Electrical Properties of Polyaniline-Manganese Chloride Composites

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Electrical and morphological properties of Polyaniline (PANI) filled with various mass fractions of manganese chloride ($MnCl_2$) synthesized in aqueous hydrochloric acid (HCl) medium using ammonium persulphate as an oxidant were investigated. The sample morphology was characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Significant changes were observed in the morphology of the samples depending on the filler level. The direct current (dc) and alternating current (ac) electrical properties were investigated as a function of temperature. The dc conductivity decreased 72% with 10% filler level whereas ac conductivity has shown a 120% increase with 6% filler level at room temperature. It is shown that the alternating charge transport mechanism of the unfilled and filled polyaniline samples is consistent with correlated barrier hopping (CBH) model. Imaginary (M'') parts of electric modulus exhibited temperature-dependent dielectric relaxation behavior for both filled and unfilled PANI samples. POLYM. ENG. SCI., 51:617–623, 2011. © 2010 Society of Plastics Engineers

INTRODUCTION

In recent years, conducting polymers have widely been investigated due to their increasing number of applications in transistors, rechargeable batteries, chemical sensors, diodes, microelectronics etc. [1–10] Polyaniline is one of the most studied conducting polymers because of its low cost, excellent environmental stability, high electronic conductivity, and relative ease of the synthesis. Polyaniline has four different states (leucoemeraldine base, emeraldine base, pernigraniline base, and emeraldine salt). Among the above forms of PANI, only the emeraldine salt form is conductive and it can be synthesized by a simple electrochemical or chemical oxidation of aniline in an acidic medium [1, 2, 5–21].

The addition of metal cations to the polymer significantly modifies the morphological structure and physical properties such as electrical and optical. The filling process in this respect can be rather crucial for some technological applications. Although a number of the studies have dealt with the effect of metal salts [3, 5, 6, 8, 11, 21–24], no previous study to the best our knowledge, has been reported on the effect of manganese chloride on the morphological and electrical properties of PANI. In this work, we synthesized PANI with various mass fractions of $MnCl_2$ by using chemical method. The structure of the samples was investigated by FTIR and SEM. The ac and dc conductivity and dielectric measurements of the samples were carried out at different temperatures.

EXPERIMENTAL

Synthesis of Filled and Unfilled Polyaniline Samples

PANI in emeraldine salt form was synthesized via chemical oxidation polymerization. Ammonium persulphate (Merck, Germany) was used as an oxidant. Five milliliter aniline was first dissolved in 1.5 M, 70 mL HCl (Merck, Germany). Following this, 10 g ammonium persulphate dissolved in 20 mL deionized water was added into this solution and stirred at constant speed. Polymerization was performed for 5 h at room temperature. The sample was filtered by using a coarse filter paper (Macherey-Nagel, 751/75/20, Germany). The sample left in the filter was then washed three times sequentially with deionized water. The green colored pure PANI powder was obtained after drying. $MnCl_2$ (Merck, Germany) solutions with mass fractions of 2%, 6%, and 10% were prepared separately prior to the filling process. The $MnCl_2$ solutions in the amount of 5 mL from each concentration mentioned above were added during the chemical polymerization of PANI to obtain PANI-$MnCl_2$ composites. The filled samples were also filtered and dried as described above.

