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AC electrical and dielectric properties of PVC-MWCNT nanocomposites

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Abstract

AC electrical and dielectric properties of polyvinyl chloride (PVC) with multi-walled carbon nanotube (MWCNT) nanocomposites for different concentrations (0, 0.05, 0.005, and 0.0005 wt%) and temperatures (298, 323, 343 and 353K) in the frequency range (10^3, 10^4, 10^5, 10^6 and, 10^7 Hz) were investigated. The nanocomposites of PVC with MWCNTs were prepared in THF solution, followed by film casting. Electrical conductivity measurements increase with the increase of the amount of MWCNTs. The dielectric investigations show decrease in the real and imaginary parts of the composite with increasing the MWCNTs concentration.

Keywords: Carbon nanotubes; Poly(vinyl chloride); Nanocomposites; Electrical properties

Introduction

Since the discovery by Iijim's in 1991 (Cassell *et al.,*1999) of carbon nanotubes (CNTs) in arc-discharge soot materials, nanotubes have simulated intensive studies for their high strength and adsorbents properties in many potential applications which include mechanical, electronic, catalysis, sensors (Qian *et al.,* 2002; Cline, 2004; Height *et al.,* 2004; Komarov & Mironov, 2004; Lohl *et al.,* 2007). The CNTs are found in two general morphologies, single -walled (SWCNTs) and multi- walled (MWCNTs). SWCNTs are hollow single cylinders of a graphene sheet, which are defined by their diameter and their chirality, while the MWCNTs are a group of concentric SWCNTs often capped at both ends, with diameters reaching tens of nanometers depending on the number of concentric walls (Rodney *et al.,* 2003; Massimiliano *et al.,* 2004; Micheal & Connell, 2006).

In the last decade, many researchers were interested in polymer/CNT composites and so continuous studies are needed to improve their physical properties and their applications. These studies show that the polymer/CNT composites are better than composites filled with metallic particles consisting electrical and thermal transfer mechanisms, even a small amount of CNT added to the composites will enhance these properties. The most important polymer that has CNT nanocomposites is polyvinyl chloride (PVC). PVC is one of the most important thermoplastic polymers with a lot of applications due to its considerable environmental and chemical resistance, as well as its very excellent mechanical properties, it widely used as a material in the building and construction industry, for window profiles, floor coverings, wall papers, or pipes (Elliott ,1987). Broaza *et al.* (2007) found that the electrical conductivity of PVC / MWCNT nanocomposite would increase if MWCNT homogenously distributed in the PVC matrix. Mamunya *et al.* (2008) studied the electrical and thermophysical behaviour of PVC/MWCNT nanocomposites by percolation theory, they found that electrical conductivity of the PVC/CNT composites depends on the content of CNTs enabling to reveal the ultra-low value of the percolation threshold which is 0.00047 while for thermal conductivity the content of CNT does not reveal any percolation behaviour in the vicinity of electrical percolation concentration but exhibit minimum in the region of low content of CNTs. Li *et al.* (2009) studied the positive and negative temperature coefficients effects on some electrical properties for pristine and oxidized MWCNT/PVDF composites, they found that the composites conductivity increases slowly with increasing MWCNT volume fraction while the dielectric constant increases with MWCNT volume fraction. Shi *et al.* (2009) studied the electrical and dielectric properties of MWCNT/PANI composite, they showed that in dc conductivity the typical percolation acts with low percolation threshold of 5,85wt% MWCNT content. While the dielectric constant for the nanocomposite increase as MWCNT increase.

The present work is focused on the study of the electrical conductivity and dielectric properties for PVC/MWCNT nanocomposites, to show the effects of MWCNTs concentrations and temperature of these nanocomposites.

Material preparation

MWCNTs were synthesized by the chemical vapor deposition (CVD) method. N-type silicon (111) substrate was thermally oxidized; thick Fe film was thermally deposited on SiO_2/Si substrate. Argon and acetylene were used as reactor gases within the temperature range (750-850 ^{0}C).The CNTs grown on catalyst particles were examined by transmission electron microscope (TEM) to study the characteristics of CNTs.

The PVC (BDH chemical, England) in powdered form with density 1.390 kg/m^3, was used as a polymeric matrix for preparation of the composite. MWCNTs was dissolved in 25ml of tetrahydrofuran (THF) and sonicated for 2h to disperse the individual nanotubes. One gram of PVC was dispersed in (25ml) THF, and the solution was slowly mixed at room temperature. The composite of the PVC with MWCNT, (0.05, 0.005 and 0.0005 wt %) were prepared in the form of thin films cast from PVC solution in THF.

