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Enhanced Dielectric Properties of Polyaniline/Silver/Carbon Nanotubes Nanocomposite

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ABSTRACT

Current researches had shown that the electrical conductivity of most polymers depend on the method of its preparation and type of fillers. This research therefore aimed at studying the electrical properties of polyaniline carbon nanotubes nanocomposite prepared by hand mixing and decoration methods. The effect of preparation method on electrical properties of polyaniline containing Carbon Nanotubes (CNTs) and silver nanoparticles was studied. The formation of Ag NPs was confirmed by XRD. The AC-conductivity, dielectric permittivity (ε') and dielectric loss (ε") of (CNTs/PANI/Ag) nanocomposites have been measured in the temperature range from 298 to 433 K and frequency range from 10 to 100 kHz. The Ag-CNTs improved the electrical conductivity and dielectric properties of polyaniline. The electrical conductivity of the CNTs/Ag/PANI nanocomposite prepared by decoration method is higher than composites prepared by mixing method.

Keywords: Polyaniline, Silver, Carbon Nanotubes, AC-Conductivity, Dielectric Permittivity, Dielectric Loss

1. INTRODUCTION

Most of polymer materials have very high electrical resistance. In electronic industries, polymer materials are being widely used to produce numerous parts such as circuit boards, IC chip trays, encapsulants for electronic device, housings of personal computers, frames of monitors, keyboards, mouses and so on. Many of these applications take the advantages of polymer materials as good insulators, but some applications require polymer materials to be electrically conductive (Xin and Li, 2011). For example, conductive polymers can be used for electromagnetic shielding, anti-static electricity, printed circuit boards, electrodes of electrochemical devices such as fuel cells. However, there are only few types of inherently conductive polymers commercially available but they usually have poor processability because they are not thermoplastic (Xin and Li, 2011). For example, Polyaniline (PANI) is a well known conducting polymer but its application is limited as PANI is not thermoplastic and a doping process is necessary to induce electrical conductivity. A common approach to development of conductive thermoplastics is achieved through adding conductive fillers into a non-conductive polymer matrix. The commonly used conductive fillers usually used include metal powder, metal fibers, Carbon Nanotubes (CNTs), carbon fibers, carbon black, graphite and so on (Kar and Choudhury, 2013; Nguyen and Shim, 2011). These conductive filler/polymer composites have attracted much attention recently due to their high potentials in industrial applications. In all the conductive fillers mentioned above, CNTs exhibit fascinating electronic and mechanical properties because of their unique molecular structures. The combination of CNTs and other kind of nanoparticles is particularly useful to integrate the properties of two components in hybrid

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materials (Xu *et al*., 2014). Many studies have been devoted for fabrication of metal nanoparticles-decorated CNTs for unique electrical, magnetic and optical properties (Chen *et al*., 2013). Among them, silver-decorated CNTs (Ag-CNTs) have gained extensive attention due to their potential applications as catalyst (Xin and Li, 2011), optical limiters and advanced materials (Long *et al*., 2011). There are several methods of preparing Ag-CNTs materials, including vapor deposition (Lawal and Wallace, 2014) and surface chemical reduction (Alimohammadi *et al*., 2012). However, all these methods cannot get satisfactory results. In most cases, agglomeration of silver nanoparticles is still a problem and consequently few silver nanoparticles are decorated onto CNT surfaces, leading to poor synergic effects of the Ag-CNTs nano-hybrids, especially in the electrical conductivity (Xin and Li, 2011).

In the present work, CNTs/PANI/Ag NCs was prepared by hand mixing and decoration method. The electrical and dielectrically properties of the CNTs/PANI/Ag NCs were investigated.

