

Studies on the Dielectric Properties of Poly(*o*-toluidine) and Poly(*o*-toluidine-aniline) Copolymer

Honey John,¹ Rinku M. Thomas,¹ K. T. Mathew,² Rani Joseph¹

¹Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682 022, Kerala, India

²Department of Electronics, Cochin University of Science and Technology, Cochin 682 022, Kerala, India

Received 1 April 2003; accepted 23 October 2003

ABSTRACT: Poly(*o*-toluidine) (PoT) and poly(*o*-toluidine *co* aniline) were prepared by using ammonium persulfate initiator, in the presence of 1M HCl. It was dried under different conditions: room temperature drying (48 h), oven drying (at 50°C for 12 h), or vacuum drying (under vacuum, at room temperature for 16 h). The dielectric properties, such as dielectric loss, conductivity, dielectric constant, dielectric heating coefficient, loss tangent, etc., were studied at micro-

wave frequencies. A cavity perturbation technique was used for the study. The dielectric properties were found to be related to the frequency and drying conditions. Also, the copolymer showed better properties compared to PoT alone. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 592–598, 2004

Key words: Polyaniline; poly(*o*-toluidine); conductivity; frequency; poly(*o*-toluidine *co* aniline)

INTRODUCTION

The recent widespread use of conducting polymers, especially polyaniline, for various technological applications such as energy storage devices, sensors, and above all as a strong electromagnetic inductive (EMI)^{1,2} material has recently attracted significant attention with a growing interdisciplinary trend. Electrically conductive polymers are new and very effective materials for antistatic purposes. Polyaniline especially has been found to be a very effective material for antistatic applications.³ Electrically conducting polymers differ from inorganic crystalline semiconductors in two ways: they are molecular in character and also they lack long-range order.

Of the large variety of conducting polymers, polyaniline (Pani) has received much attention because of its unique reversible proton doping, high electrical conductivity, and ease of bulk preparation. However, to make polyaniline technologically viable, processability and thermal stability of the polymer have to be improved. Copolymerization may be a simple and convenient method to accomplish this task. The dc conductivity of poly(aniline *co o*-anisidine),⁴ poly(aniline-*co*-toluidine),^{5,6} and poly(aniline-*co*-*N*-butylaniline),^{7,8} copolymers investigated earlier yielded fruitful results.

Currently, an understanding of transport mechanisms in conducting polymers and the potential use of polymers as EMI shielding and absorbing materials have encouraged the measurement of dielectric behavior at high frequencies. Nagai and Rendell⁹ have summarized the theoretical and experimental aspects of ac conductivity and dielectric relaxation of polymers. Some studies on dielectric behavior of conducting polymers at microwave frequencies have been reported.^{10–14}

In this paper we report on the synthesis and dielectric properties in a microwave field, of poly(*o*-toluidine) (PoT) alone and its copolymer with aniline.

EXPERIMENTAL

Aniline and *o*-toluidine (reagent grade) were distilled prior to use. HCl and ammonium persulfate were used as received.

Preparation

Preparation of polyaniline

Chemical oxidative polymerization of aniline was carried out using ammonium persulfate as initiator in the presence of 1M HCl at 0–5°C. The reaction was carried out for 4 h. Polyaniline was also prepared at room temperature. The polymer formed was dried in an oven at 50°C for 12 h and pelletized. The dielectric conductivities of both samples were measured using a cavity perturbation technique.

Correspondence to: R. Joseph (rani@cusat.ac.in).

Preparation of poly(*o*-toluidine)

Chemical oxidative polymerization of *o*-toluidine was carried out using ammonium persulfate as initiator in the presence of 1M HCl. The polymerization was carried out for about 4 h at room temperature. It was then filtered washed and dried under different conditions: room temperature (48 h), in an oven (at 50°C for 12 h), or in a vacuum (at room temperature, under vacuum for 16 h). The dielectric properties and conductivities of these samples were measured using the cavity perturbation technique.

