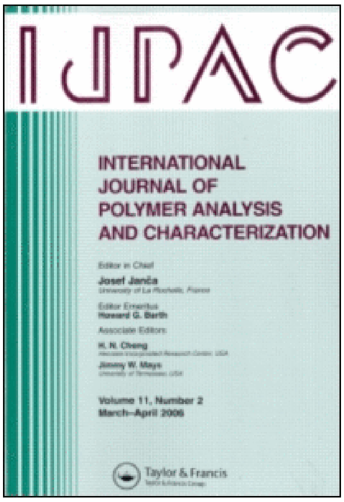

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Dielectric Properties Investigation of Polyaniline Prepared by Using Fenton's Reagent

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Abstract: The frequency dependence of the dielectric properties and dc conductivity (σ_{dc}) of polyaniline samples that have been prepared in a conducting state by a chemical method using Fenton's reagent were investigated. These samples were prepared at constant molar ratio H_2O_2/aniline ($r = 1$) and at different concentrations of both H_2O_2 and aniline (0.2 M, 0.4 M, and 0.5 M). The measurements were carried out using the complex impedance technique in the frequency range 0.12 to 100 KHz at the temperature range from about 278 to 311 K. It has been found that the concentrations of H_2O_2 and aniline have a noticeable effect on the dielectric properties. All samples have only one activation energy for one phase of material except at 0.5 M, implying several activation energies and consequently several phases in the material.

Keywords: Dielectric properties; Fenton's reagent; Polyaniline

INTRODUCTION

The dielectric properties of polymer materials play an important role in device applications such as high-performance capacitors, electrical cable insulation, and electronic packaging and components. The detailed

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investigation of the dielectric loss, electrode, and interfacial polarization effects of polymers is of great importance.

Polyaniline (PANI) is a favorable polymer to work with because of its good environmental stability, good redox reversibility, and good electrical conductivity. These properties provide possible applications in battery electrodes,[1,2] electrochromic devices,[3,4] photoelectric cells,[5,6] light-emitting diodes,[7] and biosensors.[8,9]

Polyaniline is generally prepared by the oxidative polymerization of aniline by ammonium peroxydisulfate (APS).[10–13] Ammonium peroxydisulfate is a strong oxidant, and the polymerization of aniline is an exothermal reaction, so the reaction heat is difficult to control, leading to a wide molecular weight distribution. Post-treatments become complicated because the inorganic by-product (ammonium sulfate) exists in the product.[14] On the other hand, H_2O_2 reduction product is only H_2O, thus greatly simplifying the post-treatment. Another advantage is the possibility of recycling the reaction medium because it does not contain any harmful components to aniline polymerization.

Sun et al.[14,15] have studied the aniline polymerization in the bulk using H_2O_2 as an oxidizing agent and $FeCl_2$ as catalyst. The optimum reaction conditions for the PANI powder formation were studied, and these authors also mentioned that if the polymerization of aniline is carried out by using only H_2O_2 as an oxidant, small yield PANI is obtained, even after 24 h, and hence they added the catalyst. Inoue et al.[16] reported the oxidation of aniline using H_2O_2 in the presence of Fe^{2+} to prepare PANI powder; its conductivity was 10^{-6}–10^{-9} Scm^{-1}. Such low conductivity was attributed to the deprotonation of PANI, since PANI was treated using a boiling aqueous solution of ammonium hydroxide before measurement of conductivity.

In our previous work,[17] we studied the synthesis of PANI films using quartz crystal microbalance to observe the formation of the PANI powder in the bulk. The powder had very low conductivity value compared to that obtained by APS. The charge-transfer mechanism of conducting polymers including PANI has been investigated using dielectric relaxation behavior and ac conductivity measurements.[18–23] Based on these investigations, no work was done to study dielectric properties of PANI powder obtained by Fenton's reagent. Therefore, the present study aimed to investigate the dielectric properties of the powder. The molar ratio (r) of H_2O_2/aniline was kept constant at a value of unity as recommended by Sun et al.[14] and the concentrations of H_2O_2 and aniline were 0.2, 0.4, and 0.5 M.

EXPERIMENTAL SECTION

Chemicals

Aniline (ADWIC, Egypt) was distilled twice under atmospheric pressure. H_2O_2 (ADWIC, Egypt), ferrous sulfate ($FeSO_4 \cdot 7H_2O$) (Qualikems, India), and sulfuric acid were used without further purification. Freshly distilled water was used to prepare all aqueous solutions.