2. MATERIALS AND METHODS

2.1. Synthesis of CNTs/PANI/Ag NCs

2.1.1. Synthesis of PANI/Ag NCs

Aniline (Aldrich) was dissolved in 1 M nitric acid, as was silver nitrate (Aldrich). The solutions were mixed to start the oxidation at room temperature. The concentration of aniline was 0.4 M, the silver nitrate- to-aniline molar ratio was 2:5. The reaction was slow, characterized by an induction period extending for weeks. So it is activated by exposing to UV light (Blinova *et al*., 2009). Green solids produced in the oxidation were collected on filter and washed several times by distilled water and dried at room temperature.

2.1.2. Synthesis of CNTs/PANI/Ag NCs

CNTs/PANI/Ag NCs was prepared by hand mixing method and decoration method.

In hand mixing method experiment CNTs with an average diameter of (10-20) nm a length of (0.5-200) lm from Ahwahnee Technology Inc. was used as nanotube starting materials. 3 mg of PANI/Ag NCS and 1 mg CNTs were mixed in the reaction vessel. 2 mL of dicholoroethan was then add to mixture and sonicated for about 20 min. The mixture was left at room temperature for solvent evaporation.

In decoration method, PANI/Ag NCS was dissolved in DMF and the fillers CNT's was added in the solution and then ultrasonicated at 20 kHz and 24 W for 10 min to ensure that the fillers was homogeneously mixed with the CNTs (Xin and Li, 2011). DMF was then evaporated and the composite was dried at 50°C for 6 h.

2.2. Electrical Properties

The AC-conductivity, dielectric constant ε' and dielectric loss ε" as a function of temperature and frequency were measured. This is carried out using programmable automatic LCR meter (PM636 Philips) at frequencies of 10-100 kHz and temperature range of 298-433 K. The effect of preparation method on the electrical properties was studied.

2.3. XRD Analysis

X-ray powder was used to character the surface structure characterization of the prepared CNT/PANI/Ag NCS using Diano Corporation USA diffract meter with the Co-radiation ($\lambda = 0.179$ nm).

3. RESULTS AND DISCUSSION

3.1. XRD Study

Figure 1 shows the X-Ray Diffraction (XRD) patterns of the CNTs/PANI/Ag NCs prepared at different conditions. It is observed that the Ag exhibited the four main crystallographic planes. Ag (111), Ag (200), Ag (220) and Ag (311) represent the silver metal crystals with face-centered cubic symmetry, which is in good agreement with the literature (Xin and Li, 2011). The CNTs showed the XRD peaks that corresponded to the C (100) and C (102) planes of crystalline graphite-like structures (Khan *et al*., 2014). The broad peak at 2θ of 13.4° can be ascribed to the periodicity parallel and periodicity perpendicular to the PANI chains. The reduction in peak height of the CNTs planes in the CNT/PANI/Ag NCS composites prepared by decoration method (**Fig. 1b**) may be caused by the tube wall defects in the acid treatment and polymer grafting processes (Xin and Li, 2011).

The average crystallite size of the silver was calculated using the Scherrer Equation (1) (Ristic *et al*., 2002):

$$D = \frac{0.94\lambda}{\beta\cos\theta} \tag{1}$$

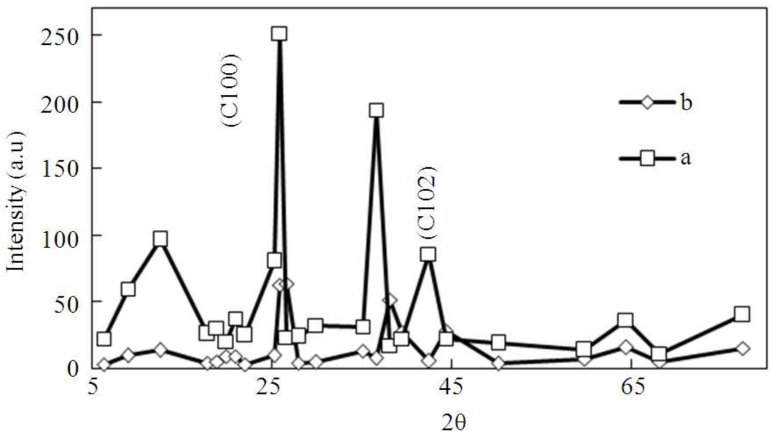


Fig. 1. XRD patterns of CNT/PANI/Ag NCS prepared by (a) mixing method and (b) decoration method

