A study on aminated PVC/oxidized MWCNT composites

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ABSTRACT

Aminated PVC was obtained from bonding of 3-(dimethylamino)-1-propyl amine to the PVC with the aid of a nucleophilic substitution reaction. It was determined by titration that the amine compound was bound to PVC 10.8% in mole. The four different composites (wt 2, 5, 8 and 11% oxidized MWCNT) were prepared using aminated PVC and, MWCNT which contains acid groups bonded (oxidized MWCNT) on its surface. PVC, aminated PVC and the composites were characterized using FT-IR spectroscopy. SEM-EDX of aminated PVC, and SEM images of aminated PVC/5% oxidized MWCNT and aminated PVC/11% oxidized MWCNT composites were examined. Differential scanning calorimeter (DSC) measurements showed that amine substitution reaction in PVC reduced the glass transition temperature (Tg) of PVC. Amination reaction reduced thermal stability of PVC, but still thermal stabilities of the composites were lower than that of PVC. The dielectric constant values at low frequencies decrease with increasing applied field frequency, and then remain. The dielectric constant increase with increasing temperature for the composites, except composite containing 11% of oxidized MWCNT. A.C. conductivities for the all composites increased rapidly with increasing frequency up to 800 Hz, then they increased slowly up to 4000 Hz at room temperature. A.C conductivities of all composites almost remained constant between 310 and 360 K with increasing temperature.

Key words: Aminated PVC, oxidized MWCNT, thermal, electrical, SEM.

INTRODUCTION

The characteristic properties of metal nanoparticles and nanocomposites have been the subject of study for a long time because of their unique electrical, thermal, mechanical, electronic and optical properties. Carbon nanotubes (CNTs) are ideal fillers for polymer composites due to their high Young’s modulus combined with good electrical and thermal conductivity (Mamunya, 2011). Poly(vinyl chloride) (PVC) is chosen as the host polymer matrix, because of its wide range of applications, low cost, chemical stability, biocompatibility and sterilizability (Wilkes et al., 2005). To improve the thermal and mechanical properties of PVC, additives such as wood flour (Djidjelli et al., 2002), wood fibers (Matuanaet al., 1998), clay (Peprnicek et al., 2006), and calcium carbonate (Sun et al., 2006) have been used as additives to PVC. Carbon black (Yazdani et al., 2014) and other conjugated polymers, such as polyaniline (Tao et al., 2015; Conn et al., 1995) and polypyrrole (Ouyang et al., 1996), were incorporated in the PVC matrix in order to improve the electrical conductivity. CNT have also been identified as a suitable filler material for PVC (Annu et al., 2014; Al-Ramadhan et al., 2012). In PVC/MWCNT composites, dielectric constant increased with increasing MWCNT contents, but decreasing with increasing frequency (Saeed et al., 2015). AC electrical and dielectric properties of PVC-MWCNT nanocomposites were investigated (Abdullah et al., 2011). The result obtained was due to polarization effect. The electrical and thermophysical behaviour of PVC-MWCNT nanocomposites have also been studied (Mamunya et al., 2008). Absorbance spectra of MWCNT-doped PVC films having different
concentrations were recorded, and it was observed that absorbance increased with increase in MWCNT concentration (Abdullah et al., 2013). The effects of dispersing agents such as oleic acid and methyl oleate for proper distribution of MWCNT in the PVC matrix were investigated (Skorczewska et al., 2011), and it was found that they were effective for proper distribution. In recent study on the influence of MWCNT on the Processing Properties and Structure of PVC Composites was published (Skorczewska et al., 2018).

In this study, compositions were prepared from multi-walled carbon nanotube containing a certain percentage of acid groups on the surface (oxidized MWCNT) and amine compound bound PVC (aminated PVC). So, it was aimed to prepare homogeneous composites by interacting easily the amine groups in PVC with the acid groups in MWCNT. FTIR and SEM, SEM-EDX characterization was performed. Thermal and electrical properties of these composites were investigated.

### MATERIALS AND METHODS

Oxidized multi wall carbon nanotube (MWCNT) containing 2.5% carboxyl group was obtained from Nanografi Co. Ltd. 3-(dimethylamino)-1-propylamine, and other chemicals were purchased from Sigma-Aldrich.

### Synthesis of aminated PVC

Amination of PVC was performed according to the procedure given in literature (Balakrishnan et al., 2005). Briefly, 5 g of PVC was accurately weighted and mixed with 40.4 mL of 3-(dimethylamino)-1-propylamine and 9.6 mL distilled water in 100 mL volumetric flask. The mixtures were sonicated for 5 min and then passed into argon gases. They were placed into oil bath for 1 h at 80°C and then filter by washing with distilled water. The cured product was immersed in ethanol for overnight, decanted and dried at room temperature for 24 h and then dried again in a vacuum at 45°C for 48 h.