Sample Preparation

A series of solutions were made in which the molar ratio (r) of H_2O_2/aniline was kept constant at a value of unity. To achieve that, the concentration of both H_2O_2 and aniline was changed simultaneously to 0.2 M (sample (a)), 0.4 M (sample (b)), and 0.5 M (sample (c)) in 0.3 M sulfuric acid solution and at 0.001 M ferrous sulfate. The PANI powder precipitated in the bulk of the solution was collected from the reaction medium after the polymerization process was terminated by filtration, then washing with 0.3 M sulfuric solution and then acetone. The obtained PANI samples have green color except at 0.5 M (sample (c)), which has brown color.

The dielectric properties were investigated by using the complex impedance technique (lock-in amplifier, SR 510 Stanford Research System, Model SR830 DSP); the details of the circuit used were previously published elsewhere.[24] All measurements were carried out in frequency range 0.12 to 100 KHz and at temperatures from about 278 to 311 K. Also, the reversibility behavior of dielectric properties with temperature was checked, and the data were the same for increasing and decreasing temperatures. The values of dc conductivity (σ_{dc}) at different temperatures were obtained by extrapolation to zero frequency.

RESULTS AND DISCUSSION

Dependence of Dielectric Constant ε' on Frequency

Figures 1(a)–1(c) show the frequency dependence of ε' at different temperatures for samples (a), (b), and (c), respectively. These figures are plotted on a log-log scale because of high values of ε' obtained at low frequencies. The values of ε' for all samples are very high at low frequencies and high temperatures, then decrease with increasing frequency. Such high values of ε' may be due to the interfacial effects within the bulk of the samples and also may be partially due to the electrode effects. This is attributed to

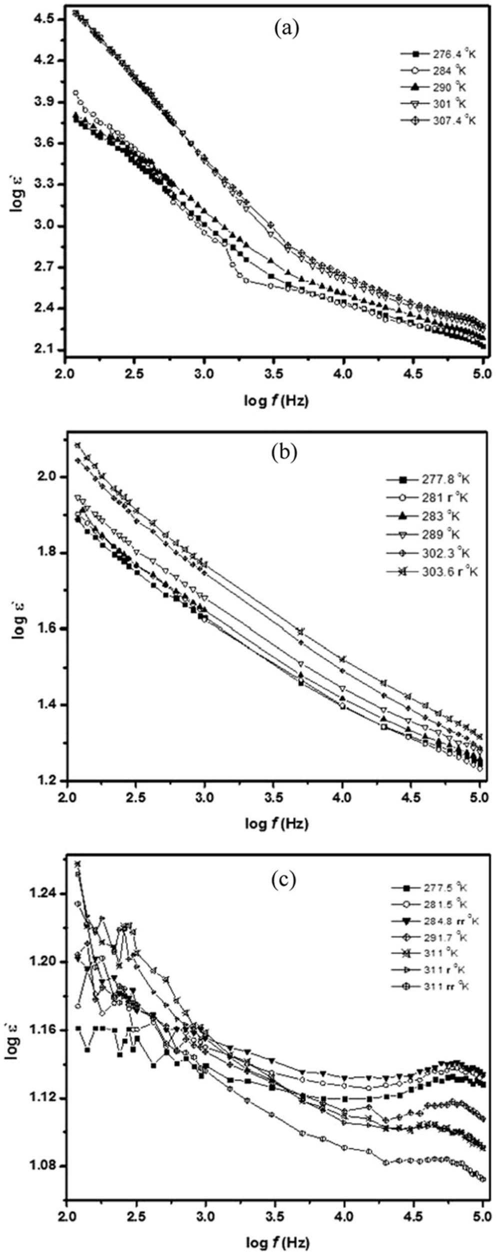


Figure 1. Logarithmic plots of ε' at different concentrations of H_2O_2 and aniline: (a) 0.2 M, (b) 0.4 M, and (c) 0.5 M.

the long-range drift of ions, and, consequently, the barrier layer formation on the electrode surface results in large values of ε' and dielectric loss ε'',[25,26] when an electric field is applied to the sample. At high frequencies, the periodic reversal of the electric field occurs so fast that ion diffusion in the direction of the field can no longer follow the field variation. Consequently, the polarization due to the charge accumulation decreases, leading to a decrease in the values of ε' and ε''.[27,28]

