Dielectric relaxation in polyvinyl alcohol–polypyrrole–multiwall carbon nanotube composites below room temperature

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Abstract
Polyvinyl alcohol–polypyrrole–multiwall carbon nanotube composite polymer films have been synthesized by a chemical oxidative polymerization technique. Dielectric properties have been measured in the frequency range from 20 Hz to 1 MHz and in the temperature range \(77 \leq T \leq 300\) K. Electric modulus vector analysis gives the presence of dielectric relaxation peaks for different composites from which the activation energies have been calculated.

Keywords: polyvinyl alcohol, polypyrrole, VRH theory, charge transport, dielectric properties

Classification numbers: 5.10, 5.14

1. Introduction
Recently the study of conjugated conducting polymers has become a subject of interest in research and industry due to their extensive use as materials for corrosion inhibitors, compact capacitors, antistatic coating, electromagnetic shielding and smart windows [1–3]. Most conducting polymers have an extended \(\pi\)-conjugation system with single and double bond alterations along with a polymeric backbone. They behave like semiconducting materials with low charge carrier mobilities. Among such materials, polypyrrole (PPy) has been considered as one of the better materials due to its good environmental stability, easier synthesis technique and relatively high conductivity as compared to other derivatives, although it has certain limitations such as insolubility and relatively poor mechanical strength [4–6]. Thus, attempts have been made to overcome such limitations by blending PPy with other polymeric materials such as polyvinyl alcohol (PVA) [7], polymethyl methacrylate (PMMA) [8], polyvinyl chloride (PVC) [9] etc, in order to achieve good mechanical strength. Advantages including flexible molecular chains, good adhesion to electrodes and its ductile nature have made PVA a desirable material to be incorporated with PPy [5]. Carbon nanotubes (CNTs), on the other hand, are a material with excellent stability and good conductivity, due to which they have been used as an excellent reinforcing material. Their large aspect ratio has made CNTs an effective filler in different matrices such as polymers etc [10]. It has also been observed that the introduction of CNTs into the polymer matrix improves the stability of mechanical and electrical properties [11,12]. The improvement of stability may be due to the formation of a \(\pi–\pi\) bond between the delocalized \(\pi\) electrons of the conducting polymer and the delocalized \(\pi\) electrons of the p-orbital of the carbon atoms of the CNT [13]. The technique of preparing blends of conductive filler and insulating matrix is becoming more popular due to the retention of the matrix properties as well as higher conductivity. Many investigations have been carried out to synthesize PVA–PPy composites and reveal their structural, mechanical, thermal and electrical properties with different
conducting fillers, but the influence of CNTs on the properties of PVA–PPy composites has not been reported to date.

In the present work PPy has been blended with PVA and multiwall CNT (MWCNT) has been added by an in situ chemical oxidative polymerization method. The dielectric properties of such composites have been measured in the temperature range $77 \leq T \leq 300 \text{ K}$ and in the frequency range of $20 \text{ Hz}–1 \text{ MHz}$.

2. Sample preparation and experimental techniques

Pyrrrole monomer, cetyl trimethylammonium bromide (CTAB), MWCNT (Nanocyl 7001), polyvinyl alcohol (PVA), ammonium peroxysulfate (APS), ethanol and acetone have been used as received from the manufacturer. Both double distilled pyrrole and water were used in our study.

