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Activation Behaviour and Dielectric Relaxation in Polyvinyl Alcohol and Multiwall Carbon Nanotube Composite Films

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Abstract

The dc and ac electrical transport property of Polyvinyl Alcohol-Multiwall Carbon Nanotubes (PVA-MWNT) composites has been investigated within a temperature range $77 \leq T \leq 300\text{K}$ and in the frequency range 20Hz to 1MHz. The temperature variation of dc conductivity gives the presence of two different activation energies. The dielectric properties of the samples have been explained in terms of electric modulus vector. The dielectric relaxation has been explained in terms of interfacial polarization occurring in between the insulating PVA matrix and MWNT conductive filler. The variation of the relaxation time with temperature also indicates the presence of two different activation energies.

Keywords: A. Polyvinyl Alcohol; A. Multi walled Carbon nanotubes; B. Chemical synthesis; D. Electric modulus; D. Interfacial Polarization

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1. Introduction

During the last two decades, Carbon Nanotube (CNT) has become a prominent conductive filler with potential applications in the field of emitters, nanoelectric devices, probe tips for scanning probe microscopes and Nanotube based composites[1-2]. The ability of good electrical conducting property and enhanced mechanical properties of CNTs has made them popular among the scientists. On the other hand, polymers like polyvinyl alcohol (PVA), polyurea urethane, methyl cellulose, polymethyl methacrylate (PMMA) are regarded as the polymeric materials with low electrical properties but significant mechanical properties. These types of materials are used as a matrix where the conductive fillers are introduced to enhance the electrical properties. Introduction of CNTs in the matrix of such materials not only improves the mechanical properties, but also a large enhancement in electrical properties is noticed [3-6]. In this work, Poly (vinyl alcohol) (PVA) is used as a matrix material for its high solubility in water and alcohol. So the PVA/CNT composites can be fabricated very easily through water, alcohol and surfactant medium [7-11]. In the recent past, an extensive investigation has been made to explore the properties of PVA/CNT composites [12-20] describing the synthesis and characterization of the PVA/CNT composites and to find their mechanical properties. Only a few works give the information regarding the electrical and dielectric properties of PVA/CNT composites. Zhang et al [21] describes the electrical and dielectric properties of PVA/MWNT composites above room temperature. But a systematic study of electric and dielectric properties of PVA/MWNT composites below room temperature is still unavailable.

This work deals with the synthesis and electrical transport properties of polyvinyl alcohol and Multiwall Carbon Nanotube composites below room temperature. An extensive dielectric relaxation study has been made to investigate the dc conductivity and dielectric properties of the PVA-MWNT composites in the temperature range 77-300K and in the frequency range 20Hz -1MHz.

2. Sample Preparation and Experimental Techniques

Polyvinyl alcohol (PVA), Cetyltrimethylammonium bromide (CTAB), Multiwall Carbon nanotubes (MWNT: Nanocyl 3100), ethanol are used as received from the market. Double distilled water is used for the experiment.

In situ chemical oxidative polymerization technique has been adopted to synthesize the composites of PVA and MWNT. 1, 3, 5, 7 and 10% (by weight) MWNT are dispersed in 120 mg of cationic surfactant CTAB and 1(M) HCl solution with help of a sonicator to obtain a well dispersed solution. The prepared solutions are then cooled down to 1-5°C in ice chamber prior to use. Different PVA solutions are prepared by a mixture of ethanol and water with 99, 97, 95, 93 and 90% (by weight) of PVA. The mixture is heated with continuous magnetic stirring at 80°C till a clear transparent solution is obtained. This solution is then cooled to room temperature by stirring. 50 ml 99 % PVA solution is mixed with 50 ml 1 % MWNT solution under continuous magnetic stirring in an ice chamber. After 24 hours, the homogeneous mixture is taken in a petridish in an oven at 40°C. A black film is obtained which is washed several times with water and ethanol to remove the residual solvent, unreacted parts and so on. Finally it is dried at 40°C in an oven. Sample containing 1 wt% MWNT is marked as PM1. Similarly samples having 3%, 5%, 7% and 10% mwnt content are considered as PM3, PM5, PM7 and PM10 respectively.

Morphology of the sample is taken by a Field Emission Scanning Electron Microscope (FESEM) of the model Carl Zeiss Supra 40 vp. The temperature dependent dc conductivity measurements have been done on the composite samples in the temperature ranging from 77K to 300K. The electrical conductivity of the samples was measured by a standard four probe method after good contact was ensured with highly conducting graphite adhesive (Electrodag 5513, Acheson, Williston, VT) and fine copper wires as the connecting wires. The dc conductivity was measured with an 8^{1/2} – digit Agilent 3458A multimeter. The temperature dependence of the conductivity was studied with a liquid nitrogen cryostat. For the control and measurement of the temperature, an ITC 502S Oxford temperature controller was used. To measure the dc response, films of size 1 cm x 1cm of the samples was taken.