The values of ε' and ε'' (the figure of ε'' relations is not shown) decrease as the concentrations of both H_2O_2 and aniline increase. It can be seen that sample (c) has the lowest ε' and ε'' values of all the samples. This observation may be attributed to the fact that the number of reoriented dipoles is much lower than in other PANI samples. This sample is different in structure and color (brown) because it contains high fraction of oligomers of PANI and cross-linking of PANI molecular chain[14,29]; this observation was also evidenced in a previous work.[17]

Dependence of Electric Modulus M' and M'' on Frequency

Interfacial polarization arises mainly from the existence of polar and conductive regions dispersed in relatively less polar and insulating matrix. This phenomenon is particularly important in conjugated polymers and may interfere in the relaxation process analysis. Therefore, it was decided to study the "electric modulus" formalism,[30] and, hence, the conductivity relaxation[31–34] of the polymer can be investigated. An advantage of using the electric modulus to interpret bulk relaxation properties is that the variation in the large values of permittivity and loss at low frequencies are minimized.[35]

Many authors prefer to describe the dielectric properties of these systems by using the electric modulus M' and M'' formalism.[23,36] The complex electric modulus is derived from the complex permittivity, according to the relationship defined by Macedo et al.[25] The real and imaginary parts of the electric modulus M' and M'' can be calculated from ε' and ε'', as follows[37]:

$$M' = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon'')^2} \quad M'' = \frac{\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2} \tag{1}$$

M' and M'' representations of dielectric process give some idea of relaxation of dipoles that exists in different energy environments, independent of the strong effect of dc conductivity, which often masks the actual dielectric relaxation processes.

The calculated values of M' and M'' were plotted against the frequency as shown in Figure 2, where M' exhibits a part of a sigmoid shape for all samples. The almost zero values of M' at low frequency

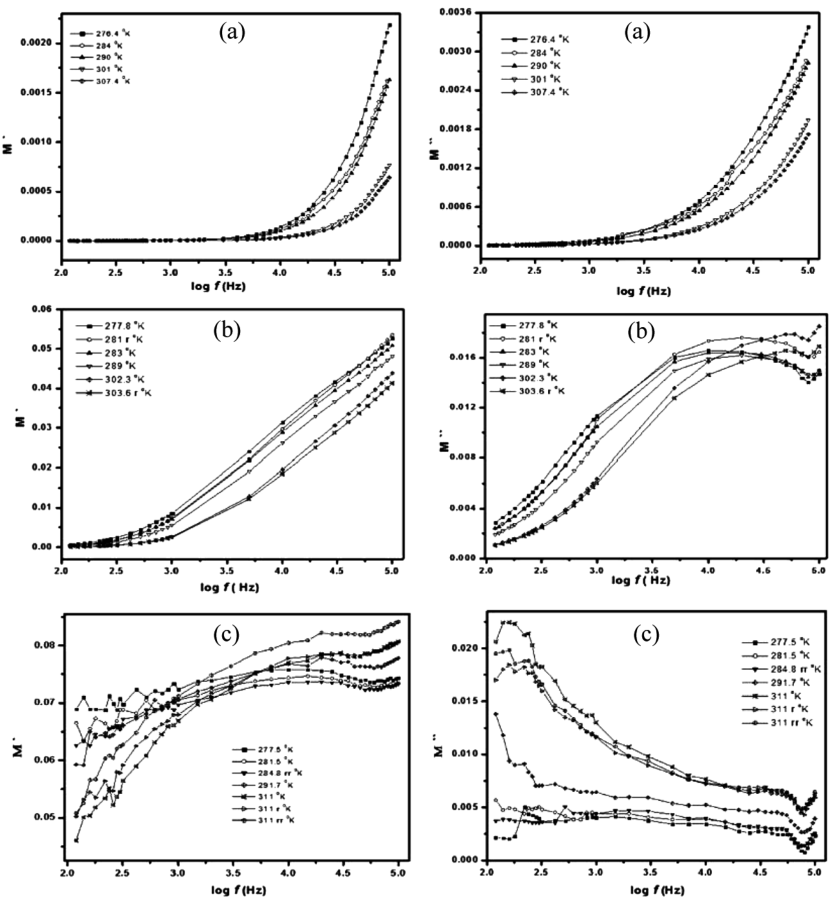


Figure 2. Frequency dependence of M'' and M' at different temperatures of and at different concentrations of H_2O_2 and aniline: (a) 0.2 M, (b) 0.4 M, and (c) 0.5 M.