Composites of polypyrrole with MWCNT in PVA were synthesized by an in situ chemical oxidative polymerization method. $10\%$ PVA solution was prepared in water with constant stirring at $80\text{ °C}$ and then it was cooled to room temperature for use. MWCNTs were dispersed in an acidic solution of CTAB which was used as a cationic surfactant. $1.136 \text{ g}$ CTAB and $60 \text{ mg}$ of MWCNT were added to $300 \text{ ml}$ $1 \text{ M HCl}$ and the mixture was sonicated in order to obtain a well-dispersed suspension. In this suspension $25 \text{ ml}$ of precooled $0.5 \text{ M pyrrole}$ and $25 \text{ ml} 0.5 \text{ M APS}$ were added in an ice chamber with continuous magnetic stirring. A black colored solution was obtained. $10 \text{ ml}$ PVA solution was added into the resultant black solution after an hour of mixing and the solution was left in the refrigerator at $0–5 \text{ °C}$ for $24 \text{ h}$ to complete the polymerization process. Then the solution was put on a glass plate. A film was obtained after drying at room temperature. It was washed with water and acetone repeatedly to remove oligomers and any unreacted monomer. It was dried at $303 \text{ K}$ for overnight. For comparison purposes, four different samples were prepared with $0, 10, 20$ and $30\%$ of MWCNT. The samples were numbered as PPyC0, PPyC10, PPyC20 and PPyC30 for $0, 10, 20$ and $30\%$ of MWCNT, respectively. The concentrations of pyrrole, HCl, APS and PVA remained the same for all samples. PVA was used as a binding material. The sample characterization and experimental techniques were given in our previous study [14].

3. Results and discussion

The dc conductivity with different contents of MWCNT in the PVA matrix was measured in the temperature range $77 \leq T \leq 300 \text{ K}$. The room temperature (300 K) conductivity increases from $6.86 \times 10^{-4}$ to $4.32 \times 10^{-2} \text{ Ω}^{-1} \text{ m}^{-1}$ with increasing MWCNT content from $0\%$ (PVA–pyrrole composite without MWCNT) to $10\%$ by weight. The composites with lower MWCNT have very few conductive networks [15]. However, with an increasing content of MWCNT in the polymer matrix, more and more conductive networks are formed, resulting in a sharp increase in the conductivity of the composites. Figure 1 shows the temperature variation of dc conductivity for all the samples. The dc resistivity of the samples decreases with increasing temperature, i.e. semiconducting behavior is observed for all the samples. Also there is a decrease in resistivity of the samples with increasing MWCNT content. The graph of $\ln[\rho(T)]$ versus $10^3/T$ in figure 1 indicates the presence of two different slopes which can be explained by studying the activation behavior of the composites. The activation energy of all the investigated samples was calculated by the Arrhenius equation

$$\rho(T) = \rho_0 \exp(E_a/k_B T), \quad (1)$$

where $\rho_0$ is the resistivity at infinite temperature, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant and $T$ the absolute temperature. $E_a$ can be calculated from the slopes of the straight line plot of $\ln[\rho(T)]$ with $1/T$. The values of the activation energy of all the samples are shown in table 1. The activation energy increases with the increase of MWCNT content in both temperature ranges. It may happen due to the interaction of MWCNT (with its large activation energy) and the insulating polymer matrix. Again, the composites have smaller activation energies at lower temperatures than at higher temperatures. This anomalous behavior of the composites suggests the presence of more than one conduction mechanism. Within the composites, a thin layer of insulating polymer is separated and due to this a potential barrier is created with respect to internanotube hopping. At lower temperatures, a weak interaction between the polymer and MWCNT produces a larger barrier height so that the conduction process along the MWCNT dominates. However, the barrier height between the nanotubes may decrease with increasing temperature and the thermal fluctuation induced tunneling [16,17] among the nanotubes may play an additional role in the conduction process. Thus, it may be concluded that, at higher temperatures, conduction along the MWCNT as well as between MWCNTs through the polymer take place. As a result, two activation behaviors in the composites have been observed, resulting in a deviation from the linear behavior of $\ln[\rho(T)]$ versus $1/T$ plot at low temperature.

The capacitance ($C_p$) and the dissipation factor ($D$) of all the investigated samples were measured with increasing frequency ($f$) from $20 \text{ Hz}$ to $1 \text{ MHz}$. The dielectric parameter
shows the decrease of \( \varepsilon' \) with increasing frequency. The real part \( \varepsilon' \) is the component for energy storage while the imaginary part \( \varepsilon'' \) is the component for energy dissipation. The electrical relaxation process may be successful only if it is followed by the polarization cloud. The relaxation time \( \tau \) can be obtained from the peaks of the \( \varepsilon'' \) – \( f \) plots.