Measurements

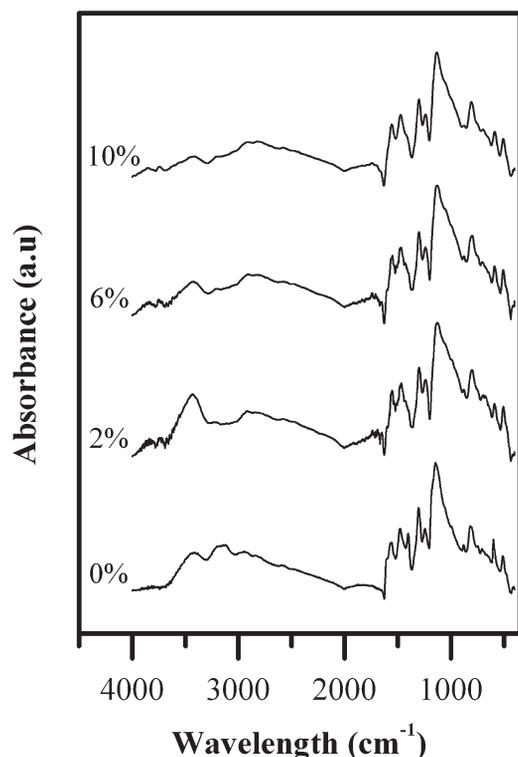The samples were characterized by infrared spectroscopy using a Shimadzu FTIR 8201 spectrophotometer in

FIG. 1. FTIR absorbance spectra of unfilled- and MnCl₂-filled PANI.

the range of 4000–400 cm^{-1}. Measurements were performed in KBr pellets. Philips XL30SFEG SEM-EDX scanning electron microscope, operating at an accelerating voltage of 20 kV was used to observe the morphology of the samples.

For the electrical measurements, the pellets of 13 mm diameter were formed with thicknesses varying up to 0.5–0.8 mm by applying a pressure of eight tones using a cold-press. The surfaces of the samples were coated with silver paste on either side and a guard ring was used for the protection of the side surfaces. Electrical measurements were performed in the temperature range of 303–373 K in a vacuum of 10^{-3} Torr. The temperatures were controlled by using a temperature controller (OXFORD-ITC 502).

The dc measurements were carried out using a Keithley 6487 Picoampermeter by employing the two-probe technique. Dielectric parameters such as the capacitance (C_p) and dielectric loss factor (tan δ) were measured by an LCR meter (AGILENT 4284A) in the frequency range from 10^4 to 10^6 Hz.

The dc and ac conductivity (σ_{dc} and σ_{ac}), the real (ε') and imaginary (ε'') parts of complex dielectric constant ($\varepsilon^* = \varepsilon' + \varepsilon''$) and the dielectric loss factor were calculated from the relations $\sigma_{dc} = dI/AV$, $\varepsilon' = C_p d/\varepsilon_0 A$, tan $\delta = \varepsilon''/\varepsilon'$, $\sigma_{ac} = \omega C_p d$ tan δ/A, where A is the cross-sectional area, V is the potential across the sample, d is the sample thickness, I is the current flowing across the sample, C_p is the capacitance, ε_0 is the vacuum permittivity, and ω is the angular frequency.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy

Characteristic peaks of polyaniline were observed in all FTIR spectra for all samples (see Fig. 1). The absorption band at 820 cm^{-1} is associated with C—C and C—H for a benzenoid unit [8, 14]. The peak at 1143 cm^{-1} corresponds to the in-plane bending of C—H [6, 11]. The peaks at 1244 and 1304 cm^{-1} are related to C—N stretching mode for the quinoid and benzenoid units [6, 11, 14, 22]. Aromatic ring stress, N—H deformation and C=N stretching gives absorption in the region from 1600 up to 1450 cm^{-1}. The characteristic peaks at 1558 and 1477 cm^{-1} are due the presence of quinoid and benzenoid rings, respectively [7, 14, 16, 18, 21]. The absorption band at 2939 cm^{-1} is associated with C—H stretching vibration and N—H stretching vibration peak is observed in the region 3500–3000 cm^{-1} [5, 8, 16, 17, 21, 22, 25].

The clear shifts were observed in the FTIR spectra of the filled PANI samples. For instance, the absorption bands at 819, 1143, and 2939 cm^{-1} belonging to unfilled PANI shifted to 806, 1132, and 2910 cm^{-1}, respectively by a 10% filler level. This is due to the fact that metal cations become adsorbed as a result of electrostatic interaction with chloride ions (Cl$^-$) on the surface of the polymer molecules (see Fig. 2).