indicate the disappearance of electrode polarization.[38] For samples (a) and (b) both M' and M'' increase with increase in frequency and decrease with increase in temperature. For sample (c), M'' decreases with increasing frequency and increases with increase in temperature indicating that sample (c) has a different structure than the others as previously mentioned.[17] As shown in Figure 2 for sample (b), M'' exhibits only one peak, which shifts to higher frequencies with increasing temperature, implying higher energies of the current charge carriers at higher temperatures. These peaks are related to relaxation process.[38] On the other hand, for sample (a) it seems that the peaks of M'' may be

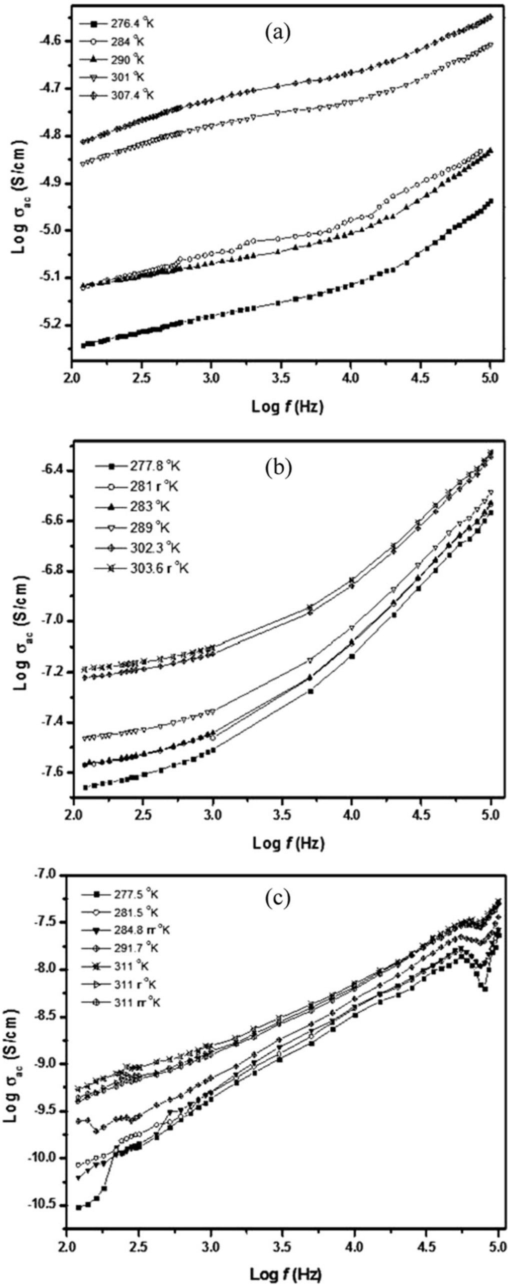


Figure 3. Frequency dependence of log σ_{ac} at different temperatures and at different concentrations of H_2O_2 and aniline: (a) 0.2 M, (b) 0.4 M, and (c) 0.5 M.

above our experimental frequency limit (100 KHz). In contrast, in sample (c) the peaks were shifted to lower frequencies.

Dependence of ac Conductivity σ_{ac} on Frequency

Figure 3 shows the σ_{ac} of PANI samples as a function of frequency (double logarithmic scale) and at different temperatures. It was observed in all samples that for low frequencies up to 1 KHz the real part σ_{ac} becomes almost frequency independent and its value is equal to the dc conductivity at the respective temperature. At high frequencies the conductivity becomes frequency dependent.

The total conductivity $\sigma(f)$ at a given temperature and frequency can be expressed as

$$\sigma(f) = \sigma_{dc} + \sigma_{ac}(f) \tag{2}$$

where σ_{dc} is the dc electrical conductivity and $\sigma_{ac}(f)$ is the ac conductivity. The frequency variation of $\sigma_{ac}(f)$ at a particular temperature for a disordered semiconductor obeys the following power-law:

$$\sigma_{ac}(f) = Af^{s} \tag{3}$$

where A is a constant dependent on temperature and the exponent $s \leq 1$.

It is also noticeable that σ_{ac} of all samples shows significant temperature dependence except for sample (c), where the temperature dependence decreases such that all curves become closer to each other.