Figure 2. Variation of the real part of permittivity with frequency for different samples.

Figure 3. Variation of the imaginary part of the permittivity with frequency for different samples.

As a function of frequency, \( \varepsilon'' \) is described by the complex permittivity in the form

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega),
\]

where the real part \( \varepsilon'(\omega) \) is the component for energy storage and the imaginary part \( \varepsilon''(\omega) \) is that for energy loss, in each cycle of the electric field. In order to investigate the dielectric properties of the composite samples, the dielectric constant \( \varepsilon'(\omega) \) were calculated using the expression \( \varepsilon'(\omega) = C_{pd}/\varepsilon_0 A \) where \( d \) and \( A \) are sample thickness and surface area of the sample, respectively, and \( \varepsilon_0 \) is the free space permittivity. Again the dielectric loss \( \varepsilon''(\omega) \) has been calculated using \( \varepsilon''(\omega) = D\varepsilon'(\omega) \) where \( D = \tan\delta(\omega) \) is the tangent delta. The variation of \( \varepsilon' \) with \( f \) for different samples at room temperature (\( T = 300 \) K) is shown in figure 2. All the samples have a strong frequency dispersion of permittivity in the low frequency region followed by a nearly frequency-independent behavior above \( 10^4 \) Hz. The electrical relaxation process may be the reason behind the decrease of \( \varepsilon' \) with the increase in frequency. Also the value of \( \varepsilon' \) increases with the addition of MWCNT in the lower frequency and becomes nearly the 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 [18]. An electric relaxation time \( \tau \) 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 \( \varepsilon'' - f \) plot [19].

Figure 3 shows the decrease of \( \varepsilon'' \) with increasing \( f \) for different samples. The magnitude of \( \varepsilon'' \) may be regarded as the contribution of three distinct effects—dc conductance, interfacial polarization and the usual dipole orientation or Debye loss [20]. The possible cause of this decrease of \( \varepsilon'' \) with increasing frequency may be attributed to the interfacial polarization. Again in the measured frequency region, no peak was observed for the \( \varepsilon'' - f \) plots. In general, interfacial polarization is masked by the conduction due to the conductive part of the disordered systems [15]. In such cases, the dielectric properties of the samples can be described by the complex electric modulus formalism [21]. Electric modulus \( M \) can be defined as

\[
M^* = \frac{1}{\varepsilon^*} = M' + iM'',
\]

where \( M' \) and \( M'' \) are the real and imaginary part of the dielectric modulus given by

\[
M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2},
\]

\[
M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}.
\]

From the imaginary part of electrical modulus \( M'' \), the relaxation time of the orientation of dipoles can be obtained. Variation of the real part of the electric modulus (\( M' \)) with frequency for different samples at room temperature is plotted in figure 4 where no characteristic peak is observed for any of the samples. The peak for linear frequency \( f_p \) can be obtained from the graph \( M' \) versus log frequency.

Figure 5 shows the variation of \( M'' \) with frequency, \( T = 200 \) K for all the samples. All the curves have a loss peak

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**Table 1. Activation energies for the relaxation mechanism in different PVA–PPY–MWCNT composites.**