To measure the dielectric response of the investigated samples, 1 cm x 1cm size of the samples was taken and graphite adhesive were coated on both side of the samples with attaching Copper leads. The samples were kept inside the cryostat for the change in temperature which varies from 77K to 300K. An Agilent 4384A LCR meter was used to find the capacitance and dissipation factor as a function of frequency in the range of 20 Hz to 1MHz

3. Results and Discussions

Fig.1 shows the FESEM micrograph of PVA-MWNT samples (PM1 and PM3). It is observed from PM1 that the sample has rod like morphology. As observed from the image, the diameter of the rod is 60-80 nm and length os of 1-2 μm . Diameter of the PVA-MWNT composite has been increased than pure MWNT [22] and it may be due to uniform distribution of polymer on the surface of pure MWNT i.e. the MWNTs are coated by polyvinyl alcohol.

The dc conductivity with different content of MWNT in PVA matrix has been measured in the temperature range $77 \leq T \leq 300\text{K}$. The room temperature (300K) conductivity increases from 7.82×10^{-7} to $2.60 \times 10^{-5} \Omega^{-1}\text{m}^{-1}$ with increasing MWNT content 1 to 10% by weight. The composites with lower MWNT have very few conductive networks [21]. However, as the content of MWNT in PVA matrix increases, formation of more and more conductive networks increase the conductivity of the composites in a sharp manner. The variation of dc conductivity with temperature for all the samples is shown in Fig.2. All the samples show semiconducting behavior as the dc resistivity of the samples decreases with increasing temperature. The resistivity of the samples also decreases with increasing MWNT content. A graph of $\ln[\rho_{\text{dc}}(T)]$ versus $1000/T$ in Fig.2 indicates the presence of two different slopes. This existence of two different slopes can be explained by the study of activation behavior of the PVA-MWNT composites. The activation energy of all the investigated samples has been calculated by the Arrhenius equation

$$\rho(T) = \rho_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (1)$$

where ρ_0 is the conductivity at infinite temperature, E_a is the activation energy, and k_B is the Boltzmann constant. E_a can be calculated from the slopes of the straight line plot of $\ln[\rho(T)]$ with $1/T$. The values of activation energy of all the samples vary from 3 to 18.5 meV in the temperature range $77 \leq T \leq 150\text{K}$ and 74 to 91 meV in the temperature range $150 \leq T \leq 300\text{K}$. It is also observed that in both the temperature range the activation energy increases with the increase of MWNT content. This is due to interaction of MWNT having large activation energy with the insulating PVA matrix. On the other hand the activation energy of

the composite at lower temperature is smaller than that of higher temperature. From this anomalous behavior, one may expect the presence of more than one conduction mechanism. In such system, the nanotubes are separated by a thin layer of insulating polymers, which acts as a potential barrier to internanotube hopping. At lower temperature, interaction between polymer and MWNT is not prominent i.e. barrier height is large so the conduction process is dominated through the MWNT only. However, with increasing temperature the barrier height between the nanotubes may decrease and due to which, the thermal fluctuation induced tunneling [23, 24] among the nanotubes may play an additional role of the conduction process. Thus it may be concluded that, at higher temperature, the conduction along MWNT and between MWNTs through polymer take place. As a result, a deviation from the linear behavior of $\ln\rho(T)$ v.s. $1/T$ plot has been observed at low temperature and resulting two activation behavior in the composites.

The capacitance (C) and the dissipation factor (D) of all the investigated samples have been measured with increasing frequency (f) from 20 Hz to 1MHz. The real and imaginary components of the dielectric permittivity have been calculated by the following relations

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \quad (2)$$

$$\varepsilon'' = \varepsilon' D \quad (3)$$

where ε' , ε'' and ε_0 are the real, imaginary and free space permittivity respectively, A is the area of the electrodes and d is the thickness of the investigated samples. Fig.3 shows the variation of ε' with f for different samples at room temperature. In all the cases, a strong frequency dispersion of permittivity is observed in the low frequency region followed by a nearly frequency independent behavior above 10^4 Hz. The decrease of ε' with increase in frequency may be attributed to the electrical relaxation process. It is seen that with addition of MWNT, the value of ε' increases in the lower frequency and nearly same in the higher frequency region. Within a disordered material, the hopping of the charge carriers to a new site can be successful only if it is followed by the polarization cloud around the charge carriers [25]. An electric relaxation time τ is required for the mutual movement of the charge and the associated polarization cloud. The relaxation time can be obtained from the peaks of the ε'' -f plot [26]. Fig.4 shows that the value of ε'' decreases with increasing f for different

samples. The magnitude of ε'' may be regarded as the contribution of three distinct effects, DC conductance, interfacial polarization and the usual dipole orientation or Debye loss [27]. It appears that ε'' increases with decrease in frequency revealing that there exhibits the interfacial polarization in the composite. On the other hand, no peaks would not be observed in ε'' -f plots in the measured frequency region. In general, the conduction due to the conductive part of the disordered systems masks the interfacial polarization [21, 26]. In such cases, the dielectric properties of the samples can be described by the complex electric modulus formalism [28]. Electric modulus (M) can be defined as

$$M^* = \frac{1}{\varepsilon^*} = M' + iM'' = \frac{1}{\varepsilon' - i\varepsilon''} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \quad (4)$$

Variation of M'' with frequency at room temperature (T=300K) for all the samples have been shown in Fig.5. A loss peak is found in all the curves which may be due to the interfacial polarization at a particular frequency range for each bulk composite. At a certain temperature, the intrinsic immobilized free charge can move freely under the influence of applied field. The free charge is blocked at the insulating matrix and conductive filler and as a result, the dielectric difference between them produces interfacial polarization. With increasing MWNT content, the relaxation peaks shifts towards the higher frequency side. As a result of the increase of MWNT content, more and more free charges may accumulate on the interface resulting in a decrease of relaxation time and thus, the relaxation process shifts towards the higher frequencies [21].