where, D is the crystal size of Ag, λ the wavelength of X-ray (0.179 nm), θ half diffraction angle of peak (in degree) and β the true half peak width. The average size of the Ag determine through the (111) plane is 38 and 81 nm for CNTs/PANI/Ag NCs prepared by decoration and hand mixing method, respectively. This means that method of preparation affect on particle size of Ag.

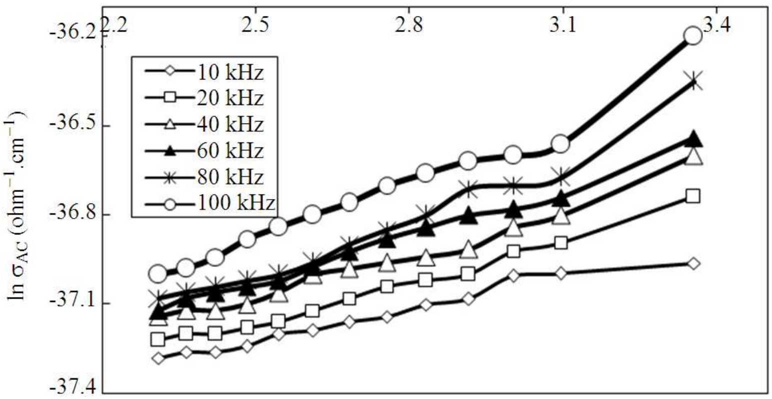
3.2. AC Electrical Conductivity of CNTs/Polymer Composites

Pure PAI is excellent conducting materials and have electrical conductivity of 10-17 ohm cm^{-1} (Xin and Li, 2011). To improve it electrical conductive, electrically conductive fillers must be added. The electrical conductivities of all the composites prepared in this work are shown in **Fig. 2** as a function of frequency and temperature. Depending on the preparation method, the values of electrical conductivity are different. In order to distinguish the effects of two different methods of preparation on electrical conductivity of CNTs/polymer composites, we divided the composites into two groups: (a) and (b), as shown in **Fig. 2a and b**, respectively. The 1st consists of CNTs/PANI/Ag composite prepared by the solution mixing method and the 2nd consists of CNT/PANI/Ag composite prepared by decoration method. The electrical conductivity of a composite can be best described by a scaling law based on the percolation theory (Xin and Li, 2011) Equation (2):

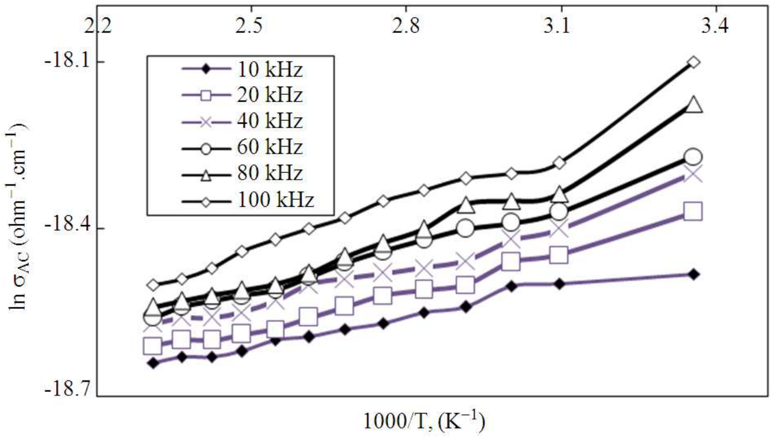
$$\sigma = \sigma_o (p - p_c)^t \quad \text{for } p > p_c \tag{2}$$