AC electrical measurements

Samples used for electrical measurements were shaped as discs of different thicknesses. The electric properties (Ac dielectric and Ac conductivity) of PVC+CNTs in the frequency range (10^3 -10^7) Hz were investigated using PM 6308 (Philips) automatic RCL meter. The samples of PVC/CNTs nanocomposites were placed in the holder. All experiments were carried out with different temperatures (298, 323, 343, and 353K). AC dielectric and Ac conductivity were calculated and plotted as a function of frequency.

Fig.1. TEM image of CNTs with diameter (30-40nm).

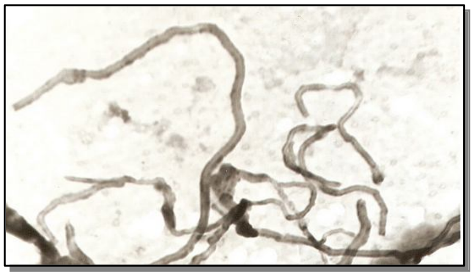


Fig.2. TEM image of CNTs with diameter (35nm).

Capacitance C, dielectric loss (ε″) and tangent (tanδ) of the investigated samples were measured directly using the automatic RCL meter. The AC conductivity $\sigma_{AC.}$, dielectric constant(ε′), and dielectric loss (ε″) of the prepared PVC/MWCNT composites were calculated from the following relations (Elliott ,1987):

$$\sigma = \frac{t}{RA},$$

$$\varepsilon' = \frac{Ct}{\varepsilon_o A},$$

$$\varepsilon'' = \tan(\delta)\varepsilon' \qquad \text{………(1)}$$

Where ε_o is the permittivity of free space = 8.85×10^{-12} F/m, t and A thickness and surface area of the sample respectively. R : resistance of the composite, ε′: dielectric constant.

AC electrical conductivity $\sigma_{AC}(\omega)$ is measured by the following equation Elliott, (1987):

$$\sigma_{AC}(\omega)=\sigma_{total}(\omega)-\sigma_{DC}(\omega) \qquad \text{…… (2)}$$

Where ω is the angular frequency (=2πf), $\sigma_{total}(\omega)$ is the measured total electrical conductivity, $\sigma_{DC}(\omega)$ is the DC conductivity which depends strongly on temperature, it dominates at low frequencies and high temperatures, Whereas the σ_{AC}, which has a weaker temperature dependence than σ_{DC}, and dominates at high frequency and low temperature. The relation for the frequency dependence AC conductivity is given by:

$$\sigma_{AC}(\omega)=A_1\omega^s \qquad \text{………(3)}$$

A_1 is a constant, and (S) is a function of temperature which is determined from the slope of a plot ln $\sigma_{AC}(\omega)$ versus ln(ω) (Elliott, 1987), then the value of S can be calculated from ;

$$S=\frac{d[\ln \sigma_{ac}(\omega)]}{d[\ln(\omega)]} \qquad \text{………(4)}$$

Fig.3. Variation of σ_{AC} of PVC/MWCNT with Frequency for different concentration at: a-298K, b-323K, c-343K, d-353K

