EFFECT OF MnO₂ NANOWIRE ON RHEOLOGICAL AND DIELECTRIC PROPERTIES OF PVDF/CNT HYBRID NANOCOMPOSITES

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Abstract

Poly (vinylidene fluoride) (PVDF) matrix hybrid nanocomposites incorporating MnO₂ nanowire (MnO₂NW) and Carbon nanotubes (CNT), were fabricated by melt mixing in a batch mixer followed by hot pressing. Dielectric properties of fabricated nanocomposites were studied in X-band frequency (8.2-12.4GHz). The conductive CNT increased the dielectric permittivity of the PVDF by serving as a nanocapacitor. Increasing CNT loading enhanced dielectric loss due to the formation of a conductive network. Adding MnO₂NW increased the dielectric permittivity while decreasing dielectric loss. Rheology coupled with dielectric properties and electrical conductivity measurements of the nanocomposites showed the effect of MnO₂NW, as secondary nanofillers, on the CNT percolative network. We attribute the superior dielectric properties of the hybrid nanocomposites to the role of MnO₂NW on improving the dispersion state of CNT (confirmed by rheology) and also its barrier role on hindering the CNT network formation.

Introduction

Polymer nanocomposites containing carbon nanofillers have been widely used as potential high dielectric permittivity (high-κ) materials for high-tech applications such as fabrication of advanced electronics and film capacitor, etc. [1-3]. High-κ polymer nanocomposite can be fabricated by dispersion of conductive fillers in polymer matrix. The dielectric constant of nanocomposites enhances one or several orders of magnitude at percolation threshold due to insulation-conduction transition. Conductive polymer nanocomposites (CPNs) consisting of carbon nanofillers can deliver high dielectric constants at low filler contents which intact high flexibility, processability and mechanical properties of polymer matrix. Therefore, a great deal of attention has been focused on CPNs containing carbon nanofillers. For example, high-κ CPNs were fabricated by embedding graphene [4-6] or carbon nanotubes (CNTs) [7-10] in the polymer matrix.

The geometry of the conductive filler plays a crucial role in the dielectric properties of composites. Fillers with higher aspect ratios can improve the dielectric constant of the composites more efficiently as compared to spherical particles because of their lower percolation threshold than that of spherical particles [11, 12]. So, Carbon nanotubes (CNTs) can be promising options to fabricate CPNs, owing to their large aspect ratio and high electrical conductivity. There are numerous studies incorporating of CNTs to make high-κ CPNs [10, 13-15]. Despite the success of several studies in development of high-κ CNT/polymer nanocomposites, their high dielectric loss at percolation threshold is the main issue. Formation of 3D conductive network by direct contact between CNTs at percolation threshold, facilitates charge transfer and consequently generate very high dielectric loss. So, obtaining CPNs with both high dielectric permittivity and low dielectric loss values at the same time is still challenging. Surface modification of CNT (such as functionalization or coating with other materials) has to be taken into account in order to achieve high-κ CPNs with low dielectric losses. However, CNT surface modifications can significantly raise the production costs and also high loading of modified CNTs is also required to gain acceptable dielectric properties [16, 17]. Preparing hybrid nanocomposites by adding secondary filler are of great interest to overcome the aforementioned problems [18-20]. In this approach, the contact between neighboring CNTs can be suppressed by applying second filler. Furthermore, by choosing a ferroelectric material, a desirable high-κ CPN can be expected due to the increased permittivity and reduced loss, simultaneously [19, 21].

To this end, we have designed and fabricated CNT/MnO₂ nanowire (MnO₂NW)/PVDF to obtain a promising dielectric hybrid polymer nanocomposite based on the following reasons: (i) a better dimensionality match can be achieved if both fillers share the same geometry. It is postulated that incorporation of 1D secondary filler (MnO₂NW) would be more effective to disrupt conductive network formation of CNTs in comparison with nanoparticles. [19, 21-23], (ii) MnO₂ is also known for its high theoretical specific capacitance, low cost, natural abundance, and environmentally friendly nature [24, 25]. So, by employing MnO₂NW we expect not only to reduce the dielectric loss since its barrier role between CNTs, but also to increase dielectric constant owing to its properties. Moreover, It is well established that the dielectric properties of CPNs strongly rely on the dispersion state of the fillers in the nanocomposite [2, 11]. Different methods such as electron microscopy have been used to study the dispersion state of CNTs. Although electron microscopy is a strong technique for filler dispersion studies, but it is not enough. Lertwimolnun and Vergnes [26] have shown that rheometry can be a powerful tool for characterizing the state of dispersion of nanoparticles in a polymer matrix.
Generally speaking, the linear viscoelastic behavior of nanocomposites shows a significant change from liquid-like flow behavior to a pseudo solid-like behavior, depending on the concentration and the state of dispersion. The solid-like behavior of nanocomposites is often attributed to the existence of a percolation network formed by nanoparticles. So, morphological and rheological properties of the CNT/MnO₂NW hybrid nanocomposites were used to describe the observed dielectric properties.