where, σ is the electrical conductivity of the composite, σ_0 is the coefficient, p is the filler's volume fraction, p_c is the percolation threshold, the exponent t is related to sample dimensionality, i.e., t = 1, 1.33, or 2.0 for one, two, or three dimensions, respectively (Xin and Li, 2011). The electrical conductivity can be significantly increased by several orders of magnitude when the percolation threshold p_c is achieved due to the formation of infinite conductive networks by filler particles. Below the percolation thresholds, the conductivity of composite increased as frequency increased. In the vicinity of the percolation threshold, we observed that electrical conductivity became independent of frequency at the lower measured frequencies. This conductivity is identified as the DC conductivity, σ_{DC}. This suggests that the ohmic element plays an important role at low frequencies. At higher frequencies, however, conductivity values experienced a power law like behavior of $\sigma(\omega) \propto \omega^s$ where s<1 (Xin and Li, 2011). The complex conductivity response of conductor-dielectric mixtures, such as CNTs/ PANI/Ag NCs, is often analyzed in terms of the Resistance-Capacitance (R-C) percolation model. In this model conducting and dielectric properties of the mixture are represented by a network of idealized resistors and capacitors (Xin and Li, 2011). It is well known that the AC conductivity is the sum of all dissipative effects including an actual ohmic conductivity caused by migrating charge carriers as well as a frequency-dependent dielectric dispersion (Xin and Li, 2011). The frequency dependence of the total AC conductivity can then be represented by the following Equation (3):

$$\sigma(\omega) = \sigma_{DC} + \sigma_{AC} = \sigma(0) + A\omega^s \tag{3}$$



(a)



(b)

Fig. 2. Effect of temperature on AC-electrical conductivity (at different frequencies) for CNTs/PANI/Ag prepared by mixing method (a) and decoration method (b)

where, ω is the angular frequency, σ_{DC} is the frequency independent conductivity or DC conductivity (at $\omega \rightarrow 0$), A is a constant dependent on temperature T and s is an exponent dependent on both the frequency and temperature with values in the range of 0-1 (Wu *et al*., 2009). **Figure 2a and b** shows that CNTs/PANI/Ag NCs, the conductivity value keeps almost unchanged at low temperatures and begins to increase as the temperature increase, which is attributed to the metallic behavior of CNTs (Wu *et al*., 2009). The rapid increase in conductivity at higher temperature should not be ascribed to pure CNT, but rather to be associated with the mobility of PANI macromolecule chains.

In the solution mixing method, the silver nanoparticles were able to contribute a lot to the electrical conductivity of CNTs/PAI composite due to the high conductivity of silver (σ_{Ag} = 6.30-105 ohm cm^{-1}). This is showing the advantage of Ag-CNTs as effective conducting filler for improvement of electrical conductivity of the polymer.

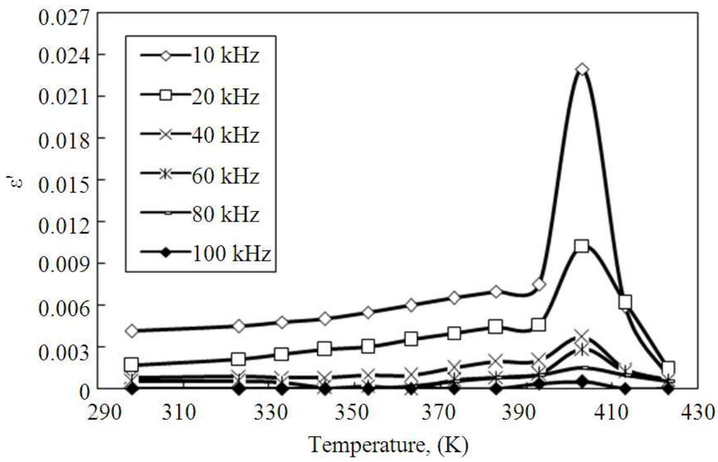
In the decoration method, as we can see from **Fig. 2b**, the conductivity in this composite is higher than composite prepared by mixing method. The reason can be considered from the differences between these two preparation methods. In the decoration method, the mixing was done using DMF, which could cause some of the silver ions nanoparticles to become silver. As silver ions are not electrically conductive, it cannot contribute to electrical conductivity of composite.