Scanning Electron Microscopy

SEM micrographs in Fig. 3 show dispersion of PANI particles. While the SEM of pure PANI displays a block like structure alongside various aggregates (Fig. 3a), 2% filled sample (Fig. 3b) show that block like structures have now been replaced with smaller platelets. Furthermore, there is no distinctive and dominant inter-particle contact for pure and 2% filled samples apart from the aggregates. However, this picture changes completely for the 6% sample as seen in Fig. 3c where a smooth and homogeneous structure is now more apparent rather than the particulate appearance. The SEM image for 10% sample (Fig. 3d) appears to be rather similar to pure PANI and 2% sample.
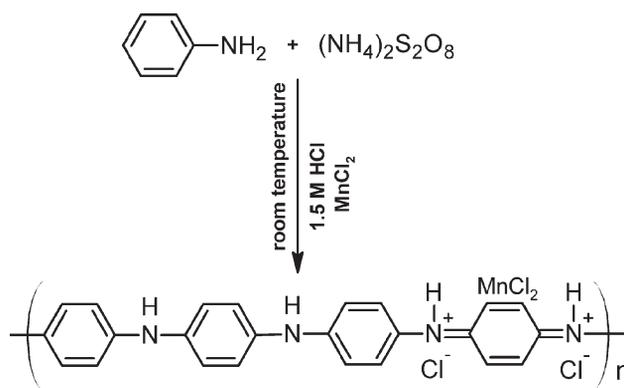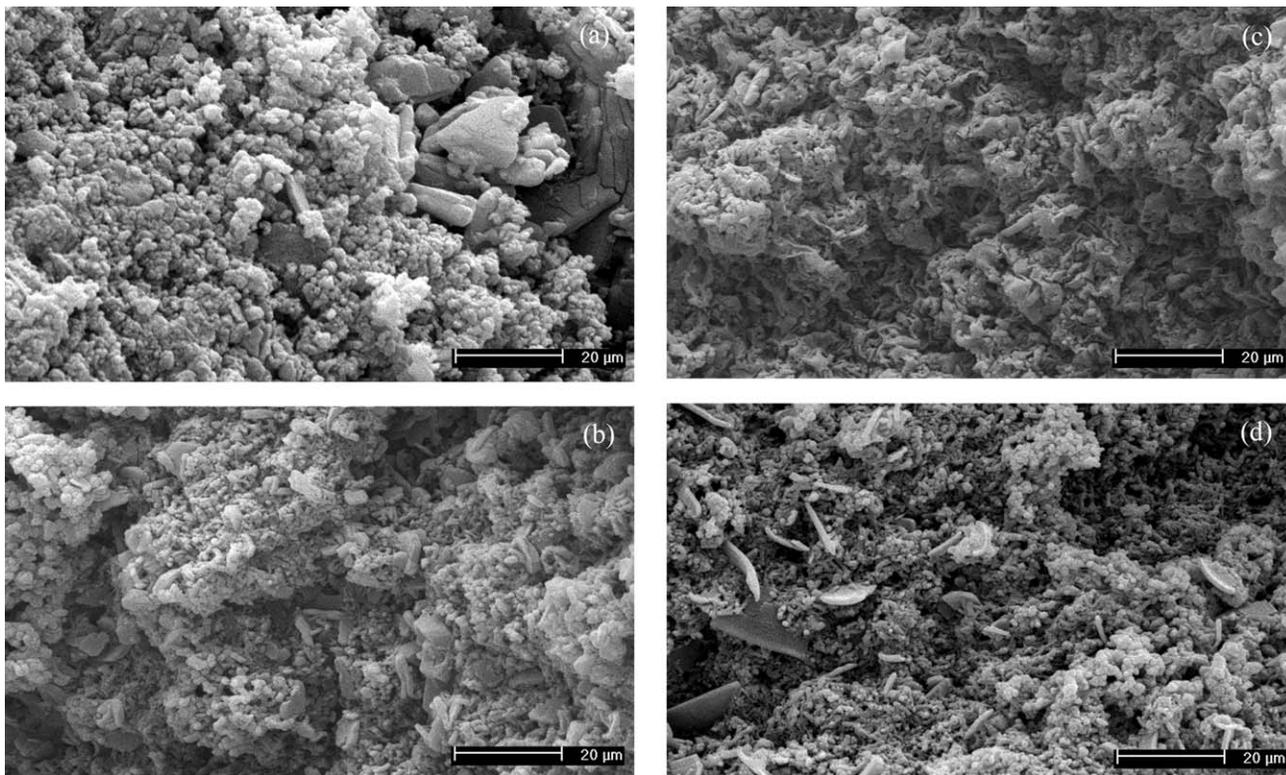

