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Dielectric, electrical and microstructural properties of unfilled and MWCNTs filled polystyrene nanocomposite prepared by *in-situ* polymerization technique using ultrasonic irradiation

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The unfilled and multi-walled carbon nanotubes (MWCNTs) filled polystyrene (PS) nanocomposites are prepared by *in-situ* polymerization technique using ultrasonic irradiation. The effect of different volume fraction (ϕ) of MWCNTs in PS has been studied with respect to their dielectric and electrical characterizations as a function of frequency and temperature. The dielectric constant of different volume fraction (ϕ) of MWCNTs shows higher value at low frequency region and it shows frequency independent behaviour at higher frequency. The *dc* conductivity is found to increase with increasing volume fraction (ϕ) of MWCNTs whereas *ac* conductivity increases with increasing frequency. The SEM image reveals uniform dispersion of MWCNTs in polymer matrix.

Keywords: Polymer nanocomposite, *In-situ* polymerization, Multi-walled carbon nanotubes, Dielectric properties, Electrical properties

1 Introduction

Researchers across the globe attracted their attention towards filler reinforced polymer composite owing to its mechanical, thermal, electrical and optical properties[1-6]. Now-a-days multi-walled carbon nanotubes (MWCNTs) have become an attractive choice as filler in polymer because of its wide ranging advantages like high electrical conductivity, chemical stability, mechanical strength and its high aspect ratio[7-13]. A variety of materials like epoxy, polymer[14-21] have been used for the filling purpose of carbon nanotubes (CNTs). Amongst these, polystyrene has become an obvious choice because of easy accessibility and fast crystallization rate. Theoretical and experimental results showed substantial interaction[22,23] between polystyrene (PS) and MWCNTs. The PS/CNT composite has wide ranging applications such as EMI Shielding materials[24-28], transparent conducting films[29,30] and sensors[31-33] etc. The miscibility of CNT in PS is quite good[34].

A variety of techniques like solution mixing/ casting[35,36], melt mixing[37,38], *in-situ* polymerization[39-41], latex technology[42], ultrasonic dispersion in solution[43,44] etc. have been utilized for the preparation of polymer nanocomposite. Out of these techniques, in the present investigation, *in-situ* polymerization technique using solution form of monomer has been used and the mixing and polymerization have been done by using ultrasonic irradiation. Also emphasis has been given to study the incorporation of different volume fraction (ϕ) of non-functionalized MWCNTs as filler in polystyrene. The dielectric behaviour, *ac* as well as *dc* conductivity, loss tangent for different volume fraction (ϕ) of filler as a function of frequency have been carried out at predetermined temperature of 25°, 50° and 75°C, respectively. The hardness of the polymer nanocomposite for different volume fraction of MWCNTs has also been carried out.

2 Experimental Details

In the present investigation, PS (99%) was purchased from Alfa Aesar having density 0.906 g/ml, MWCNTs (Premium grade) was purchased from Reinste Nano Venture Pvt. Ltd, India with purity >95%. The benzoyl peroxide (BPO) (polymerization initiator) was supplied from HPCL, Mumbai (India).

The nanocomposite was made by *in-situ* polymerization using ultrasonication technique (Transonic Ultrasonicator, power-250 Watt, frequency 25-28 kHz). Different volume fraction (ϕ) of MWCNTs was mixed with the monomer (Styrene) in a sealed test tube. The test tube was sonicated at room temperature for 50 min for proper mixing of MWCNTs in monomer. Polymerization initiator BPO (0.5 wt% of monomer) was then added in the test tube and the bath temperature was increased in a controlled manner up to the optimized temperature of 72°C for the polymerization to start. Sonication was continued at the same temperature for about two hours till the MWCNTs containing monomer becomes heavily viscous in nature. Thereafter, the test tube containing viscous composite was left for cooling to room temperature. The resultant unfilled as well as MWCNTs filled polymer composite was cut into pellets for characterization purpose.

SEM images were recorded using Scanning Electron Microscope (Model-SS100 Pemptron, Korea) in order to study the microstructural details. For dielectric measurement of virgin PS and MWCNTs-PS nanocomposite samples, both the surface of the pellets were made conducting by applying colloidal silver paste (TED PELLA, INC.) and cured at room temperature. Capacitance (*C*) and conductance (*G*) measurements were performed in two probe sample holder using high frequency LCR meter (Wayne Kerr 6500 P, frequency range: 20 Hz-5 MHz). Measurement operational controls and data recording were done through the computer at different temperatures (25°, 50° and 75°C) as well as at different frequencies. Dielectric constant ε' was calculated from the measured *C* using the following equation:

$$\varepsilon' = \frac{C \times d}{\varepsilon_0 A} \qquad \ldots(1)$$

where *C* is the capacitance in farad, ε_0 is the permittivity of free space (8.85×10^{-12} F/m), *d* is the thickness of the samples (in meter), *A* is area of the surface (in meter^2) and tanδ was calculated using the following relation:

$$\tan\delta = \frac{G}{\omega C} \qquad \ldots(2)$$

where $\omega=2\pi f$, *f* is the frequency, in Hz and G is the conductance, in sm.