3.3. Dielectric Properties

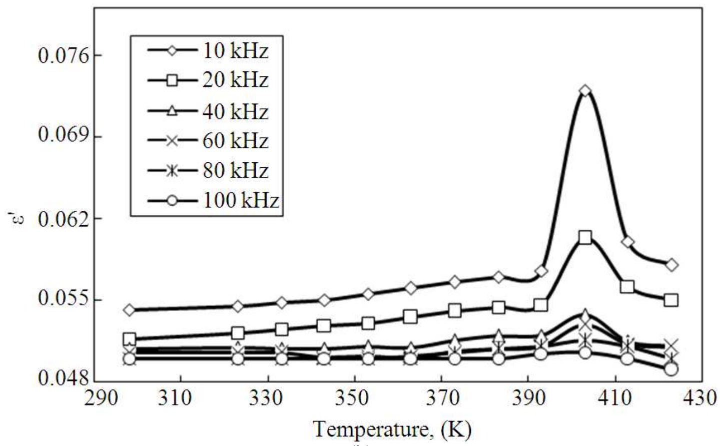
Conducting polymer composites possess a frequency (ω) dependent, complex dielectric constant (Chanmal *et al*., 2011) Equation (4):

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon'' \quad (4)$$

The real part ε' represents the relative dielectric constant and the imaginary part ε" accounts for the dielectric loss. **Figure 3 and 4** present the frequency and temperature dependence of dielectric constant and dielectric loss of CNTs /PANI/Ag prepared at different conditions. The measurement results of temperature dependence of dielectric constant and dielectric loss can be helpful to confirm the mechanism of the dielectric behavior. To investigate the dielectric behavior of the CNTs/PANI/Ag composites were calculated in the frequency range from 10 to 100 kHz. **Figure 3** shows that the ε' of the composites in the low frequency and high temperature region greatly enhances due to the Maxwell-Wagner polarization originating in the insulator-conductor interfaces or formation of large number of minicapacitors network in nanocomposites (Chanmal *et al*., 2011). In the case of MWS polarization, charges are trapped at the interface having material with different relaxation time arising due to difference in the dielectric permittivity and conductivity (Chanmal *et al*., 2011). This leads to enormous increase in the permittivity and strong dependence of dielectric permittivity in the low frequency region. At low frequency, a high value of ε' of composites was observed because at low frequencies, polarization follows the change of the electric field and dielectric loss is minimum and the contribution the dielectric constant is maximum. At high frequencies, the electric field changes too fast for the polarization effects to appear. In this case, the contribution to the ε' is minimal and there are almost no dielectric losses in the system. A high value of ε' would be beneficial in capacitor applications.



(a)



(b)

Fig. 3. Effect of temperature on dielectric constant (at different frequencies) for CNTs/PANI/Ag prepared by mixing method (a) and decoration method (b)