FIG. 2. The reaction mechanism of MnCl₂-filled PANI.

FIG. 3. Scanning electron micrographs of (a) PANI, (b) PANI-MnCl$_2$ (2%), (c) PANI-MnCl$_2$ (6%), and (d) PANI-MnCl$_2$ (10%).

DC Electrical Measurements

Typical I–V curves given in Fig. 4 for unfilled and filled PANI samples are for only around the room temperature (303 K) where we see that it displays an Ohmic behavior.

However, all the other samples also exhibit an Ohmic behavior at the temperatures range used. The dc conductivity based on the above Ohmic behavior decreased significantly with increasing filler level (see Fig. 5).

This is because the mobility of electrons is being restricted due to more electrostatic interactions caused by the filling process leading to a decrease in conductivity. This decrease was ~72% at 303 K and 53% at 373 K for the sample with the highest filler level (10%) compared with the unfilled sample.

It is clear in Fig. 5 that dc conductivities of the filled samples increase with increasing temperature. This could be due to increased mobility of charge carriers in the structure as a result of weakened electrostatic interactions due to higher temperatures. However, it should be noted that the conductivity of the unfilled PANI sample where there is no MnCl$_2$ is virtually constant and does not change with the temperature.

Dielectric Measurements

The ac conductivity dependence on frequency at different temperatures for both filled and unfilled PANI sam-ples displays the same behavior (see Fig. 6). Although the ac conductivity was not affected by the frequency, it takes higher values with increasing temperature. The ac conductivity of polymers is usually described by the power law of frequency [3, 4, 12, 13, 24, 26, 27]. The total measured conductivity at a given temperature is
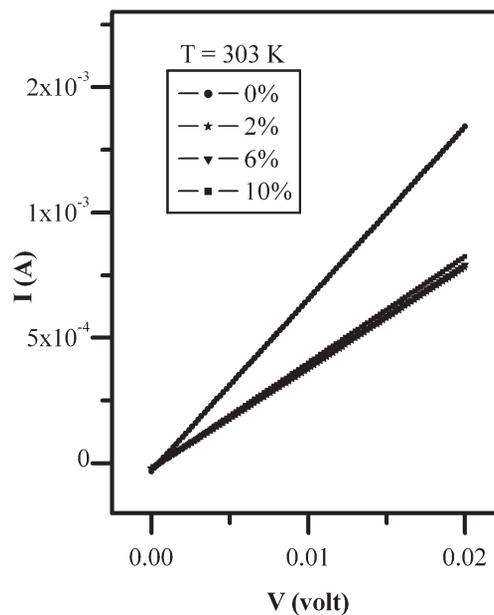