The frequency dependence of imaginary part of the electric modulus (M'') of the sample PM10 at different yet constant temperature is shown in Fig.6. The relaxation peaks shifts towards the higher frequency side with increasing temperature. The motion of the polymer chains increase due to increase in temperature and accumulation of the free charges occurs at the interface within the sample. Also there is an increase of the charge carrier mobility. As a result, the relaxation time decreases and there is a shift of the loss peak towards the higher frequency side with increase in temperature.

The spectra for $M''(f)$ at a fixed temperature T = 300K for different composite samples have been scaled in Fig.7. In the scaling process $M''(f)$ are scaled by M''_{\max} , while the frequency axis is scaled by the relaxation frequency f_{\max} . It is noted that the spectra for different compositions do not merge on a single master curve, which implies that the

conductivity relaxation depends on the MWNT content in composite. The normalized plots of M''/M''_{\max} with $\ln(f/f_{\max})$ at different temperatures for a representative PM10 composite have been scaled in Fig.8. We observe that the spectra for $M''(f)$ for different temperatures merge on a single master curve. This means that all dynamic processes occurring at different temperatures exhibit similar activation energy. Such results were also observed for other composites. The average activation energy E_a for carrier hopping which contributes to the relaxation behavior can be obtained by an analysis of the temperature variation of the relaxation time τ_m given by Arrhenius equation,

$$\tau_m = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (5)$$

where τ_0 is the pre-exponential factor, E_a is the activation energy, and k_B is the Boltzmann constant and T the absolute temperature. The values of τ_m corresponding to the maxima in Fig.7 can be evaluated by the relation

$$f_{\max} = 1/2\pi\tau_m \quad (6)$$

where f_{\max} is the frequency at which the maximum M'' occurs and τ_m is the corresponding relaxation time. In Fig.9, the values of $\ln(\tau_m)$ as a function of inverse temperature have been plotted. The points indicate the experimental data whereas the solid lines indicate the least square fitting obtained from the Eq.(5). The graph in Fig.9 shows the presence of two slopes for all the samples which indicate the presence of two activation energies as obtained in the case of dc activation behavior. The value of the slopes at lower temperature region (77-150K) is small whereas the value of the slopes becomes higher at the higher temperature region (150-300K). This gives a change in the slope and hence the activation energy changes during the temperature region 150-200K, which is confirmed by Fig.2. The value of the activation energy has been calculated from the slopes, the values of which are 2 to 5 meV in the temperature range 77 to 150K and 14 to 30 meV for the temperature range 150 to 300K. A strong charge transfer due to delocalization of charge carriers accumulated on the interface along a long range conjugated length is indicated by the low values of the activation energy [29-32]

4. Conclusions

The composites of PVA/MWNT have been synthesized by an in situ chemical oxidative preparation technique and the study of activation behavior and dielectric relaxation has been done in an extensive manner within a temperature range 77-300K and in the frequency range 20Hz-1MHz. The temperature dependence of dc conductivity gives the presence of two different activation energies. The same is obtained from the plot of characteristic relaxation time versus temperature variation.

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Figure Caption

Fig.1 FESEM micrograph of different PVA-MWNT samples (PM1 and PM3).

Fig.2 The Temperature dependence of dc conductivity of different PVA/MWNT composites. The solid line is fitted to Eq.(1).

Fig.3 The frequency dependence of the real part of complex permittivity for the different PVA/MWNT composites at T=300K.

Fig.4 The frequency dependence of the imaginary part of complex permittivity for the different PVA/MWNT composites at T=300K.

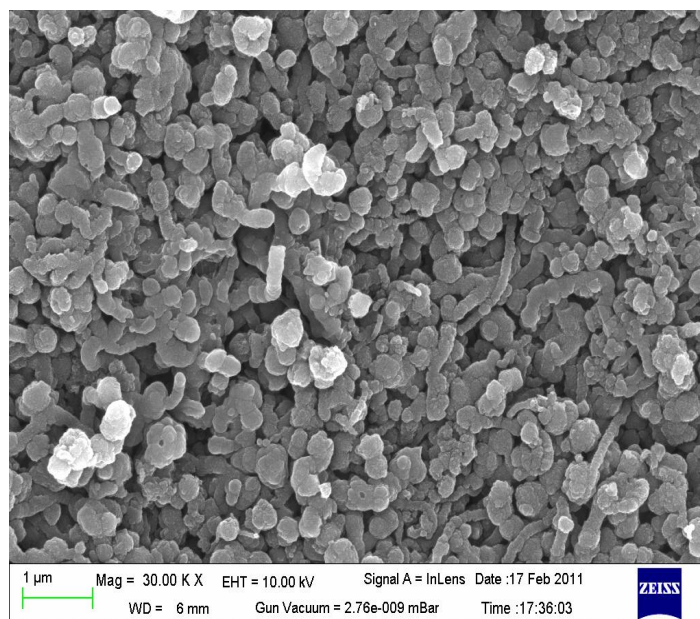
Fig.5 The frequency dependence of the imaginary part of complex electric modulus for the different PVA/MWNT composites at T=300K.