The *dc* conductivity is calculated by the following equation:

$$\sigma_{dc} = \frac{d}{RA} \qquad \ldots(3)$$

where *d* is thickness and *R* is the resistance.

The *ac* conductivity is also, calculated by the following equation:

$$\sigma_{ac} = G\frac{d}{A} \qquad \ldots(4)$$

where symbols have usual meanings.

3 Results and Discussion

Figure 1 shows the D-shore hardness of virgin PS and MWCNTs filled PS as a function of volume fraction (ϕ) of MWCNTs. A sharp decrease in hardness is clearly noticeable in the range 0.01-0.02 volume fraction (ϕ) range and thereafter, moderate decrease up to 0.05 volume fraction (ϕ) is observed. The decrease in the hardness with increase in volume fraction of MWCNTs may be attributed to the decreased particle to particle interaction among styrene particle and MWCNTs because of blending of styrene particles by MWCNTs within the composite which prevent the strong bonding among these particles.

Figure 2(a, b and c) show the variation of the dielectric constant as a function of alternating frequency at room temperature 25°, 50° and 75°C, respectively. It is evident from the graphs that the value of dielectric constant is high at low frequency and decreases sharply up to 1kHz then remains

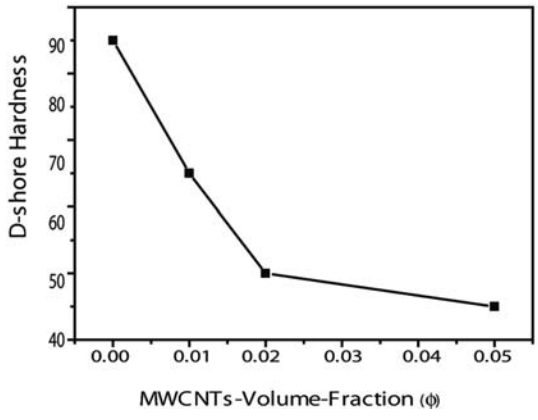

Fig. 1 — D-shore hardness as a function of MWCNTs volume fraction(ϕ) for PS-MWCNTs composites

constant almost up to 5 MHz.The value of έ at room temperature is higher for 0.05 ϕ but for 50°C and 75°C this value is higher for 0.01 ϕ. The increase in the value of έ at lower frequency could be attributed to Maxwell-Wagner's interfacial polarization in heterogeneous composite system. The higher value of έ at low frequency could also be accounted for the tendency of induced dipoles in polymer matrix to orient themselves in the direction of applied field[45]. The value of έ is found to be the higher at lower frequency region, which makes the nanocomposites suitable for utilization as a charge storing device at lower frequency region. The dielectric constant is found to be low frequency dependent while invariable towards high frequency. This could be attributed to the orientation of the dipole and conduction of the charge carriers at higher frequency[46].

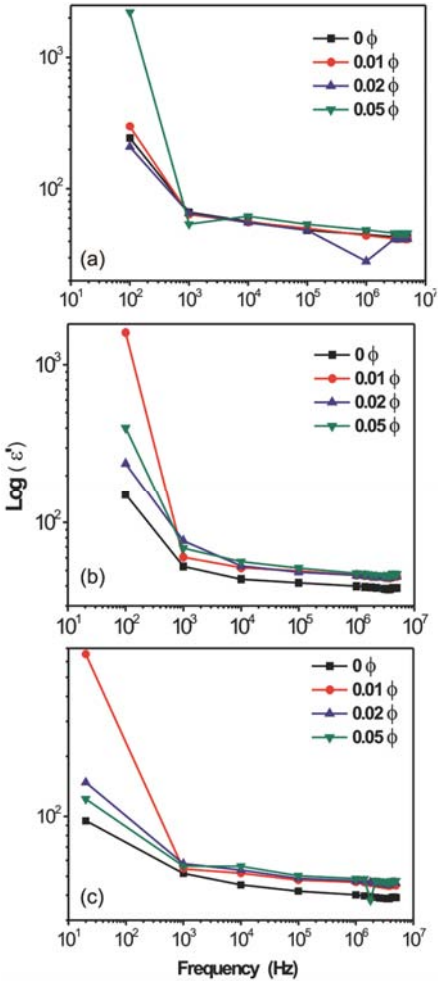

Fig. 2 — Variation of dielectric constant with frequencyfor PS with different MWCNTs volume fraction (ϕ) composites at (a) 25°C, (b) at 50°C and (c) at 75°C temperature