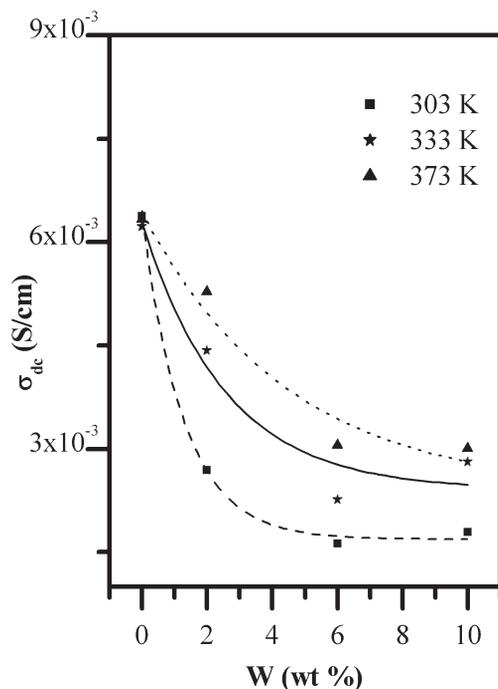FIG. 4. Voltage-current characteristics of unfilled and filled PANI samples at 303 K.

FIG. 5. Variation of dc conductivity depending on the filler level at different temperatures.

$$\sigma(\omega) = \sigma_{dc} + a\omega^s \qquad (1)$$

where a is a temperature dependent constant and s ($s \leq 1$) is an exponent. The second term in *Eq. 1* represents the frequency dependent conductivity.

There are various theoretical models such as small polaron tunneling (s increases with temperature), electron
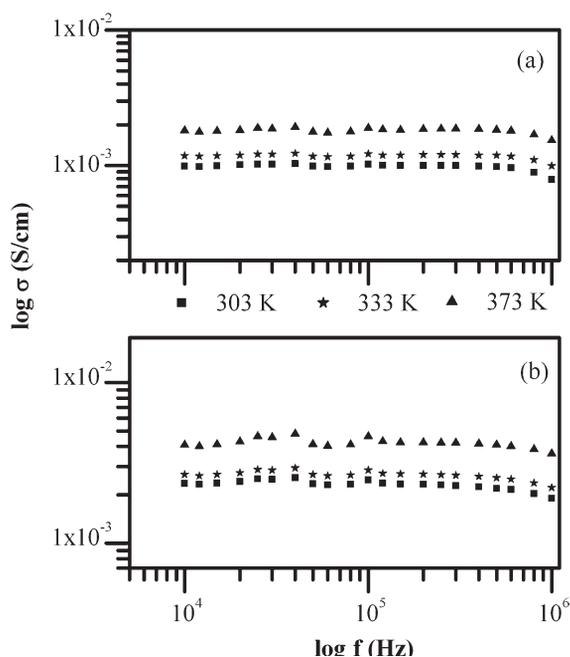

FIG. 6. Frequency dependence of ac conductivity at different temperatures for (a) 10% filled and (b) unfilled PANI.
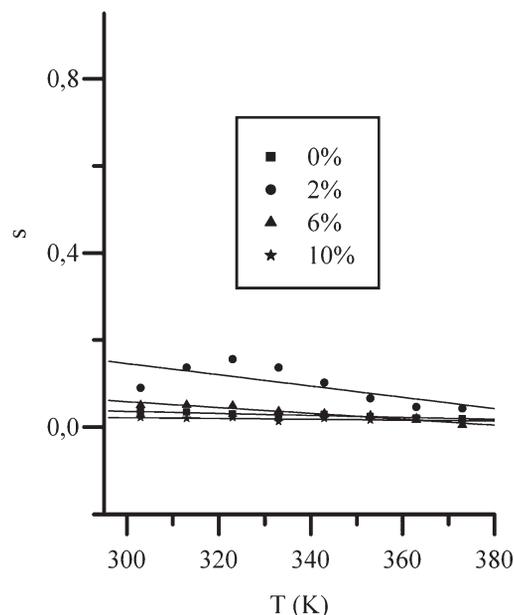
FIG. 7. Frequency exponent (*s*) versus temperature for unfilled PANI and PANI filled with various filler levels of $MnCl_2$.

tunneling (s is independent of temperature), and CBH model (s decreases with temperature) that can provide explanation for ac conductivity [3, 4, 12, 13, 24, 26, 27]. The value of s can be calculated from Fig. 6. To determine which model is consistent with the conductivity mechanism, the variation of the frequency exponent s with the temperature is important (see Fig. 7).