Fig.6 The frequency dependence of the imaginary part of complex electric modulus at various temperatures for the sample PM10.

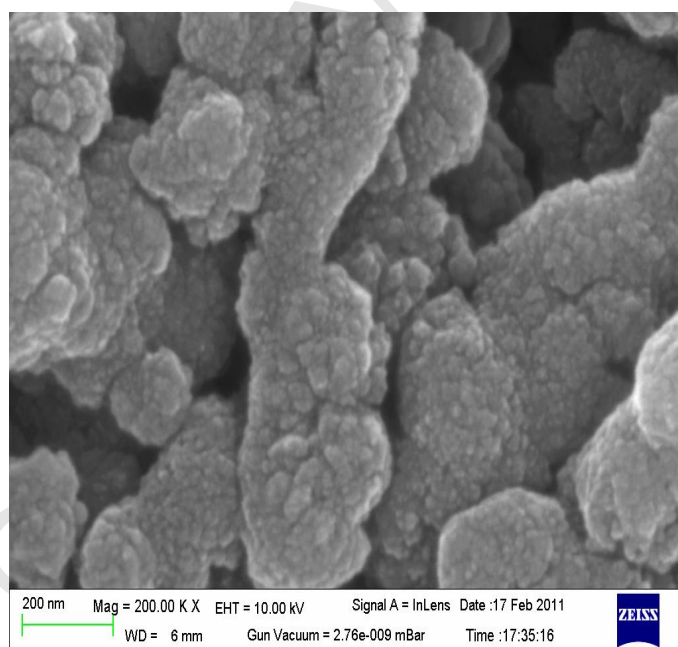
Fig.7 Normalized plots of M''/M''_{\max} with $\ln(f/f_{\max})$ of the different PVA/MWNT composites at T=300K.

Fig.8 Normalized plots of M''/M''_{\max} with $\ln(f/f_{\max})$ of the sample PM10 at different constant temperatures.

Fig.9 Arrhenius plots of the relaxation time with $1000/T$ of different PVA/MWNT composites. The solid line is fitted to Eq.(5).