Materials

MnO₂ nanowire synthesis: In this study, hydrothermal method was used to synthesize MnO₂ nanowires. First, 0.608 g KMnO₄ (Sigma Aldrich, ACS reagent ≥99.0%) was dissolved in 70 ml distilled water and agitated vigorously for 30 min. Then, 1.27 ml HCl (EMD Chemicals, 37%) was added to the solution and mixed for additional 10 minutes. The solution was transferred to a 100 mL Teflon lined stainless steel autoclave and kept at 140°C for 12 h in oven. Then autoclave was cooled down over night to room temperature. After cooling, precipitates were collected, filtered and rinsed several times with distilled water to reach neutral pH 7. Finally, the collected powder was dried for 4h at 80°C.

Nanocomposite Preparation: PVDF (3M Canada, PVDF 11008/0001) was selected as polymeric matrix owing to its high dielectric constant, ferroelectricity and high breakdown strength. To fabricate nanocomposite samples, APAM (Alberta Polymer Asymmetric Minimixer) was facilitated to melt mix PVDF with fillers at 240°C and 235rpm. To prepare nanocomposite samples for dielectric studies two types of samples were fabricated: first, binary nanocomposites of PVDF/CNT and PVDF/MnO₂NW were prepared at two different concentrations (0, and 2) with 15 min mixing. For CNT/MnO₂NW/PVDF hybrid nanocomposites, two samples with different MnO₂NW/CNT weight ratios (1, and 2) were fabricated. First, PVDF was masticated for 3 min, followed by addition of CNTs and mixing for 7min. Finally, MnO₂NW were added and mixed for additional 8 min for CNT/MnO₂NW hybrid nanocomposites. A Carver compression molder (Carver Inc., Wabash, IN) was used to make circular samples at 240°C and 35 Mpa for 10 min. The diameter and thickness of the samples are 25 mm and 0.2 mm respectively.

Characterization

Transmission Electron Microscopy: The structure of MnO₂NW was studied by high-resolution transmission electron microscopy (HRTEM). The TEM used in this study was Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, OR) at 200 kV acceleration voltage with a standard single tilt-holder. The images were captured by a Gatan UltraScan 4000 CCD Camera (Gatan, Pleasanton, CA). In order to investigate CNT dispersion in PVDF, TEM was carried out on ultramicrotomed sections which prepared using a Leica EM UC6 microtome setup in nitrogen atmosphere.

X-ray Diffraction: Rigaku ULTIMA III X-ray diffractometer with Cu K-alpha radiation was used to record XRD spectra. The scans were recorded in the range of 2θ = 0.92–90 degrees using a 0.02 degree step and a counting time of 1.0 degree per min at 40 kV and 44 mA.

Electrical Conductivity and Dielectric Properties: To measure electrical conductivity of nanocomposite samples with conductivity less than 10⁻⁶ S·cm⁻¹, Keithley 6517A electrometer was used. The Keithley 6517A electrometer was connected to a Keithley 8009 test fixture and equipped with Keithley 6524 high resistance measurement software. For conductivities higher than 10⁻⁶ S·cm⁻¹, Loresta GP resistivity meter (MCP-T610 model, Mitsubishi 48 Chemical Co., Japan) connected to an ESP four-pin probe (MCP-TP08P model, Mitsubishi Chemical Co., Japan) was used. Dielectric properties were measured in the X-band frequency range (8.2-12.4 GHz) with E5071C network analyzer (ENA series 300 kHz to 20 GHz). The samples were sandwiched between two waveguides of the network analyzer.

Rheometry: Rheological measurements were performed on PVDF, PVDF/2.0wt%CNT, PVDF/2.0wt%MnO₂NW, PVDF/2.0wt%CNT/2.0wt%MnO₂NW and PVDF/2.0wt%CNT/4.0wt%MnO₂NW nanocomposites using an Anton-Par MCR 302 rheometer at 240°C using 25 mm parallel-plate geometry with a gap of 200 μm under nitrogen.