For all samples, it is seen that s values tend to decrease with the temperature. Considering these variations, it is possible to say that CBH model is more appropriate. According to this model, the charge carrier hops between the sites over the potential barrier which separates them. The frequency exponent s for such model is

$$s = 1 - \frac{6k_B T}{W_M + k_B T \ln(\omega\tau_0)} \qquad (2)$$

where W_M is the effective barrier height, k_B is Boltzmann's constant ($k_B = 86.13 \ \mu e \ VK^1$), τ_0 is the relaxation time, and T is the temperature. The data was fitted to *Eq. 2* since s is independent of frequency. The slope of the graph of $1-s$ versus T given in Fig. 8 would be equal to $6k_B/W_M$. The calculated W_M values are related to the filler level as it is 2.24 eV for the pure PANI, 0.4, 0.77, and 5.6 eV for 2%, 6%, and 10% $MnCl_2$ filler levels, respectively.

The effect of the filling process on the ac conductivity for different temperatures at two frequencies shows a rather similar frequency independent behavior (see Fig. 9). However, an interesting point is that the highest conductivity is observed at around 6% at approximately room temperature. Over 120% increase was obtained in the ac conductivity at 303 K with 6% filler level for 1 MHz. Furthermore, the conductivity decreases with increasing temperature contrary to the other samples. This behavior of
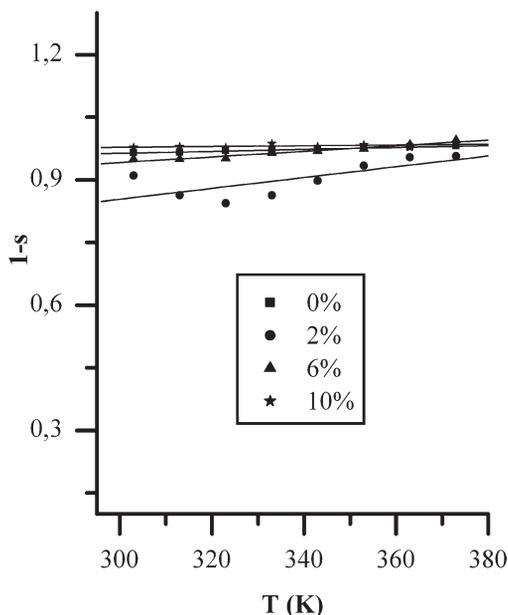
FIG. 8. Plots of $1 - s$ versus T for unfilled PANI and PANI filled with various filler levels of $MnCl_2$.

6% sample is thought to be due to its different morphological structure which was explained in detail previously.

To analyze the dielectric properties, the complex dielectric constant (ε^*) is generally converted to the complex electric modulus (M^*) since it is not suitable to describe the electrical properties of conjugated polymers [4, 12, 15]. The real (M') and imaginary (M'') parts of

the electric modulus can be calculated from ε' and ε'', as follows:

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \quad \text{and} \quad M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \qquad (3)$$

The frequency dependence of the imaginary component of the modulus shows shifts at different temperatures for both unfilled and 10% filled samples (see Fig. 10). It is observed that the relaxation peaks shift towards high temperatures due to the increase in the frequency for all samples. This is due to the temperature-time equivalency in the dielectric relaxation behavior [9, 12, 28]. The temperature dependency of the relaxation time is usually analyzed using Arrhenius' law:

$$\tau = \tau_0 \exp\left(\frac{E}{k_B T}\right) \qquad (4)$$

where E is the activation energy of relaxation process, τ_0 is the relaxation time, k_B is the Boltzmann's constant, and T is the temperature. Frequencies where peak maxima occur were determined in order to calculate the relaxation time for each sample (see Fig. 10). The τ relaxation time was then calculated by employing $\omega\tau = 1$ relationship. The temperature dependencies of the relaxation times are given in Fig. 11 for unfilled and filled PANI samples. The parameters E and τ_0 obtained by fitting the curves in Fig. 11 are listed in Table 1.