PM1



PM3

Fig.1

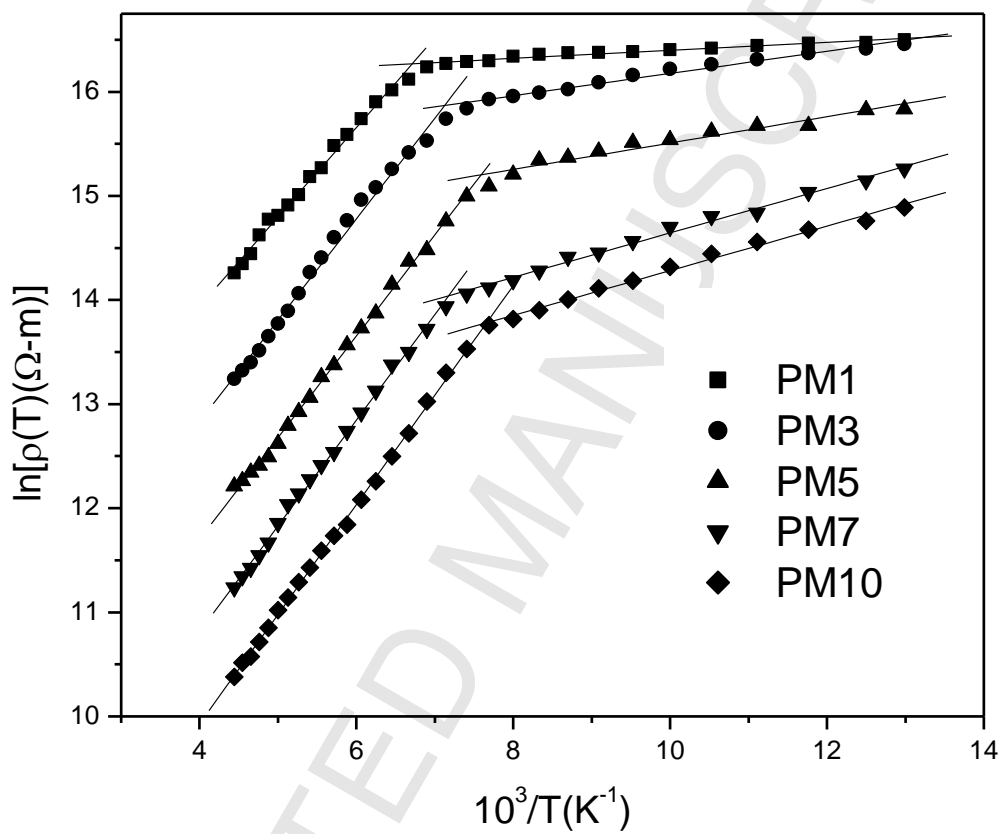


Fig.2

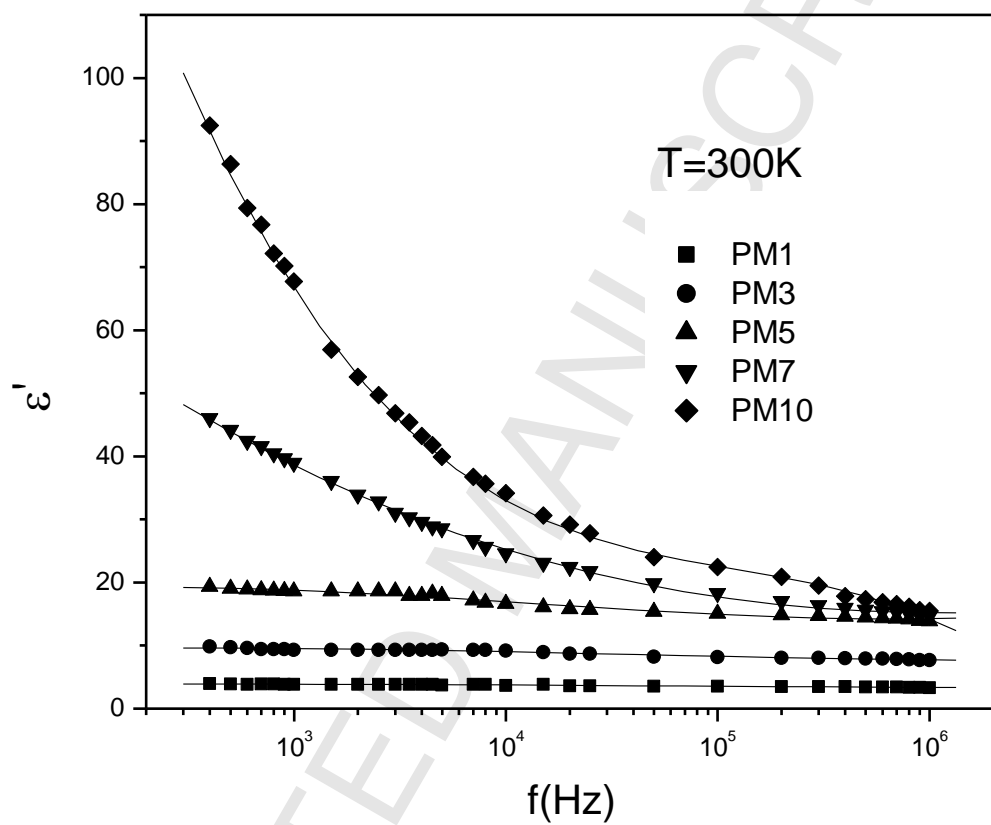


Fig.3

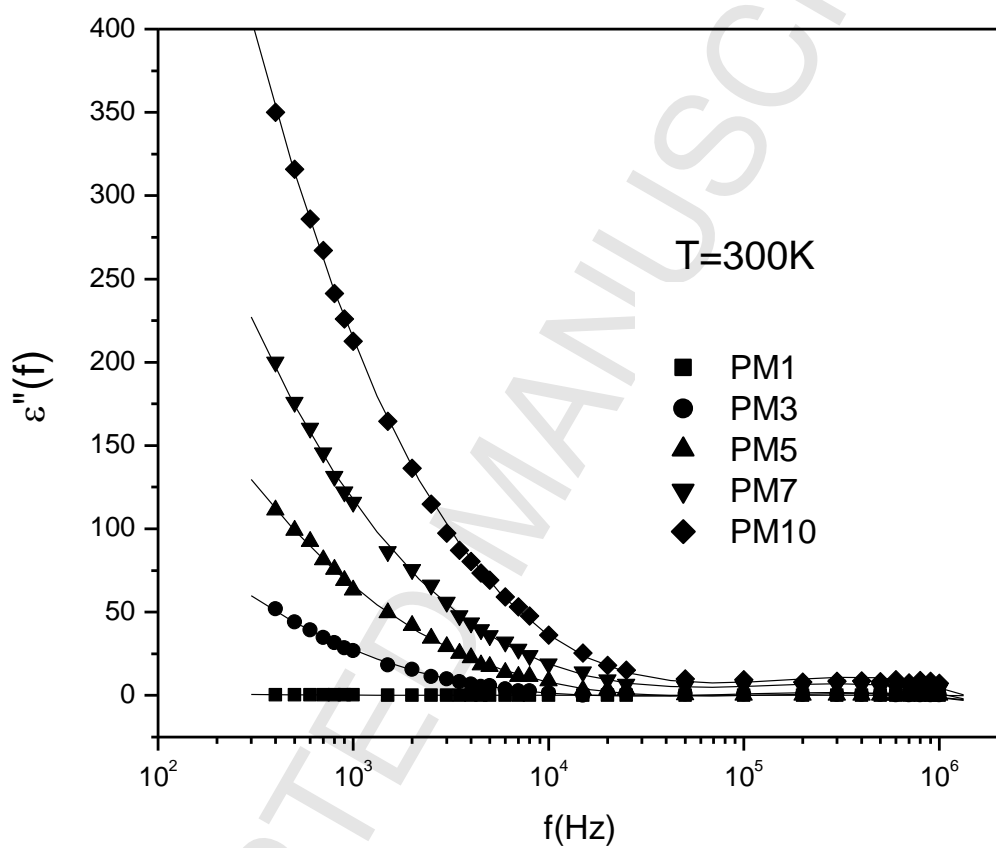


Fig.4

