposites by measuring electrical resistance (R) and converting it to electrical conductivity ($\sigma$) via [31]:

$$\sigma = \frac{L}{R \cdot A}$$  \hspace{1cm} (2)

where L and A are the thickness and surface of the samples, respectively. On the other hand, this figure demonstrates the calculated result which was carried out in our previous work [9]. Regarding this figure, it can be deduced that the experimentally found EPT region for this nanocomposite is almost in accordance with the calculated one that is about 0.28 w%.

From the quantum mechanics point of view, to explain the abrupt change in the electrical conductivity of the PS-MWCNT nanocomposites at the EPT region, it can be mentioned that, at a particular temperature the probability of an electron hopping from one localized state to another, depends on two parameters which are the spatial separation of the sites or tunneling distance (R) and their energy separation (W). In a truly amorphous system, these variables are random and independent. The hopping probability (P) is dependent on both these quantities [32]:

$$P \sim \exp \left[ -\frac{2\alpha R - W}{kT} \right]$$  \hspace{1cm} (3)

It can be deduced that adding of MWCNTs to the PS matrix, decreases W and also R for electrons due to creating traps between the valence band and conduction band of the polymer. In fact, the hopping probability is increased, subsequently. Thus, adding the MWCNTs to the PS matrix resulted in a drastic increment in the electrical conductivity of the nanocomposite in the EPT region. The addition of more MWCNTs over the EPT region does not change the electrical conductivity because the electrons taking the easiest conductive path, and shows a tendency to saturation [33].

To gain deeper insight into the different processes for fabricating the PS-MWCNT nanocomposite samples with low EPT, a
significant number of measurements have been carried out using various experimental setups. Table 1. shows the electrical conductivity results for the same nanocomposite obtained through the experiments and published by other researchers. The value of electrical conductivity measured for PS-MWCNT in this work is remarkably greater than the results published in other articles, which confirms that this method, solution mixed, is a suitable technique for fabrication of the same nanocomposite due to the higher uniformity.

3.5. Effect of Temperature on Electrical Resistance

Figure 5 plotted the electrical resistance of the different nanocomposites with the MWCNT content above the EPT region versus temperature. It is obvious that increasing the MWCNT content in the sample leads to a decrease in the electrical resistance of the nanocomposites, which can be observed comparing the vertical axes of Figs. 5a, 5b, and 5c.