Preparation of poly(*o*-toluidine-*co*-aniline)

The copolymer was prepared by the chemical oxidative polymerization of equal proportions of aniline and *o*-toluidine using ammonium persulfate as initiator in the presence of 1M HCl. The polymerization was carried out for about 4 h at room temperature. It was then filtered, washed, and dried under different conditions as described for *o*-toluidine. The dielectric properties and conductivities of these samples were measured using the same technique.

Experimental set up and theory

The experimental set up¹⁵ consists of a HP8510 vector network analyzer, sweep oscillator, S-parameter test set, and rectangular cavity resonator. The measurements were done at 25°C in the S band (2–4 GHz). When a dielectric material is introduced in a cavity resonator at the position of maximum electric field, the contribution of magnetic field for the perturbation is at a minimum. The field perturbation is given by Kupfer et al.¹⁶

$$-\frac{d\Omega}{\Omega} \approx \frac{(\epsilon_r^- - 1) \int_{V_s} \mathbf{E} \times \mathbf{E}_0^* dV}{2 \int_{V_c} |\mathbf{E}_0|^2 dV} \quad (1)$$

Where $d\Omega$ is the complex frequency shift. V_c and V_s are the volumes of the cavity and sample, respectively. \mathbf{E} and \mathbf{E}_0 are the perturbed and unperturbed fields in the cavity. ϵ_r^- is the relative complex permittivity of the sample material. Complex frequency shift is related to the quality factor, Q , as

$$\frac{d\Omega}{\Omega} \approx \frac{d\omega}{\omega} + \frac{j}{2} \left[\frac{1}{Q_s} - \frac{1}{Q_0} \right] \quad (2)$$

Q_s and Q_0 are the quality factors of cavity with and without the sample. Quality factor Q is given by $Q = f/\Delta f$, where f is the resonant frequency and Δf is the

corresponding 3-dB bandwidth. For small samples we assume that $E = E_0$ and, for dominant TE_{10p} mode in a rectangular wave guide,

$$E_0 = E_{0\max} \sin(\pi x/a) \sin(\pi p z/d), \quad p = 1, 2, 3, \dots \quad (3)$$

From eqs. (1) to (3) the real and imaginary parts of the relative complex permittivity are given by

$$\epsilon_r' = 1 + \frac{f_0 - f_s}{2f_s} \left(\frac{V_c}{V_s} \right) \quad (4)$$

$$\epsilon_r'' = \frac{V_c}{4V_s} \left(\frac{Q_0 - Q_s}{Q_0 Q_s} \right) \quad (5)$$

The real part of the complex permittivity, ϵ_r' , is generally known as the dielectric constant and the imaginary part ϵ_r'' of the complex permittivity is related to the dielectric loss of the material.

The loss tangent is given by

$$\tan \delta = \sigma + \omega \epsilon_r'' / \omega \epsilon_r' \quad (6)$$

Here, $\sigma + \omega \epsilon_r''$ is the effective conductivity of the medium. When the conductivity σ due to free charge is negligibly small (good dielectric), the effective conductivity is due to electric polarization and is reduced to

$$\sigma_e = \omega \epsilon_r'' = 2 \times \pi \times f \times \epsilon_0 \times \epsilon_r'' \quad (7)$$

The efficiency of heating is usually compared¹⁷ by means of a comparison coefficient, J , which is defined as

$$J = 1/\epsilon_r \tan \delta. \quad (8)$$

The absorption of electromagnetic waves when it passes through the medium is given by the absorption coefficient¹⁸ (α_f), which is defined as

$$\text{Absorption coefficient } (\alpha_f) = \epsilon_r'' f / n c \quad (9)$$

where $n = \sqrt{\epsilon_r'}$ and c is the velocity of light.