### Calculation of percentage of amination on PVC

10 mL HCl solution adjusted (0.1108 M) was poured into 100 mg aminated PVC and after stirring at room temperature for 2 h, the polymer was filtered and washed with water. Washing water was combined with filtrate and was titrated with the adjusted NaOH solution (0.1079 M) in the presence of phenolphthalein as indicator:

\[
\text{HCl acid mmol number spent for amine group in PVC} = 10 \times 0.1108 - 7.4 \times 0.1079 = 0.3095 \text{ mmol.}
\]

Since the amine compound which is bound to PVC has two amine groups, the molar number of the amine compound on PVC is \(0.3095 / 2 = 0.1548\) mmol. This number is also the mmol number of the amine group bonded vinyl group:

\[
\text{Percentage of aminated vinyl group (by mol)} = \frac{0.1548}{(1.283 + 0.1548)} = 10.8
\]

Where 1.283 is the mmol number of amine compound unbound vinyl chloride.

### Preparation of composite of aminated PVC with oxidized MWCNT

According to the method adopted given in the literature (Ma et al., 2010), to prepare aminated PVC/2% MWCNT composite, 0.49 g of aminated PVC was weighed precisely and then dissolved in 10 mL THF. 0.01 g of oxidized MWCNT was added to the aminated-PVC solution and mixed with a sonicator for 1 h. The resulting composite was precipitated in ethanol and filtered. We used same procedure to prepare aminated PVC/oxidized MWCNT composites containing 5, 8 and 11% oxidized MWCNTs. All composites prepared were first dried at room temperature and then dried again in a vacuum at 45°C for 48 h.

### RESULTS AND DISCUSSION

FT-IR spectrum (Figure 1a) of PVC showed characteristic bands at 2970-2820 cm\(^{-1}\) (aliphatic C-H stretching vibration on CH\(_2\), CH), 1257 cm\(^{-1}\) (C-H bending vibration on –CHCl-) and 606 cm\(^{-1}\) (C-Cl stretching vibration). In addition, bands of water coming from KBr, which is unrelated to the structure, is observed in the O-H stretching band at 3455 cm\(^{-1}\) and the O-H bending band 1636 cm\(^{-1}\). FT-IR spectrum (Figure 1b) of aminated PVC showed characteristic bands at same wavenumbers with PVC including water bands. Aminated PVC showed weak bands related to the amine group attached to PVC at 2780 cm\(^{-1}\) (C-H stretching vibration on CH\(_3\)-N), at 1470 cm\(^{-1}\) (aliphatic C-N stretching vibration band) and 606 cm\(^{-1}\) (C-Cl stretching band relatively weaker than that of PVC). The N-H band of aminated PVC is probably under the O-H stretching band.

The SEM-EDX results of the aminated PVC are shown in Figure 2. From the SEM-EDX data, it can be seen that the atomic percentage of the nitrogen element in the aminated PVC is 15.62%. It can be estimated that the molar percentage of the aminated units in PVC is 7.81 since 2 nitrogen atoms are present in the aminated units in the aminated PVC. It is relatively comparable to the 10.8% amination found through titration. However, it can be said that the value found in the titration is closer to the true value. Because the SEM-EDX can be computed from the image taken from a specific region, it can be a zone where
Figure 1: FT-IR spectra of (a) PVC and (b) aminated PVC (KBr disc).

Figure 2: SEM-EDX results of aminated PVC.
the amination is intense or less.

FT-IR spectrum of oxidized MWCNT (Figure 3a) showed characteristic bands at 3330 cm\(^{-1}\) (O-H stretching in carboxyl group), at between 2970-2860 cm\(^{-1}\) (aliphatic C-H stretching vibration), 1727 cm\(^{-1}\) (C=O stretching band), 1636 cm\(^{-1}\) (O-H bending in probably water), 1575 cm\(^{-1}\) (C=C stretching in MWCNT) and 1180-1030 cm\(^{-1}\) (C-O stretching). FT-IR spectrum of aminated PVC/11\% oxidized MWCNT composite (Figure 3b) showed characteristic bands at 3455 cm\(^{-1}\) (O-H stretching in water), 3300 cm\(^{-1}\) (as shoulder, O-H stretching in carboxyl group), between 2970-2860 cm\(^{-1}\) (aliphatic C-H stretching vibration in aminated PVC and oxidized MWCNT), 1727 cm\(^{-1}\) (C=O stretching band in oxidized MWCNT), 1636 cm\(^{-1}\) (O-H bending in probably water), 1575 cm\(^{-1}\) (C=C stretching in MWCNT), 1180-1030 cm\(^{-1}\) (C-O stretching) and the 606 cm\(^{-1}\) band of PVC, which is not seen in the spectrum of MWCNT, and can be attributed C-Cl band in aminated PVC.