Dependence of Loss Tangent $\tan\delta$ on Frequency

The variations of $\tan\delta$ with frequency at different temperatures are illustrated in Figure 4. In most physical interpretations of relaxation processes in polymers, a peak is assigned to a particular mode of motion in the main chain such as side chain or side group in the polymer matrix.[39]

It can be seen from Figure 4 that sample (a) exhibits only one peak, which shifts to higher frequencies as the temperature increases. This transport process is mainly due to activated hopping of π-electron so that the peak of $\tan\delta$ is suggested to occur when the most probable relaxation time of the hopping electrons coincides with the applied frequency. On the other hand, sample (b) does not exhibit any peaks within the studied frequency range. It is worth mentioning that in sample (c), $\tan\delta$ shows a minimum at $\approx$75 kHz; it is believed that at this frequency $\tan\delta$ approaches that of ideal capacitor. Also, this minimum gives sample (c) a high importance in resonance circuits.

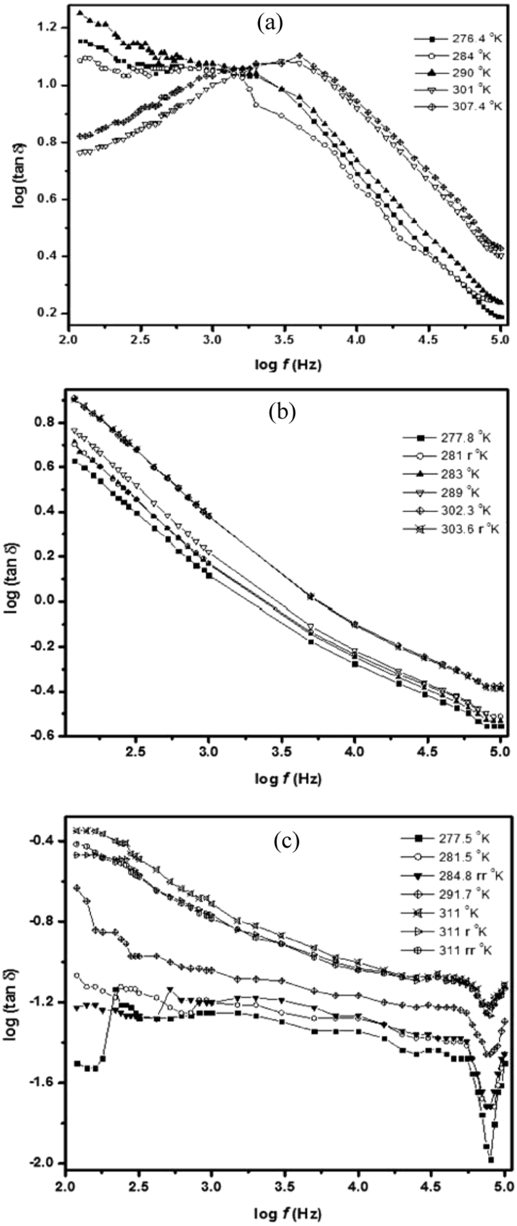


Figure 4. Variation of log (tan δ) with log frequency at different temperatures for PANI samples at different concentrations of H_2O_2 and aniline: (a) 0.2 M, (b) 0.4 M, and (c) 0.5 M.