The relaxation times of 0% (unfilled PANI), 2% and 10% filled PANI samples decreased with increasing
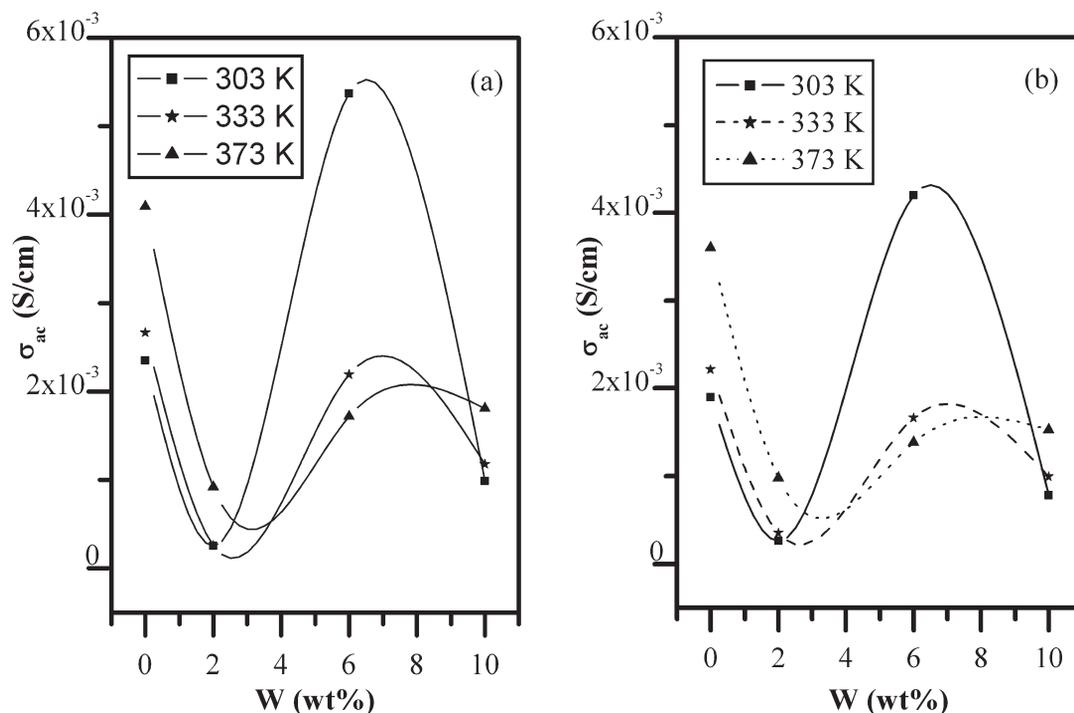

FIG. 9. Variation of the ac conductivity versus filler level for (a) 10 kHz and (b) 1 MHz at different temperatures.
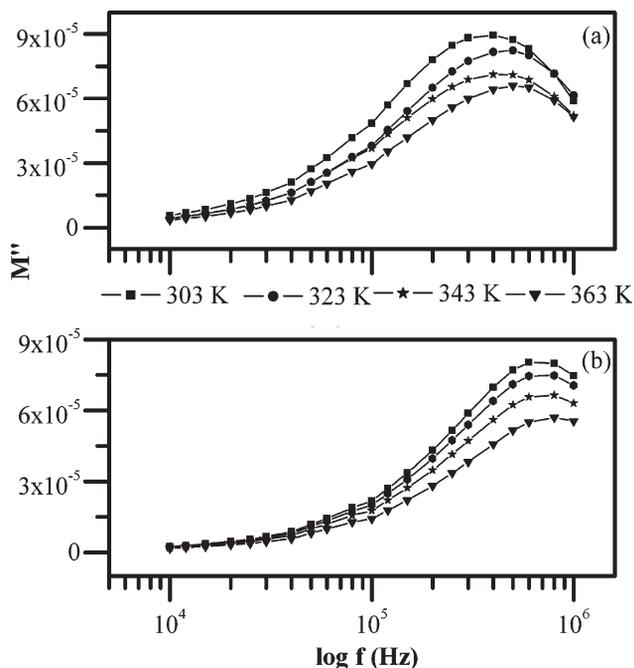
FIG. 10. Imaginary part of the electric modulus vs. frequency at different temperatures for (a) 10% filled and (b) unfilled PANI.