Penetration depth, also called as skin depth, is basically the effective distance of penetration of an electromagnetic wave into the material,¹⁹

$$\text{Skin depth } (\delta_f) = 1/\alpha_f \quad (10)$$

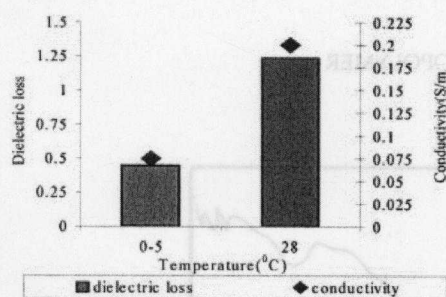


Figure 1 Effect of preparation condition on dielectric loss and conductivity at 2.97 GHz.

RESULTS AND DISCUSSION

Effect of polymerization condition on dielectric properties

Figure 1 shows the dielectric loss and conductivity of polyaniline prepared at 0–5°C and room temperature (28°C) at 2.97 GHz. It is clear from the figure that the dielectric loss and conductivity are higher for polyaniline prepared at room temperature. In a microwave field dielectric loss occurs due to the dipolar polarization. The dipolar polarization in an ac field leads to dielectric relaxation due to orientation polarization. Dielectric relaxation²⁰ is the lag in dipole orientation behind an alternating electric field and under the influence of which the polar molecules of a system rotate toward an equilibrium distribution in molecular orientation with a corresponding dielectric polarization. When the polymerization temperature of aniline is increased, head-to-head sequence of polyaniline is favored compared to head-to-tail sequence. This will induce a steric hindrance with a slight rotation of the two neighboring cycles as a consequence of this constraint. The effect of this rotation is a weaker overlap of π orbitals and therefore weaker delocalization of electrons along the chain. This leads to a high intra-chain phenomenon and will increase the dielectric loss.²¹ Therefore polyaniline prepared at room temperature (28°C) gives higher dielectric loss.

Since the conductivity in a microwave field is directly related to the dielectric loss factor, the conductivity is also higher for polyaniline prepared at room temperature.

Dielectric properties of PoT and PoT-Pani copolymer

Characterization of copolymer

Figures 2, 3, and 4 show the IR spectra of polyaniline, PoT, and poly(*o*-toluidine co aniline). The IR spectra of polyaniline and PoT are similar. The characteristic peaks of polyaniline and PoT at 1,305 cm^{-1} , due to C–H deformation, and 1,495 and 1,560 cm^{-1} , due to

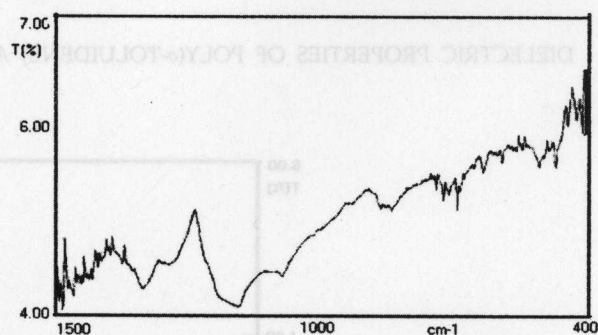


Figure 2 IR spectra of polyaniline alone.

the ring stretching modes of the quinoid and benzenoid rings, are similar in the copolymer as well. The characteristic peak at 1,150 cm^{-1} for the conducting Pani²² and PoT (1,149 cm^{-1}) salt is also present in the copolymer (1,151 cm^{-1}).

Dielectric conductivity

Figure 5(a) and (b) shows the variation of the dielectric loss of PoT alone and the PoT-Pani copolymer at different drying conditions, respectively. The dielectric loss is found to be high at lower frequency. The dielectric loss is a direct function of the relaxation process and the origin of this relaxation is due to the local motion of polar groups. The dielectric loss is very high at very low frequencies due to the free charge motion within the material.^{23,24} For very low frequencies there is time for charges to build up at the interfaces before the field changes direction and this contributes to the high dielectric loss at lower frequencies. The dielectric loss factor leads to the so-called "conductivity relaxation." The microwave conductivity is a direct function of dielectric loss. Figure 6(a) and (b) shows that the conductivity of PoT alone and copolymer at different drying conditions changes with frequency, depends upon the dielectric loss factor, and therefore shows the same behavior as the dielectric loss factor. Protonation in Pani²⁵ and PoT leads to the formation