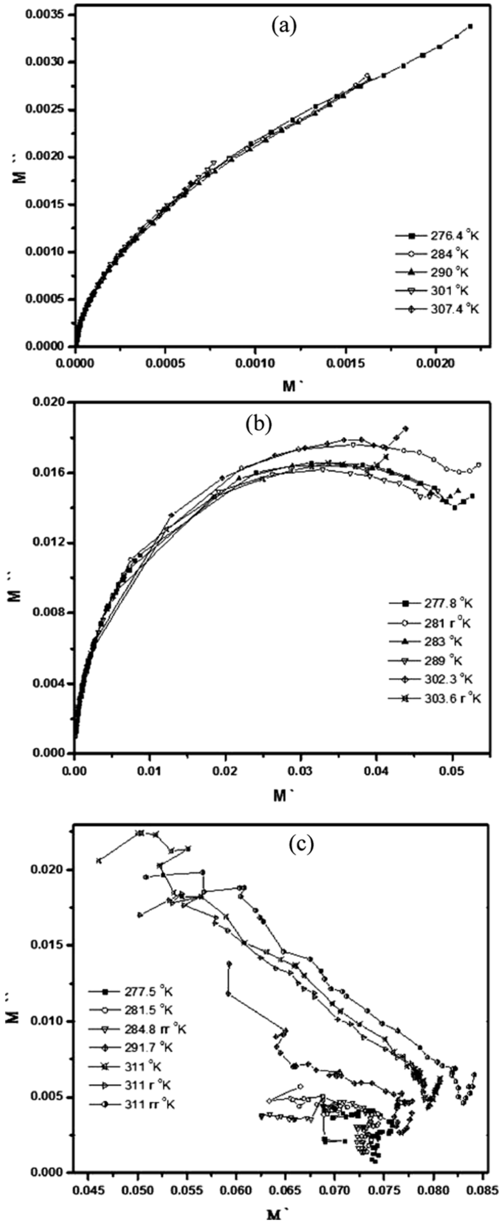
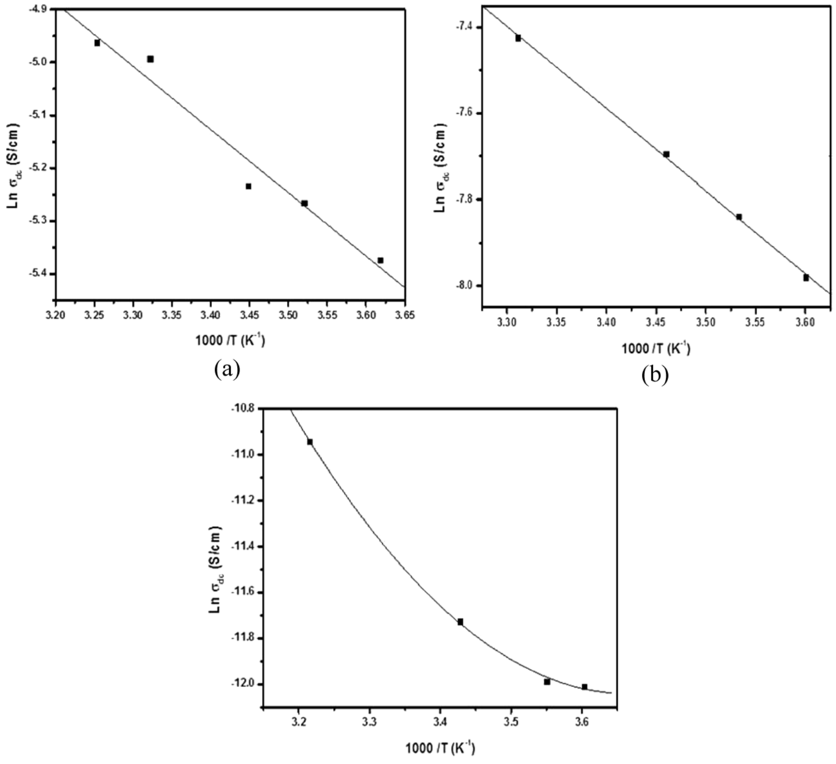


Figure 5. Complex plan for the electric modulus of PANI samples at different concentrations of H_2O_2 and aniline: (a) 0.2 M, (b) 0.4 M, and (c) 0.5 M.

Cole-Cole Diagrams

Figure 5 shows the Cole-Cole relationship (M'' versus M') in complex impedance plane, which gives evidence of relaxation process. In this diagram, the implicit variable is the frequency, which increases from right to left. It is seen from Figure 5 that samples (a) and (b) obey the Debye relation, in which the data points lie closely on only one semicircle or arc, whereas sample (c) is a multiphase material, where the data were not collected within one semicircle because every curve represents one single phase of the assumed phases. In order to have evidence for this assumption, we draw the relation between ln σ_{dc} versus 1000/T for the samples, shown in Figure 6. It is obvious that for samples (a) and (b), ln σ_{dc} changes linearly with 1000/T, implying that there is one activation energy for one phase of material, whereas for sample (c) the relation is



(a) (b)

(c)

Figure 6. Temperature dependence of σ_{dc} plotted as ln (σ_{dc}) vs. 1000/T for different PANI samples: (a) sample (a), (b) sample (b), and (c) sample (c).

a curve with multiple tangents, implying several activation energies and, consequently, several phases in the material.

CONCLUSION

In general, for nonpolar polymers, ε' and ε'' are independent of temperature, but in the case of strong polar polymers ε' increases as the temperature increases. On the other hand, in weak polar polymers, ε' and ε'' decrease with increase in temperature. All samples are strong polar polymers except for sample (c). This last sample could be classified as a weak polar polymer.

The dependence of ac conductivity on frequency indicates that the conductivity of these samples is due to hopping process. The large value of ε' on low frequency originates mainly from electrode polarization rather than from the interfacial polarization within the material. The large value of ε' is due to the motion of free charge carrier within the material. As a result, a power-law dispersion in ε' is observed, and it does not reveal any peak in the measured frequency range.