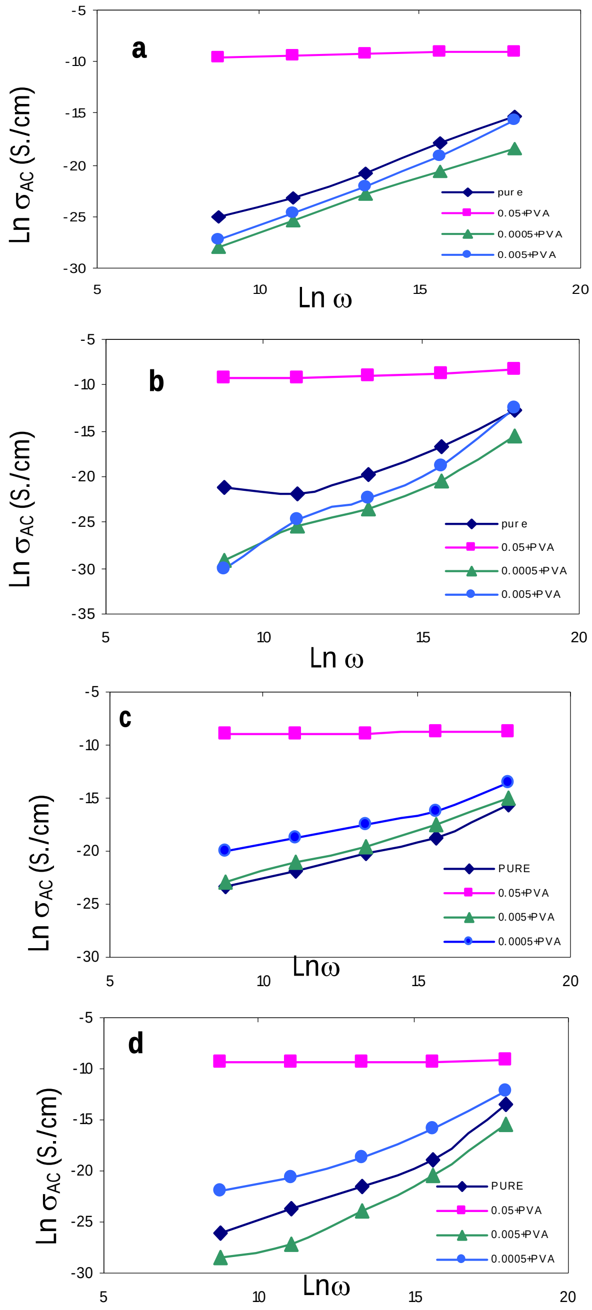


Fig.4. Variation of σ_{AC} of PVC/MWCNT with frequency for different concentration at: a-298K, b-323K, c-343K, d-353K.