From Figs 2(a, b and c), it is observed that the magnitude of increase in έ at lower frequency region decreases at higher temperature of measurement. While at higher frequencies, the value of έ is almost invariant of temperature. The increase in temperature softens the structure of the polymer which causes the possibility of connecting-sites of conducting MWCNTs within the polymer matrix which is responsible for invariant nature of έ at higher temperature. The increase in έ at 75°C at lower frequencies is not as sharp as in case of room temperature variation of έ.

Figure 3(a, b and c) shows the frequency dependence of dielectric loss, tanδ at 25°, 50° and 75°C. The variation of dielectric loss is found to be frequency dependent. At lower frequency, the value of tanδ is low (in the range of 10^{-6} to 1) which increases and becomes constant within the frequency

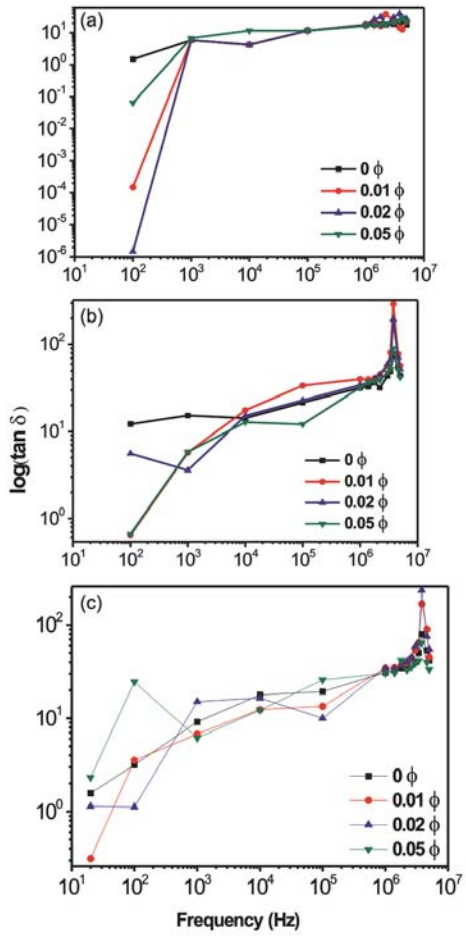

Fig. 3 — Variation of dielectric loss with frequency for PS with different MWCNTs volume fraction (ϕ) composites at room temperature (a) 25°C, (b) 50°C and (c) 75°C

range 10^3-10^6 Hz. At high frequency, a large peak in tanδ is observed for all compositions in the range 10^6-10^7 Hz but is more pronounced for 50°C and 75°C. However, the peak for tanδ is the largest for higher filler loading (0.02 ϕ) at 75°C whereas at 50°C it is the largest for 0.01 ϕ. The high dielectric loss at 3.8×10^6 Hz for 75°C could be the evidence of large leakage current in the nanocomposites. An increase in the value of tanδ is observed with temperature due to large leakage current because of the possibility of more connecting-sites of MWCNTs particles within the polymer matrix. The increase in tanδ in the range 10^6-10^7 Hz may be attributed to an increase in *ac* conductivity and shown in Fig. 4. It has also been observed that *ac* conductivity increases with filler volume fraction (ϕ) and it is the highest for 0.02 ϕ as compared to the virgin PS, which is also in conformity with tanδ plot (Fig. 4). The *ac* conductivity is observed to be frequency variant in all the cases of temperature variation i.e. at 50°C and 75°C. The *ac* conductivity is found to increase with frequency up to ~10^7 Hz then at higher frequency, it shows decreasing trend.