<table>
<thead>
<tr>
<th>Processing method</th>
<th>Electrical Conductivity (S/m)</th>
<th>CNT (w%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution mixing</td>
<td>$10^{-2}$</td>
<td>5</td>
<td>[34]</td>
</tr>
<tr>
<td>Solution mixing</td>
<td>1</td>
<td>4.8</td>
<td>[35]</td>
</tr>
<tr>
<td>Solution mixing</td>
<td>0.135</td>
<td>3</td>
<td>[36]</td>
</tr>
<tr>
<td>Solution mixing</td>
<td>$10^{-4}$</td>
<td>4</td>
<td>[37]</td>
</tr>
<tr>
<td>Solution mixing</td>
<td>$4 \times 10^{-3}$</td>
<td>19</td>
<td>[38]</td>
</tr>
<tr>
<td>Solution mixing</td>
<td>$1.46 \times 10^{-6}$</td>
<td>1</td>
<td>[39]</td>
</tr>
<tr>
<td>Solution mixing</td>
<td>0.05</td>
<td>15</td>
<td>[40]</td>
</tr>
<tr>
<td>Latex technology</td>
<td>$10^{-4}$</td>
<td>1.9</td>
<td>[41]</td>
</tr>
<tr>
<td>Solution mixing</td>
<td>$10^{-4}$</td>
<td>13</td>
<td>[42]</td>
</tr>
<tr>
<td>Mixing and subsequent compression molding</td>
<td>$9.9 \times 10^{-2}$</td>
<td>0.1</td>
<td>[43]</td>
</tr>
<tr>
<td>Transfer polymerization</td>
<td>$10^{-7}$</td>
<td>1</td>
<td>[44]</td>
</tr>
<tr>
<td>Twin-screw extruder and injection molding</td>
<td>1</td>
<td>20</td>
<td>[45]</td>
</tr>
<tr>
<td>Bulk polymerization</td>
<td>$1.48 \times 10^{-7}$</td>
<td>0.26</td>
<td>[46]</td>
</tr>
<tr>
<td>In-situ polymerization</td>
<td>$3.8 \times 10^{-4}$</td>
<td>5</td>
<td>[47]</td>
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<tr>
<td>In-situ bulk polymerization</td>
<td>$10^{-2}$</td>
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<td>[48]</td>
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<tr>
<td>Vacuum casting and hot pressing</td>
<td>6.7</td>
<td>25</td>
<td>[49]</td>
</tr>
<tr>
<td>Solution mixing</td>
<td>2.17</td>
<td>2</td>
<td>This Work</td>
</tr>
</tbody>
</table>
As can be seen in Figure 5, the increasing of the resistance with temperature in the nanocomposites is due to the fact that when temperature increases, the gap between CNTs also widens, mainly caused by the thermal expansion of the matrix, and tunneling becomes less probable, which explains the increase in the resistance with temperature. Therefore, there is a positive temperature coefficient (PTC) effect from the room temperature till ~80°C for all three nanocomposite samples containing the different weight percentages of the MWCNT. This temperature is near the glass transition temperature ($T_g$) of the PS matrix [50]. It means that the polymer reaches the softening zone and its nature going to be changed. Figures 5b and 5c indicate that after this region, the negative temperature coefficient (NTC) is dominant.

On the other hand, it seems that at ~55°C, the slope of the curve increases in all three nanocomposite samples. Several investigations reported this phenomenon for different types of MWCNT-composites [51, 52].

As mentioned before, when the temperature increases, the matrix will expand and some of the conductive chains will be broken up which results in the PTC behavior. But, the polymer matrix expansion rate is not very high in the lower temperature range, thus the PTC is observed with a smaller slope. At the higher temperature range, the matrix expansion rate became higher, therefore the PTC is observed with a higher slope [53].

The linear relationship of the resistance with temperature for these nanocomposites in the range of room temperature up to ~50°C is demonstrated inside Figure 5 for all the samples. It is obvious that for the samples containing 0.28w%, 1w%, and 2w% of MWCNT the resistance range are varying from ~3-4.2 MΩ, ~0.8-1.1 kΩ, and ~67-81Ω, respectively. This means that increasing the w% of MWCNT leads to a decrease in the measured resistance sensitivity.

On the other hand, the results showed in Figure 5 are obtained from several experiments at different times which somehow the error bar demonstrates the stability degree of the response. Also, heating the samples near the glass transition temperature ($T_g$) resulted in the deformation of the CNTs network thus, after the cooling process the amount of resistance is not the same as the previous one. Therefore, in the real mode of calorimetry process, to prevent this event, a temperature limit can be determined. Thus, according to the precision of the using ohm-meter, these nanocomposites can be used in the fabrication of a novel temperature sensor system.

4. CONCLUSION

The electrical conductivity dependence of PS-MWCNT nanocomposites to temperature was measured for different concentrations of MWCNTs namely 0.05, 0.1, 0.28, 1, 2 w%. In the fabrication step, a mixed solution method was introduced, and characterization of SEM analysis approved the uniform dispersion of MWCNTS in the polymer matrix. The determined EPT region for the nanocomposites exhibited a good agreement with other experimental works published in literatures. The variation of resistance with temperature for all the nanocomposite
samples indicates a PTC and NTC behavior before and after \( T_g \) of the PS matrix, respectively. Results showed that the resistant-temperature response function of the nanocomposite was linear between \( \pm 20 \) to \( 50 \) °C. This research work motivates the investigation in depth of the electrical and thermal properties behavior of polymer-CNT nanocomposites for calorimetric approach.

REFERENCES