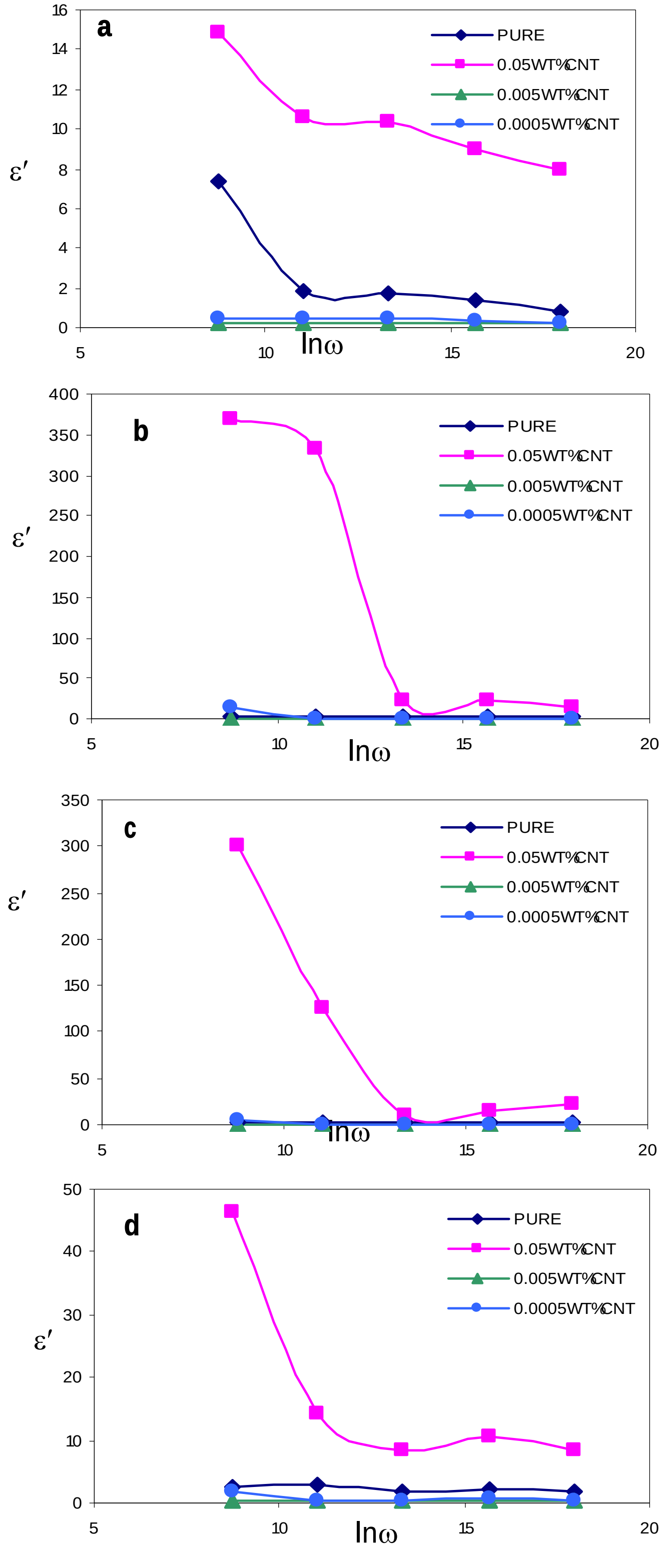
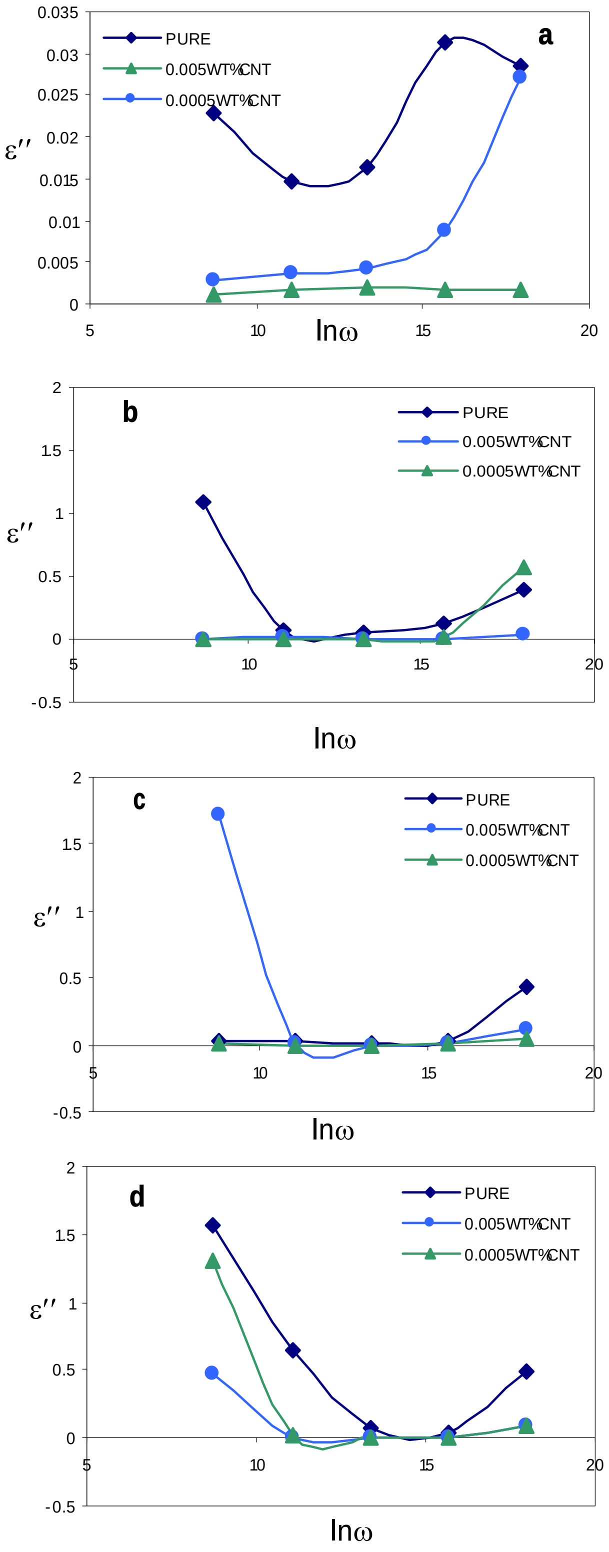


Fig.5. Variation of dielectric loss of PVC/MWCNT with frequency for different concentration at: a-298K, b-323K, c-343K, d-353K



Results and discussions

The Morphology and characterization of CNTs, which were grown on iron catalyst particles of 30nm diameter, formed on SiO_2/Si substrates using thermal CVD of acetylene for 10 min at temperature range (750-850 C^o), was studied by using Transmission Electron Microscope (TSM) as shown in Fig.1,2.

AC electrical conductivity

AC electrical conductivity of pure PVC and PVC/ MWCNT nanocomposites samples were studied as a function of frequency, concentration and temperature as shown in Fig.3. The increase of $_{AC}$ with frequency as seen in this figure is in agreement with eq. (2).

The 0.005 and 0.0005wt% MWCNT nanocomposites show a slight increase in the conductivity compared to that of the pure sample, but still the samples at this wt% remains an insulator. While at 0.05% MWCNT nanocomposites show a clear enhancement in conductivity reaching 10^{-2} $S.cm^{-1}$ which indicates the sample to be a semiconductor (Mamunya *et al.,* 2008). The reason of such behavior can be attributed to the tunneling conduction mechanisms (TCM). This behavior may be explained as: at the surface of MWCNTs the carboxylic groups decrease the tunneling current making the tunneling difficult to occurs leading to a slightly increasing of the conductivity. This process will be enhanced as CNT concentration increases (Li *et al.,* 2009). Also it can be noticed that at high content of MWCNT the nanocomposites become independent of frequency which indicates the electron type of the charge transport.