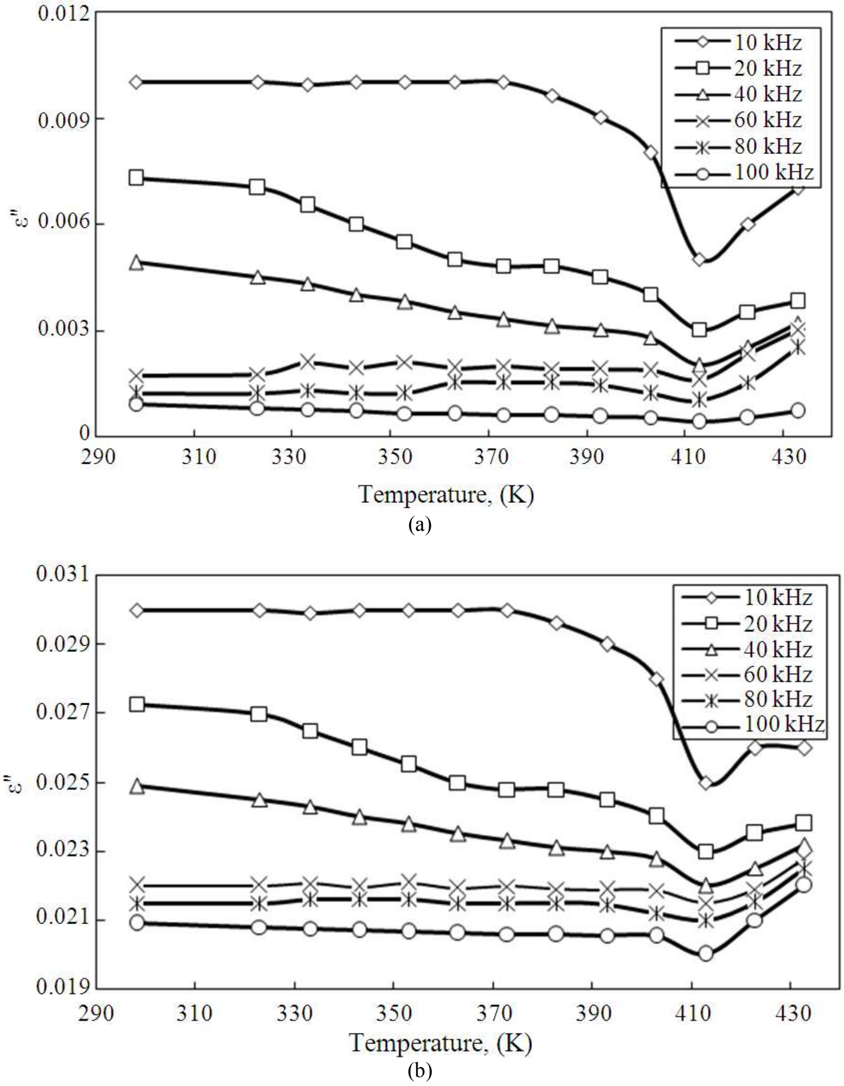


Fig. 4. Effect of temperature on dielectric loss (at different frequencies) for CNTs/PANI/Ag prepared by mixing method (b) and decoration method (a)

Figure 4 shows the dependence of dielectric loss on frequency and temperature. From which we notice that dielectric loss decrease with increasing temperature until reach 413 K then start to increase. The increase in the dielectric loss may be due to the increase in the electrical conductivity of nanocomposites which can be ascribed to the onset of percolation threshold in nanocomposites (Huang *et al*., 2009). The dielectric loss of CNTs/PANI/Ag prepared by decoration method is lower than CNTs/PANI/Ag prepared by solution mixing method. This may be due to the nature of the sample and reduction of sliver during the decoration process.

4. CONCLUSION

A novel composites consisted of MWNTs, Ag NPs and PANI were successfully synthesized using mixing and decoration methods. The XRD analyses showed that the average particle size of Ag was 38 and 81 nm for CNTs/PANI/Ag NCs prepared by decoration and hand mixing method, respectively. The conductivity of the CNTs/PANI/Ag NCs composite prepared by decoration method was much higher than that of the CNTs/PANI/Ag NCs prepared by mixing method. The dielectric properties of the CNTs/PANI/Ag NCs composites were calculated in the frequency range 10-100 kHz and temperature range 298-433 K. The difference between two methods of preparation indicated that the decoration method could give better dielectric properties because the decoration method could avoid the oxidization of silver nanoparticles.

5. ACKNOWLEDGEMENT

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