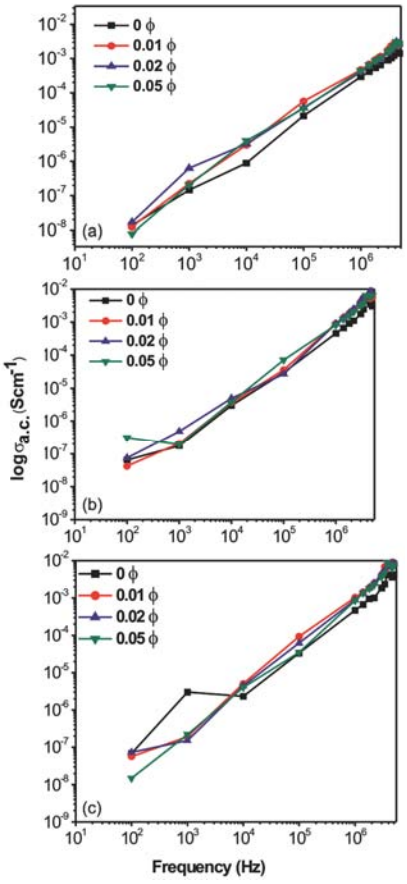

Fig. 4 — Variation of *ac* conductivity with frequency for PS with different MWCNTs volume fraction (ϕ) composites at (a) 25°C, (b) 50°C and (c) 75°C

Figure 5 shows the *dc* conductivity plot as a volume fraction of MWCNTs, it has been found that *dc* conductivity increases with increasing volume fraction (ϕ) of MWCNTs, which confirms the well dispersed MWCNTs in the polymer matrix and the increase in the electrical conductivity of the nanocomposite could also be attributed to the decrease in the average distance between the MWCNTs which allows electrons to tunnel through the polymer particles or through the direct contact[36,47,48] between MWCNTs.

Figure 6(a, b, c and d) shows the scanning electron micrograph of unfilled PS, 0.01ϕ, 0.03ϕ and 0.05ϕ

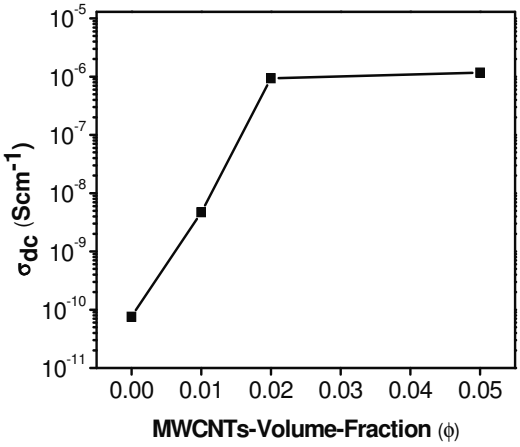

Fig. 5 — Variation of *dc* conductivity with different MWCNTs volume fraction (ϕ)for PS composite

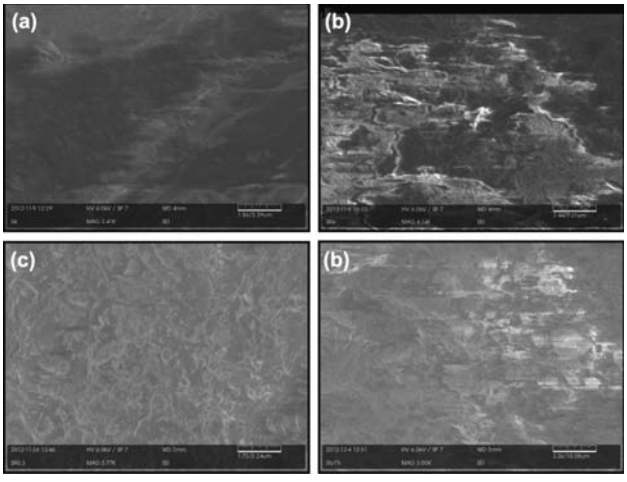

Fig. 6 — SEM micrograph of the surfaces of unfilled PS, 0.01 ϕ, 0.03 ϕ and 0.05ϕ MWCNTs filled PS (a, b, c and d)

MWCNTs filled PS, respectively. Figure 6(b, c and d) show distribution of MWCNTs the PS matrix. The microstructre of the composites shows a good wetting between MWCNTs and PS matrix. This may be attributed to the penetration of styrene into the MWCNTs during the ultrasonication process

4 Conclusions

The unfilled and MWCNTs filled PS has been synthesized by *in-situ* polymerization technique using ultrasonication irradiation. We have systematically studied incorporation of different volume fraction of MWCNTs on the dielectric behaviour, hardness, *ac* and *dc* conductivity and SEM. It has been observed that the hardness is found to decrease with increase in volume fraction of MWCNTs. It has also been observed that the *dc* as well as *ac* conductivity increases with increase in volume fraction of MWCNTs. It was observed that the *ac* conductivity increases with frequency whereas tanδ increases with frequency up to 10^7 Hz then decreased. It was also observed that the dielectric constant is high at low frequency and it is almost constant at higher frequency and also its value is found to depend on the MWCNTs volume fraction. SEM shows the homogeneous distribution of MWCNTs in the PS polymer matrix.

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