So it can be seen that the change in the electrical conductivity depends on the amount of MWCNT in the nanocomposites. At small amount, the conductivity of the nanocomposites increases with increasing frequency while at higher amount the conductivity shows a direct current and a non-dielectric behavior. This agrees with the result mentioned by other workers (Broaza *et al.,* 2007; Li *et al.,* 2008).

The temperature effect of pure and low MWCNT concentrations shows an increase in conductivity with increasing temperature which can be attributed to the movement of ions as well as to the electronic type of conductivity. At higher concentrations a different behavior is noticed where the conductivity is independent of temperature. It indicates a change of the conductivity through matrix into conductivity through filler phase (Mamunya *et al.,* 2010).

Dielectric Constant and Dielectric Loss

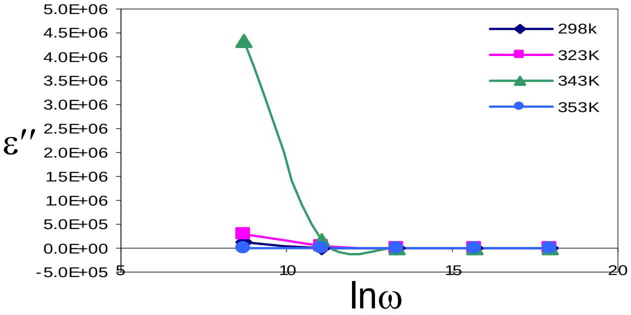
The frequency dependence of the dielectric constant (ε') and dielectric losses (ε'') of the PVC/ MWCNT nanocomposites are shown in Fig.4, 5. For pure PVC the dielectric constant decreases with increasing the frequency. The same behavior was noticed for the higher concentration of MWCNT (0.05wt%). This is because the MWCNT form large clusters. The other two concentrations (0.005 and 0.0005wt %) seem to be frequency independent. This may be attributed to that the MWCNT follows the insulating PVC matrix. This is in agreement with previous works (Li *et al.,* 2009; Shi *et al.,* 2009). Such behavior of the dielectric constant can be understood by the interfacial polarization effect (Li *et al.,* 2009). When the MWCNT distributed in the polymer matrix to form nanocomposites, it creates a lot of interfaces a large dominate of nomadic electron could provide with large π-orbital of the MWCNT. The interface polarization can take place when electrons oriented under electric field (Dang *et al.,* 2007). Further increase of CNT concentration will increase the number of interfaces but increase above a certain value will lead to the contact between the MWCNT leading to the decrease of interfaces (percolation threshold), which will resulting in the decrease of the dielectric constant.

From Fig.4 , 5 and 6, the most noticeable behavior is the increase for (ε') first followed by the decrease of (ε') with further increase of temperature. For the dielectric loss (ε'') decreasing first then increasing with temperature. The effect of temperature on the dielectric properties can be explained according to transition temperature T_t (Yu *et al.,* 2000; Bobnar *et al.,* 2007). For temperatures below T_t the filler that are connect with each other will be dispersed or separated in the polymer matrix so the interface between MWCNT and PVC increases leading to increase in (ε'), but for temperatures higher than T_t the polymer begins to melt, changing a phase of a semi-crystalline to a rubbery flow region. This leads to a decrease of the interface s between MWCNT and PVC which causes a reduction of (ε') . In such case the nomadic electrons will have high energy and even agglomerated on the interfaces at higher temperature (Li *et al.,* 2008).

Conclusion

PVC/MWCNT was prepared by the casting solution method. Electrical conductivity and dielectric properties of these nanocomposites are studied. It showed that adding MWCNT, even a small amount, will enhance the electrical conductivity while further increase will change the behavior of the composites from an insulator to a semiconductor which can be understood by TCM. The effect of temperature on electrical conductivity showed improved results especially at 353K. The dielectric

Fig.6. variation of dielectric loss of PVC/MWCNT with frequency at 0.05wt%CNT for different temperatures



constant of the nanocomposite was controlled by the amount of CNT. Where for low concentrations it showed to be frequency independent while it shows a decrease behavior for the high concentration. The effect of temperature showed an increasing of ε' with increasing temperature further increasing reducing the ε', such behavior can be attributed to interfacial polarization.

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