The changes in H_2O_2 and aniline concentrations have notable effect on dielectric properties; therefore further work to study the effect of aniline concentration alone and H_2O_2 concentration alone on the dielectric properties for the polymer is currently in progress.

REFERENCES

[1] MacDiarmid, A. G., S. L. Mu, N. L. D. Somasiri, and W. Wu. (1985). Electrochemical characteristics of "polyaniline" cathodes and anodes in aqueous electrolytes. *Mol. Cryst. Liq. Cryst.* **121**, 187–190.

[2] Novak, P., K. Muller, K. S. V. Santhanam, and O. Hass. (1997). Electrochemically active polymers for rechargeable batteries. *Chem. Rev.* **97**, 207–282.

[3] Kobayashi, T., N. Yonevama, and H. Tamura. (1984). Electrochemical reactions concerned with electrochromism of polyaniline film-coated electrodes. *J. Electroanal. Chem.* **177**, 281–291.

[4] Batich, C. D., H. A. Laitinen, and H. C. Zhou. (1990). Chromatic changes in polyaniline films. *J. Electrochem. Soc.* **137**, 883–885.

[5] Kaneko, M., and H. Nakamura. (1985). Photoresponse of a liquid junction polyaniline film. *J. Chem. Soc. Chem. Commun.* **6**, 346–347.

[6] Dong, Y. H., and S. L. Mu. (1991). Photoelectrochemical behaviour of polyaniline affected by potentials and pH of solutions. *Electrochim. Acta* **36**, 2015–2018.

[7] Karg, S., J. C. Scott, J. R. Salem, and M. Angelopoulos. (1996). Increased brightness and lifetime of polymer light-emitting diodes with polyaniline anodes. *Synth. Met.* **80**, 111–117.

[8] Bartlett, P. N., and R. G. Whitaker. (1987–1988). Strategies for the development of amperometric enzyme electrodes. *Biosensors* **3**, 359–379.

[9] Yang, Y. F., and S. L. Mu. (1997). Bioelectrochemical responses of the polyaniline horseradish peroxidase electrodes. *J. Electroanal. Chem.* **432**, 71–78.

[10] Ayad, M. M., A. F. Rehab, I. S. El-Hallag, and W. A. Amer. (2007). Preparation and characterization of polyaniline films in the presence of N-phenyl-1,4-phenylenediamine. *Eur. Polym. J.* **43**, 2540–2549.

[11] Ayad, M. M., E. A. Zaki, and J. Stejskal. (2007). Determination of the dopant weight fraction in polyaniline films using a quartz-crystal microbalance. *Thin Solid Films* **515**, 8381–8385.

[12] Ayad, M. M., and E. A. Zaki. (2008). Quartz crystal microbalance and spectroscopy measurements for acid doping in polyaniline films. *Sci. Technol. Adv. Mater.* **9**, 015007 (10 pp).

[13] Ayad, M. M., N. A. Salahuddin, A. K. Abou-Seif, and M. O. Al-Ghayesh. (2008). Chemical synthesis and characterization of aniline and o-anthranilic acid copolymer. *Eur. Polym. J.* **44**, 426–435.

[14] Sun, Z., Y. Geng, J. Li, X. Wang, X. Jing, and F. Wang. (1999). Catalytic oxidization polymerization of aniline in an H_2O_2-Fe^{2+} system. *J. Appl. Polym. Sci.* **72**, 1077–1084.

[15] Sun, Z., Y. Geng, J. Li, X. B. Jing, and F. Wang. (1997). Chemical polymerization of aniline with hydrogen peroxide as oxidant. *Synth. Met.* **84**, 99–100.

[16] Inoue, H., Y. Kida, and E. Imoto. (1966). Vulcanized aniline black. Its electrical conductivity and catalysis upon the decomposition of hydrogen peroxide. *J. Bull. Chem. Soc. Jpn.* **39**, 551–555.

[17] Ayad, M. M., and E. A. Zaki. (2008). Synthesis and characterization of polyaniline films using Fenton reagent. *J. Appl. Polym. Sci.* **110**, 3410–3419.

[18] Pinto, N. J., P. D. Shah, P. K. Kahol, and B. J. McCormick. (1996). Dielectric constant and ac conductivity in polyaniline derivatives. *Solid State Commun.* **97**, 1029–1031.

[19] Singh, R., A. K. Narula, and R. P. Tandon. (1996). A.C. conductivity of poly(N-methylpyrrole). *Synth. Met.* **82**, 63–70.