temperature. This decrease was approximately 1.5% for unfilled PANI, 7.5% for 2% $MnCl_2$ filled PANI, and 2% for 10% $MnCl_2$ filled PANI.

However, the relaxation time of 6% filled PANI sample increased about 10%. This shows that this structure, which includes dipoles associated with nitrogen and chloride on the chain segment can move with much more ease
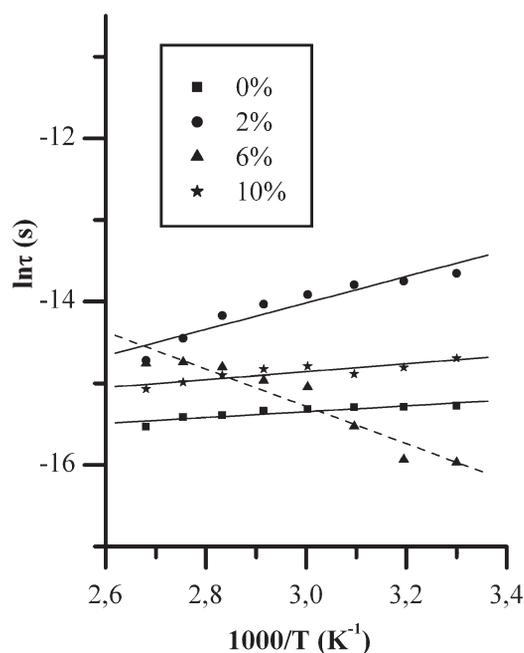

FIG. 11. Plots of ln τ versus 1000/T for unfilled PANI and PANI filled with various filler levels of $MnCl_2$.

TABLE 1. Arrhenius fit parameters τ_0 and E in Eq. 4 of filled and unfilled PANI samples.

Sample	τ_0 (s)	E (eV)
0%	7.47×10^{-8}	0.03
2%	6.38×10^{-9}	0.14
6%	6.25×10^{-5}	0.16
10%	8.42×10^{-8}	0.04

with increasing temperature in the external field compared with the other samples.

CONCLUSIONS

Polyaniline in the form of emeraldine salt synthesized by using the chemical method was filled with $MnCl_2$ at various levels. It was observed that there were clear shifts in FTIR spectra at some wavelengths depending on the filler level. The SEM micrographs revealed that 6% $MnCl_2$ filled PANI has a much more smooth and homogenous structure than the other samples.

The dc conductivity decreased significantly with the increasing filler level. This decrease was ~72% at 303 K and 53% at 373 K for the sample with the 10% filler level compared with the unfilled sample.

The frequency dependence of the conductivity was described by a power law $\sigma(\omega) = a\omega^s$. The values of the frequency exponent s for each sample decreased with increasing temperatures. It was therefore determined that the correlated barrier hopping (CBH) model describes the ac conduction mechanism best. The ac conductivity especially at room temperature was influenced by the filling process where a 120% increase was observed with just a 6% filler level.

Dielectric measurements suggested a temperature-dependent dielectric relaxation mechanism. The temperature dependency of the relaxation time was analyzed by using Arrhenius' law. While the relaxation time of 6% $MnCl_2$-filled sample increased nearly 10% with increasing temperature, the relaxation times of the rest of the samples decreased approximately between 1% and 8%.

This paper reported physical and morphological properties of various PANI-$MnCl_2$ composites for the first time as distinctive behavioral changes were observed depending on the filler level.

ACKNOWLEDGMENTS

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