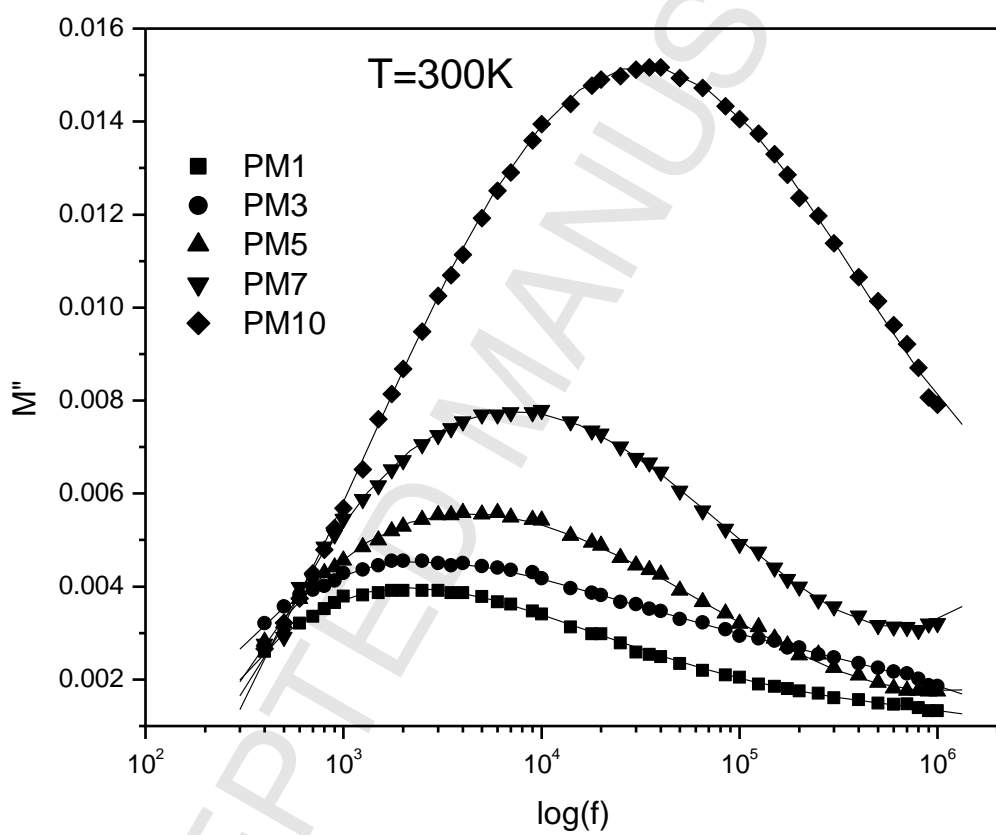


Fig.5

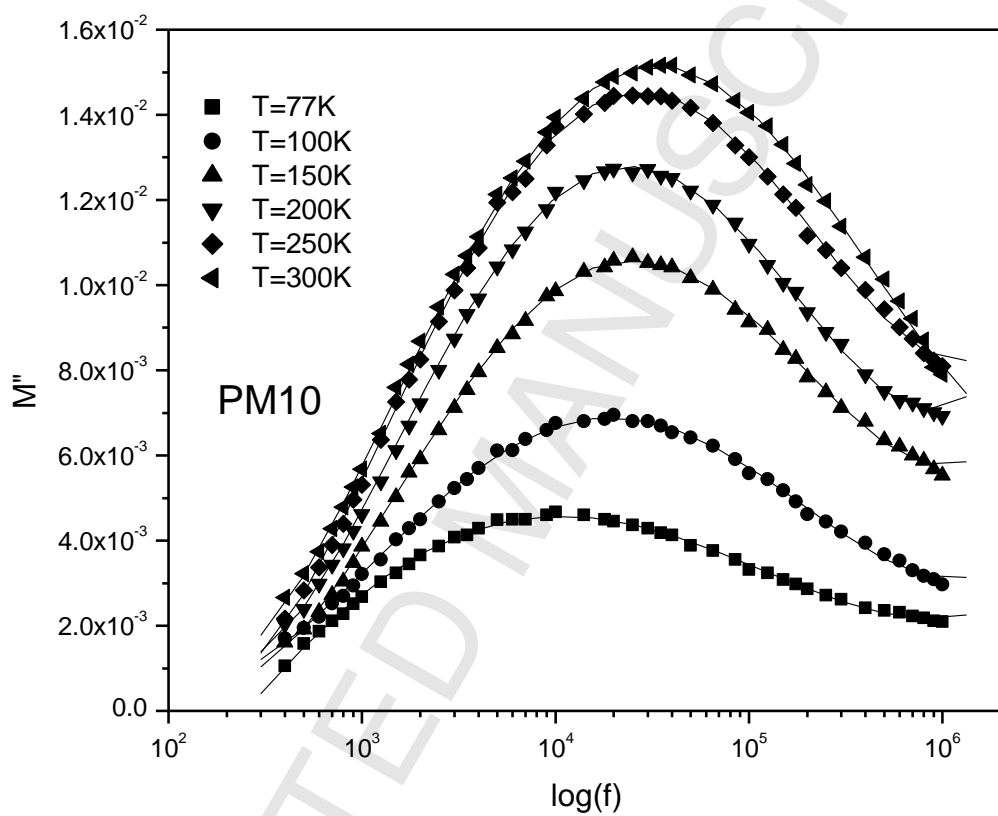


Fig.6

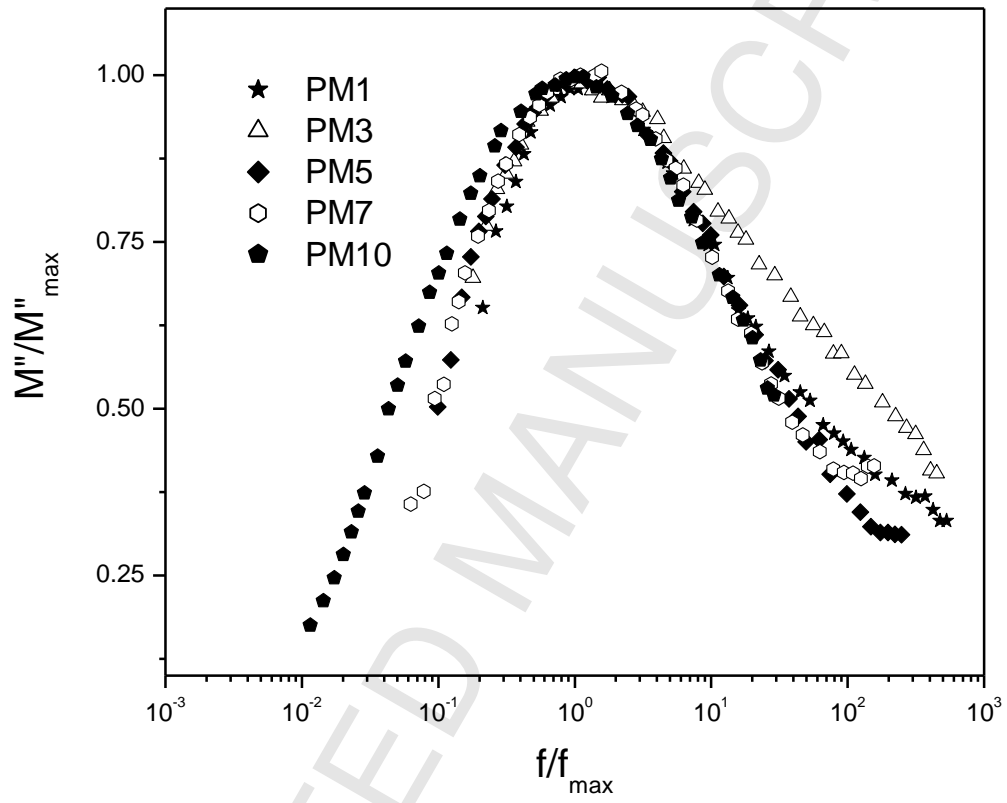


Fig.7

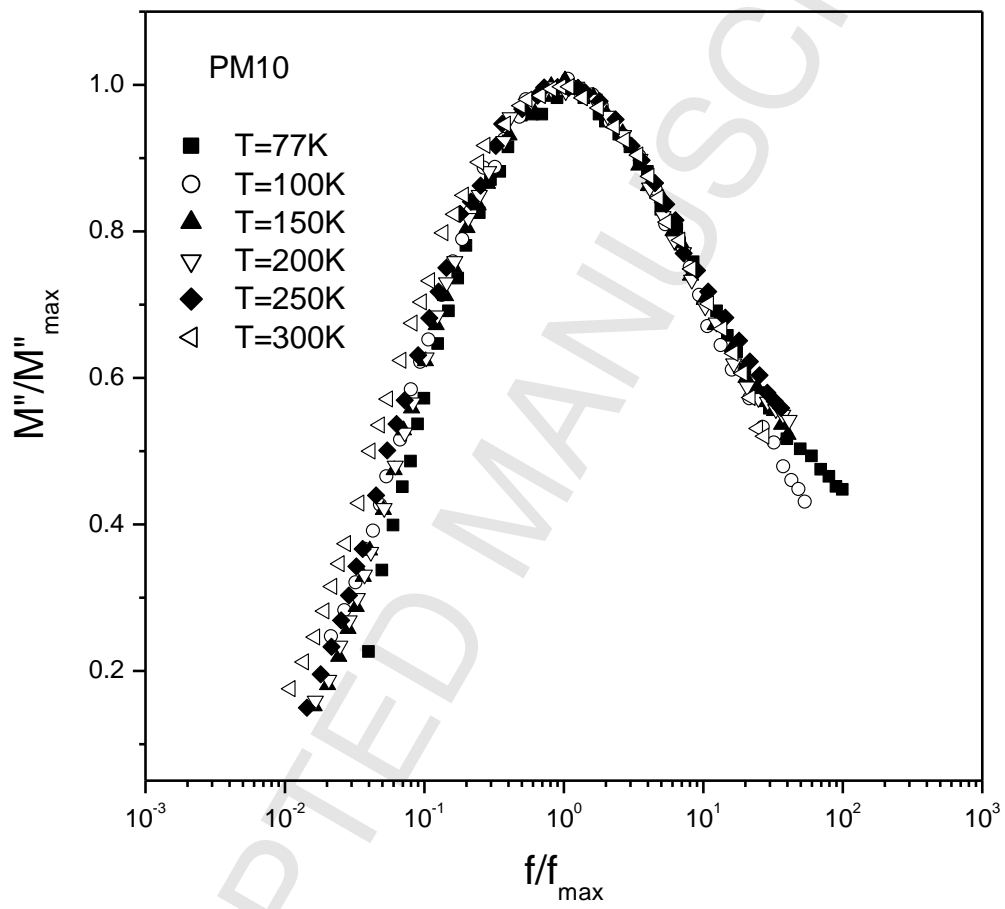


Fig.8