| Sample   | Activation energy from dc conductivity data (eV) | Activation energy from \( M'' \) relaxation data (eV) |
|----------|-------------------------------------------------|-----------------------------------------------------|
|          | 77 \( \leq T < 150 \) K 150 \( \leq T < 300 \) K | 77 \( \leq T < 150 \) K 150 \( \leq T < 300 \) K |
| PPyC0    | 0.018 0.112                                    | 0.016 0.107                                         |
| PPyC10   | 0.026 0.124                                    | 0.025 0.115                                         |
| PPyC20   | 0.027 0.125                                    | 0.028 0.122                                         |
| PPyC30   | 0.043 0.156                                    | 0.042 0.148                                         |
due to the interfacial polarization at a particular frequency range for each bulk composite. At a certain temperature, the influence of the applied field results in free movement of the intrinsic immobilized free charge. The free charges are blocked at the insulating matrix and conductive filler and as a result, interfacial polarization is produced by the dielectric difference between them. The relaxation peaks shift toward the higher frequency side with increasing MWCNT content. More and more free charges due to the increase of MWCNT content may accumulate on the interface resulting in a decrease of relaxation time. Thus, the relaxation process shifts toward the higher frequencies [15]. Figure 5 indicates the variation of the imaginary part of the electric modulus ($M''$) with the frequency of the sample PPyC20 at different but constant temperatures. The relaxation peak shifts toward the higher frequency side with increasing temperature. With an increase in temperature, the motion of the polymer chains increases and the free charges accumulate at the interface within the sample. Also the charge carrier mobility increases with an increase in temperature. As a result, the relaxation time decreases and the loss peak shifts toward the higher frequency side.

The normalized spectra for $M''(f)$ at a fixed temperature $T = 250$ K for different composite samples is shown in figure 6. In the normalization plot, $M''(f)$ are scaled by $M''_{\text{max}}$, while the frequency axis is scaled by the relaxation frequency $f_{\text{max}}$. The spectra for different compositions merge on a single master curve, which implies that the conductivity relaxation process is independent of the MWCNT content in composites. Figure 7 shows the variation of $M''$ with frequency for the sample PPyC20 at different but constant temperatures. In this case as well, the relaxation peaks shift toward the higher frequency side with increasing temperature. The increase in the mobility of the carrier electrons with increasing temperature facilitate the charge transfer process and as a result the relaxation time decreases. Due to this, the relaxation occurs at higher frequencies and thus the shift of the relaxation peak occurs.

The normalized plots of $M''/M''_{\text{max}}$ with $\ln(f/f_{\text{max}})$ at different temperatures for a representative PPyC20 composite are shown in figure 8. It is observed that the spectra for $M''(f)$ for different temperatures do not merge on a single master curve. This means that all dynamic processes occurring at different temperatures exhibit different activation energies.
Similar results were obtained for other composites. The average activation energy $E_a$ for carrier hopping contributing to the relaxation behavior can be obtained by an analysis of the temperature variation of the relaxation time $\tau_m$ given by the Arrhenius equation

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

(6)

where $\tau_0$ is the pre-exponential factor. The values of $\tau_m$ corresponding to the maxima in figure 7 can be evaluated by the relation

$$f_{\text{max}} = \frac{1}{\tau_m},$$

(7)

where $f_{\text{max}}$ is the frequency at which the maximum $M''$ occurs and $\tau_m$ is the corresponding relaxation time.

Figure 9 shows the variation of values of $\ln(\tau_m)$ with the inverse of temperature. The points indicate the experimental data and the solid lines indicate the theoretical best fits obtained from equation (6). The graph in figure 9 suggests the presence of two different slopes for all the samples, indicating the presence of two different activation energies as obtained in the case of dc activation behavior. Smaller values of the slopes were obtained in the lower temperature region (77–150 K) whereas the value of the slopes becomes higher in the higher temperature region (150–300 K). Thus a change in the slope was obtained in figure 9 and hence a change in activation energy in the temperature region 150–200 K as confirmed by figure 1. The values of the activation energy have been calculated from the slopes and are shown in table 1. 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 for the activation energy [22–25].

4. Conclusions

Composites of insulating polypyrinyl alcohol and conducting polypyrrole with different MWCNT content were synthesized by an in situ chemical oxidative preparation technique. The dc activation behavior and dielectric relaxation were investigated extensively within the temperature range 77–300 K and in the frequency range 20Hz–1MHz. The presence of two different activation energies was obtained from the temperature dependence of dc conductivity. The same is obtained from the plot of characteristic relaxation time versus temperature variation.

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