SEM images of aminated PVC/5\% oxidized MWCN and aminated PVC/11\% oxidized MWCN composites are shown in Figure 4a and b, respectively. The SEM image (Figure 4a) of the composite containing 5\% oxidized MWCNT shows...
that most of the oxidized MWCNT rods are well dispersed in the aminated PVC matrix, with a few minor irregularities. Figure 4b shows one of the fractured zone, which reveals the well dispersed oxidized MWCNT rods in the composite. The length of the rods is not very well chosen because they are embedded in the polymer matrix.

**Thermal investigation**

Differential scanning calorimeter (DSC) curves of PVC, aminated PVC and composites heated at 10°C/min are shown in the Figure 5. DSC measurements show that amine substitution reaction in PVC reduced the glass transition temperature \( T_g \) of PVC from 84.7 to 79°C. The addition of oxidized MWCNT to aminated PVC increased the \( T_g \) temperature of PVC, as details are shown in Table 1. Interaction of carboxylic acid groups on oxidized MWCNT with amine groups on PVC and chlorine-bound partial positive carbon prevents the movement of PVC chains. This phenomenon leads to a decrease in free volume in PVC and an increase in glass transition temperature.

Thermogravimetric analysis (TGA) curves of PVC, aminated PVC, aminated PVC/ 2% oxidized MWCNT composite and aminated PVC/ 5% oxidized MWCNT composite are shown in Figure 6. TGA curve of aminated

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**Figure 5**: DSC curves of PVC (a), aminated PVC (b) and oxidized MWCNT concentration (wt%) in aminated PVC/ oxidized MWCNT composites, 2% (c), 5% (d), 8% (e), 11% (f) (second cycle heating temperatures).

**Table 1**: Thermal investigation of PVC, aminated PVC and composites containing oxidized MWCNT at different percentages.

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_g ) (°C)</th>
<th>( T_i^* ) (°C)</th>
<th>50% wt loss at tem. (°C)</th>
<th>Weight loss (wt) at 300°C</th>
<th>Residue (wt%) at 500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>84.7</td>
<td>260</td>
<td>329</td>
<td>22.9</td>
<td>24.2</td>
</tr>
<tr>
<td>Aminated PVC</td>
<td>79.0</td>
<td>209</td>
<td>262</td>
<td>53.3</td>
<td>29.0</td>
</tr>
<tr>
<td>Aminated PVC/Oxidized MWCNT (wt %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>90.3</td>
<td>217</td>
<td>307</td>
<td>51.0</td>
<td>33.8</td>
</tr>
<tr>
<td>5</td>
<td>89.5</td>
<td>209</td>
<td>286</td>
<td>47.6</td>
<td>25.0</td>
</tr>
<tr>
<td>8</td>
<td>85.5</td>
<td>212</td>
<td>319</td>
<td>52.5</td>
<td>29.8</td>
</tr>
<tr>
<td>11</td>
<td>87.1</td>
<td>212</td>
<td>331</td>
<td>53.3</td>
<td>28.3</td>
</tr>
</tbody>
</table>

\*Initial decomposition temperature: The temperature at which rapid decomposition begins.
PVC shows that after a weight loss of 4.7% from 100 to 133°C, rapid decomposition started at 176°C. In the case of PVC, rapid decomposition began at 248°C (T_i, initial decomposition temperature). Amination reaction reduced thermal stability of PVC. Oxidized MWCNT increased slightly the thermal stability of aminated PVC, but still thermal stabilities of the composites are lower than that of PVC. The results obtained from TGA curves are shown in Table1 in detail.

**Electrical investigation**

For dielectric constant, dielectric loss and AC conductivity measurements, samples having 1.32 cm² area were used for all composites. Sample thickness was 0.051, 0.067, 0.067 and 0.040 cm for the composites containing 2, 5, 8 and 11% (by weight) oxidized MWCNT, respectively.