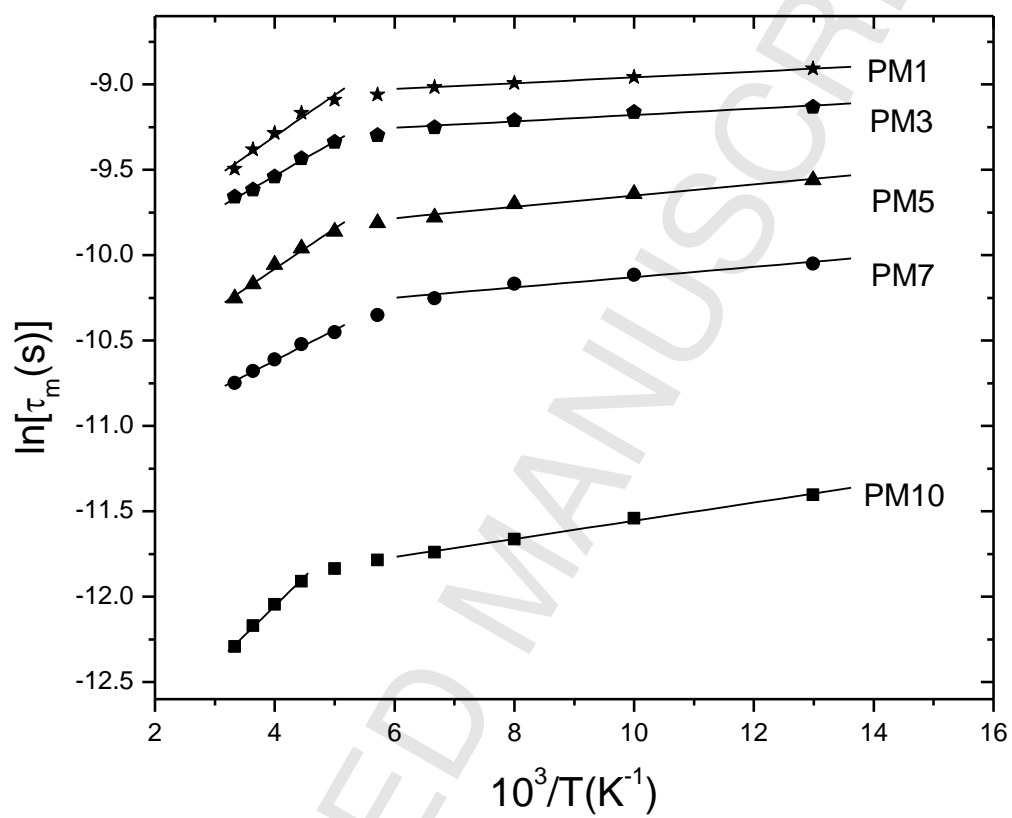


Fig.9

Highlights

> FESEM micrograph the rod like morphology where MWNTs are coated by PVA. > Temperature variation of dc conductivity gives the presence of two activation ranges. > The dielectric relaxation has been explained in terms of interfacial polarization. > Two activation energies have also been observed in the study of relaxation time.