[20] Matveeva, E. S., R. D. Calleja, and V. P. Parkhutik. (1996). Impedance study of chemically synthesized emeraldine form of polyaniline. *Electrochim. Acta* **41**, 1351–1357.

[21] Singh, R., V. Arora, R. P. Tandon, A. Mansingh, and S. Chandra. (1999). Dielectric spectroscopy of doped polyaniline. *Synth. Met.* **104**, 137–144.

[22] Capacciooli, S., M. Lucchesi, P. A. Rolla, and G. Ruggeri. (1998). Dielectric response analysis of a conducting polymer dominated by the hopping charge transport. *J. Phys. Condens. Mater.* **10**, 5595–5617.

[23] Han, M. G., and S. S. Im. (2001). Dielectric spectroscopy of conductive polyaniline salt films. *J. Appl. Polym. Sci.* **82**, 2760–2769.

[24] Abo El-Ata, A. M., and M. A. El-Hiti. (1997). Dielectric behavior in $BaCO_{2x}Fe\backslash boldmath_{12\text{-}2x}O_{19}$. *J. Phys. III* (France) **7**, 883–894.

[25] Macedo, P. B., C. T. Moynihan, and R. Bose. (1972). Role of ionic diffusion in polarization in vitreous ionic conductors. *Phys. Chem. Glasses* **13**, 171–179.

[26] Sengwa, R. J., and S. Sankhla. (2007). Dielectric dispersion study of coexisting phases of aqueous polymeric solution: Poly(vinyl alcohol) + poly(vinyl pyrrolidone) two-phase systems. *Polymer* **48**, 2737–2744.

[27] Campbell, J. A., A. A. Goodwin, and G. P. Simon. (2001). Dielectric relaxation studies of miscible polycarbonate/polyester blends. *Polymer* **42**, 4731–4741.

[28] Tsonos, C., L. Apekis, K. Viras, L. Stepanenko, L. Karabanova, and L. M. Sergeeva. (2001). Electrical and dielectric behavior in blends of polyurethane-based ionomers. *Solid State Ionics* **143**, 229–249.

[29] Stejskal, J., I. Sapurina, M. Trchova, and E. N. Konyushenko. (2008). Oxidation of aniline: Polyaniline granules, nanotubes, and oligoaniline microspheres. *Macromolecules* **41**, 3530–3536.

[30] McCrum, N. G., B. E. Read, and G. William. (1967). *Anelastic and Dielectric Effects in Polymeric Solids*. London: Wiley. pp. 108–111.

[31] Bakr, A. A., and A. M. North. (1977). Charge carrier hopping in poly(arylene vinylenes). *Eur. Polym. Sci.* **13**, 799–803.

[32] Hodge, I. M., and A. Eisenberg. (1978). Conductivity relaxation in an amorphous-iron-containing organic polymer. *J. Non-cryst. Solids* **27**, 441–443.

[33] Starkweather, H. W., and P. Avakian. (1992). Conductivity and the electric modulus in polymers. *J. Polym. Sci. B: Polym. Phys.* **30**, 637–641.

[34] Chen, S.-A., and C.-S. Liao. (1993). Conductivity relaxation and chain motions in conjugated conducting polymers: Neutral poly(3-alkylthiophenes). *Macromolecules* **26**, 2810–2816.

[35] Tsangaris, G. M., G. C. Psarras, and N. Kouloumbi. (1998). Electric modulus and interfacial polarization in composite polymeric systems. *J. Mater. Sci.* **33**, 2027–2037.

[36] Lee, H. T., K. R. Chuang, S.-A. Chen, P. K. Wei, J. H. Hsu, and W. Fann. (1995). Conductivity relaxation of 1-methyl-2-pyrrolidone-plasticized polyaniline film. *Macromolecules* **28**, 7645–7652.

[37] Ram, M. K., S. Annapoorni, S. S. Pandey, and B. D. Malhotra. (1998). Dielectric relaxation in thin conducting polyaniline films. *Polym. J.* **39**, 3399–3404.

[38] Dutta, P., S. Biswas, and S. K. De. (2002). Dielectric relaxation in polyaniline-polyvinyl alcohol composites. *Mater. Res. Bull.* **37**, 193–200.

[39] Mangion, M. B. M., and G. P. Johari. (1990). Relaxations of thermosets. III. Sub-Tg dielectric relaxations of bisphenol-A-based epoxide cured with different cross-linking agents. *J. Polym. Sci. Part B: Polym. Phys.* **28**, 71–83.