Results and discussion

The XRD pattern of as-synthesized MnO₂NWs is shown in Figure 1. The diffraction peaks can be finely assigned to the pure tetragonal α-MnO₂ [28, 29]. α-MnO₂ has higher specific capacitance and lower electrical conductivity in comparison with other crystallographic forms of MnO₂ [30]. So, α-MnO₂NW was incorporated into PVDF to not only increase the dielectric permittivity of the CNT/PVDF nanocomposite, but also works as a non-conductive barrier between CNTs to decrease the dielectric loss. TEM micrographs of MnO₂NW are shown in Figure 2a-b. The length and diameter of MnO₂NW were obtained by averaging the dimensions of more than 100 isolated NWs. The measured length and diameter of synthesized NWs were about 2.0 μm and 57 nm, respectively (aspect ratio of 35). This results revealed comparable length and geometry of CNT (CNT length: 1.5 μm) and synthesized MnO₂NW.

The frequency dependence of dielectric permittivity and imaginary permittivity at room temperature over the X-band for PVDF, PVDF/2.0wt% CNT, PVDF/2 & 4wt% MnO₂NW and PVDF/2wt% CNT/2 & 4wt% MnO₂NW hybrid nanocomposites are shown in Figure 3a-b. Neat PVDF shows an average dielectric permittivity around 3.0
at 8.2 GHz; nonetheless, addition of CNT increases dielectric permittivity to about 21.0 at same frequency. On the other side, addition of 2.0 and 4.0wt% MnO$_2$NW marginally increased dielectric permittivity to 3.7 and 5.0 at 8.2 GHz, respectively. The increase in the dielectric permittivity of CNT/PVDF nanocomposites is due to the formation of nanocapacitor structure [5, 31, 32]. The nanocapacitor structure is formed by considering each of the two neighboring CNTs as the electrodes and the very thin PVDF layer in between as nanodielectric. So called nanocapacitors will substantially increase the intensity of local electric field around CNTs, which subsequently leads to the electronic polarization of the PVDF matrix as the nanodielectric layer. In contrast to CNT, addition of MnO$_2$NW into neat PVDF slightly enhanced dielectric properties of nanocomposite revealing that MnO$_2$NW polarization is active over the X-band.

![Figure 1: XRD patterns of synthesized MnO$_2$NW.](image)

As suggested by figure 3, increasing the ratio of MnO$_2$NW/CNT enhanced the dielectric permittivity of hybrid nanocomposite. For instance, dielectric permittivity of CNT/PDVF nanocomposite at 2.0wt% of CNT was 21.0. However, by addition of MnO$_2$NW as secondary ferroelectric filler its value increased to 30.0 at 8.2 GHz for a PVDF/2wt% CNT/4.0wt% MnO$_2$NW nanocomposite that is the best result achieved in this study. The dielectric constants were dependent on frequency, showing decreases with an increase in frequency. The frequency-dependent nature of conductive polymer nanocomposites has been widely reported and is usually accredited to dissipation of the charge at the filler/matrix interface into heat [5].

On improving the dielectric permittivity of the hybrid system, two parameters came into play: namely, (i) better dispersion of CNT was achieved in the presence of MnO$_2$NW and (ii) positioning of MnO$_2$NW among CNTs. It is well established that the dielectric properties of CPNs strongly rely on the dispersion state of the fillers in the nanocomposite [2, 11]. To study the dispersion state of CNT, rheology test (stress overshoot experiment) was performed on samples with 2.0wt% CNT and different MnO$_2$NW amount. Figure 4 shows the normalized transient stress response performed on the nanocomposites as a function of shearing time. The temporal sequence of the response initiates with a linear increase in shear stress reaching a maximum value $\tau_{\text{max}}$ at $t_{\text{max}}$, and then decreases toward a steady-state value. The emergence of the stress overshoot in step rate experiments has been observed for soft glassy materials, such as emulsions [33], and also polymer nanocomposites [34, 35]. For polymer nanocomposite melts, the stress overshoot is considered as a signature for transition from pseudo-solid-like behavior under nearly at-rest condition to liquid-like behavior above a characteristic shear stress. This transition is attributed to the failure of the nanofiller superstructure and individual nanofillers orientation. When the nanocomposite is sheared, the network of the nanofillers is broken and highly anisotropic particles will be oriented in the shear direction. Thus, the stress response displays an overshoot which its magnitude shows the network strength.