**Dielectric constant, dielectric loss**

This is one of the most important properties used to determined A.C. conductivity and it is determined using the following equation:

\[ \varepsilon' = \frac{C_p}{C_o} \]

Where \(\varepsilon'\) = dielectric constant, \(C_p\) = capacitance of dielectric filled capacitor, \(C_o\) = freespace capacitor, and the dielectric constant is measured at different frequency and temperature. Variation of dielectric constant of composites of aminated PVC/oxidized MWCNTs with frequency at room temperature are shown in Figure 7. This figure shows that dielectric constant values decrease with increasing applied field frequency, between 100-500 Hz rapid for composites containing 2 and 5% of oxidized MWCNT, and between 100-800 Hz rapid for composites containing 8 and 11% of oxidized MWCNT, and then remain constant.

Dielectric loss result from the inability of polarization process in a molecule to follow the rate of change of the oscillating applied electric field. This emerge from the relaxation time (\(\tau\)) in a polymer which is the time taken for the dipoles to return to its original random orientation. It does not occur instantaneously but the polarization diminished exponentially. If the relaxation time is smaller or comparable to the rate of oscillating electric field, then there would be no or minimum loss.

**Figure 6:** TGA curves of PVC (a), aminated PVC (b), aminated PVC/2% oxidized MWCNT composite (c) and aminated PVC/5% oxidized MWCNT composite (d).
Figure 7: Variation of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of aminated PVC/oxidized MWCNTs composites with frequency at room temperature.

The dielectric loss was measured by depending on frequency (Figure 7). The dielectric loss of composite containing 11% of oxidized MWCNT which has higher dielectric constant decreases rapidly up to 500 Hz, slowly from 500 to 2000 Hz, with increasing frequency. For the other composites, the dielectric remains nearly constant with increasing frequency.

Temperature dependence of dielectric constants and dielectric losses are shown in Figure 8. The Figure shows that the dielectric constant increase with increasing temperature for the composites, except composite containing 11% of oxidized MWCNT. For 8% composite, the increase is relatively slow up to 93°C, after that it becomes rapid. For 2 and 5% composites, the increase is relatively slow up to 95°C, then it becomes rapid. These temperatures are similar to the glass transition temperature of polymer in composites.

Temperature dependence of dielectric losses for 8 and 11% oxidized MWCNT remain nearly constant up to 105-110°C, but it increases rapidly after nearly 92°C for the composites containing 2% and 5% oxidized MWCNT.

**A.C. conductivity**

A.C. conductivity is another parameter used to determine electrical properties and can be measured using the following equation:

$$\sigma_{ac} = \omega \varepsilon'' \varepsilon_0$$

where $\sigma_{ac}$ = A.C. conductivity, angular frequency $\omega = 2\pi f$, $\varepsilon''$ = dielectric loss and $\varepsilon_0$ = permittivity at free space.

The A.C. conductivity is measured at different frequencies at room temperature and different temperatures at 1 kHz frequency (Figure 9a and b, respectively). For the composites, A.C. conductivities for the all composites increase rapidly with increasing frequency up to 800 Hz, then they increase slower up to 4000 Hz at room temperature. This result means that polarization of the electrically conductive particles in the composites are faster at low frequencies but as the frequency increases, it becomes slower.

The 2% oxidized MWCNT-containing composite showed
a rapid increase in AC conductivity from room temperature to about 35°C (308 K). Then, after a very slow increase between 35 and 92°C, it was observed to increase again rapidly. The A.C. conductivity of the composite containing 5% oxidized MWCNT increased more rapidly after increasing slowly from room temperature to 92°C. It was observed that the A.C. conductivities of composites containing 8 and 11% oxidized MWCNTs did not change with temperature.

CONCLUSION

Aminated PVC was obtained from bonding of 3-(dimethylamino)-1-propyl amine to the PVC with the aid of a nucleophilic substitution reaction. The composites were prepared using aminated PVC and oxidized MWCNT. PVC, aminated PVC and the composites were characterized using FT-IR spectroscopy, SEM-EDX of aminated PVC, and SEM images of aminated PVC/5% oxidized MWCNT and...
Aminated PVC/11% oxidized MWCNT composites were examined. DSC measurements showed that amine substitution reaction in PVC reduced Tg temperature of PVC. TGA curves showed that amination reaction reduced the thermal stability of PVC. Oxidized MWCNT in the composites increased slightly the thermal stability of aminated PVC.

Dielectric constant values at low frequencies, decrease with increasing applied field frequency, and then remain. The dielectric constant increase with increasing temperature for the composites, except composite containing 11% of oxidized MWCNT. A.C. conductivities for all composites increased rapidly with increasing frequency at low frequencies, and then increased slowly up to 4000 Hz at room temperature. A.C. conductivities of all composites were nearly remained constant between 310 K and 360 K with increasing temperature.

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REFERENCES