Various level of resilience to yielding for PVDF/CNT, PVDF/MnO$_2$NW and hybrid nanocomposites were observed. According to the results, PVDF/MnO$_2$NW nanocomposites has smaller failure stress compared to PVDF/CNT and hybrid nanocomposite. It can be related to dissimilar network structure and different level of nano dispersion. It can be suggested that the concentration of MnO$_2$NW is not high enough to form a 3D network. On the other hand, higher stress for PVDF/CNT nanocomposite can be proposed to formation of a strong 3D network. Moreover, the overshoot increases for hybrid nanocomposites. it is clear that the MnO$_2$NW network is much weaker than CNT network, thus the sharp increase of overshoot for hybrid nanocomposites indicates better dispersion state of CNTs. This explanation were confirmed by TEM analysis of the samples. TEM analysis (Figure 5) revealed that adding MnO$_2$NW into the nanocomposite films improved the dispersion state of CNTs. So, higher stress overshoot is anticipated. As a consequence, secondary nanofiller (MnO$_2$NW) has a synergistic effect on dispersion state of CNTs. Hence, larger number of isolated CNTs with polymer matrix became available. So, higher dielectric permittivity is expected. Moreover, based on the nanocapacitor model, permittivity and capacitance (C) are related based on $C = e_0\varepsilon_f A/d$; where $e_0$ is the vacuum permittivity, $\varepsilon_f$ is the relative permittivity of polymer matrix, $A$ is the area of the electrical electrode, and $d$ is the distance between two electrical electrodes that are CNTs here. By replacing the PVDF medium with MnO$_2$NW/PVDF, the permittivity ($\varepsilon_f$) of the nanodielectric layer increased, enhancing the dielectric permittivity of the CNT/MnO$_2$NW/PVDF hybrid nanocomposite.

![Figure 3](image)

Figure 3-b shows that addition of MnO$_2$NW into the PVDF matrix even at high concentration (4.0% wt) has a little effect on imaginary permittivity of nanocomposite owing to non-conductive nature of $\alpha$-MnO$_2$. In contrast, addition of CNT as conductive filler into PVDF matrix can drastically increase imaginary permittivity owing to formation of conductive network. Table 1 shows the electrical conductivity of the studied nanocomposites. MnO$_2$NW/PVDF nanocomposites presented a non-conductive behavior on both concentrations. This is
attributable to the non-conductive nature of \(\alpha\)-MnO\(_2\). Addition of MnO\(_2\)NW has adverse effect on conductivity of the hybrid nanocomposite samples. In other word, MnO\(_2\)NW not only serves as dielectric but also acts as non-conductive barrier layer, hindering the formation of conductive paths and thus efficiently decreasing the leakage current. These explanations were confirmed by rheology and TEM images, an improved dispersion state of CNTs was clearly observed with the addition of MnO\(_2\)NW. It is worth noting that the comparative dimensionality of the employed nanofillers plays a leading role in their synergistic effect towards reducing dielectric loss.

Table 1. Conductivity measurement of prepared nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (S/cm)</th>
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<tbody>
<tr>
<td>PVDF</td>
<td>1.06×10(^{-15})</td>
</tr>
<tr>
<td>PVDF/2.0wt%MnO(_2)NW</td>
<td>1.24×10(^{-14})</td>
</tr>
<tr>
<td>PVDF/4.0wt%MnO(_2)NW</td>
<td>2.15×10(^{-14})</td>
</tr>
<tr>
<td>PVDF/2.0wt%CNT</td>
<td>8.62×10(^{-2})</td>
</tr>
<tr>
<td>PVDF/2.0wt%CNT/2.0wt%MnO(_2)NW</td>
<td>1.82×10(^{-2})</td>
</tr>
<tr>
<td>PVDF/2.0wt%CNT/4.0wt%MnO(_2)NW</td>
<td>1.91×10(^{-5})</td>
</tr>
</tbody>
</table>

**Conclusions**

The effect of MnO\(_2\)NW on the dielectric properties of CNT/PVDF hybrid nanocomposites was studied using rheology. Results showed that adding MnO\(_2\)NW can be used as an effective secondary filler for CPNs fabricated by CNTs. Matched dimensionality between CNT and MNO\(_2\)NWs and enhanced dispersion of CNT at the presence of MNO\(_2\)NWs are responsible for higher dielectric permittivity. The outstanding dielectric properties of developed hybrid nanocomposites at low nanofiller contents suggest them as promising materials for flexible capacitors, such as embedded capacitors in printed circuit boards.

**References**

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Fig. 2 TEM images of MnO$_2$NW at (a) low and (b) high magnification.

Fig. 3. (a) Dielectric permittivity ($\varepsilon'$) and (b) imaginary permittivity ($\varepsilon''$) of PVDF/CNT, PVDF/MnO$_2$NW and PVDF/CNT/MnO$_2$NW.
Fig. 4 Normalized shear stress as a function of shearing time for prepared nanocomposites.

Fig. 5 TEM micrographs of morphology of (a & b) PVDF/2.0wt% CNT and (c & d) PVDF/2.0wt% CNT/2wt% MnO₂NW. Better dispersion state of CNT in the presence of MnO₂NW is observed.