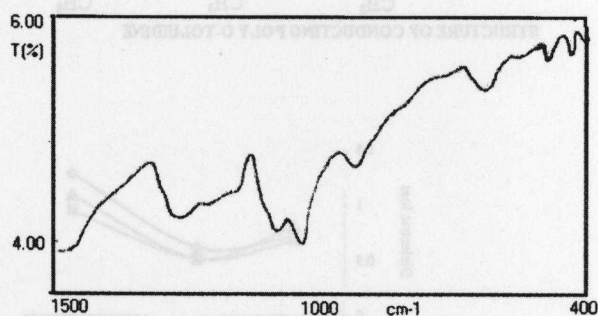


Figure 3 IR spectra of poly(*o*-toluidine) alone.

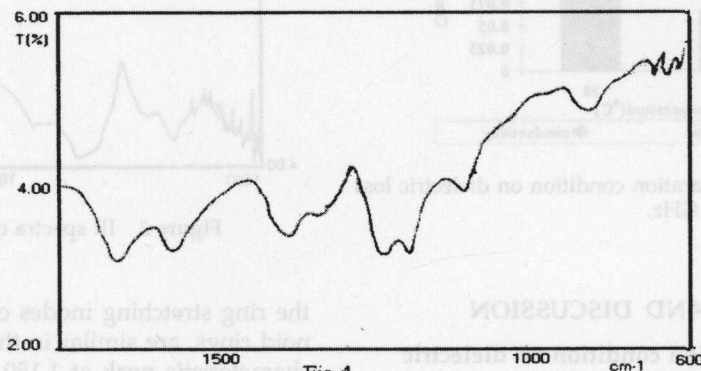
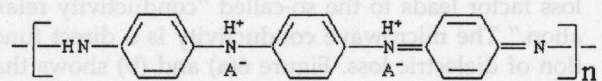


Figure 4 IR spectra of poly(*o*-toluidine *co* aniline).

of radical cations by an internal redox reaction, which causes reorganization of the electronic structure to give semiquinone radical cations. The degree of protonation and the electronic conductivity thus become a function of dopant concentration.

It is evident from the experiment that there is a loss of dopant molecules under vacuum and during high-temperature drying, which will reduce the dielectric loss, which, in turn, reduces the conductivity. The figures also show that the microwave conductivity of the room temperature dried sample is greater compared to the oven dried sample, which, in turn, is superior to the vacuum dried sample.



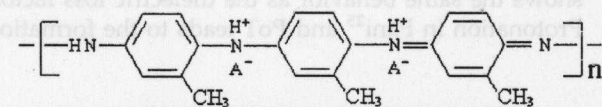
EXPECTED STRUCTURE OF CONDUCTING COPOLYMER

Dielectric constant (ϵ'_r)

Figure 7(a) and (b) shows that the dielectric constant is higher at very low and at very high frequencies. The alternating accumulation of charges, at the interphases between different phases of materials, due to the orientation polarization of the dipoles under the influence of an alternating field, causes a high dielectric constant.

Loss tangent ($\tan\delta$)

Figure 8(a) and (b) shows the variation of loss tangent with frequency of PoT alone and PoT:Pani copolymer. For a good dielectric material loss tangent ($\tan\delta$), which is defined as ϵ''_r/ϵ'_r , is directly related to the dielectric loss factor and hence will show the same behavior as that of the dielectric loss factor.



STRUCTURE OF CONDUCTING POLY *o*-TOLUIDINE

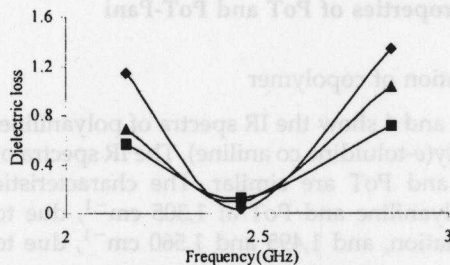
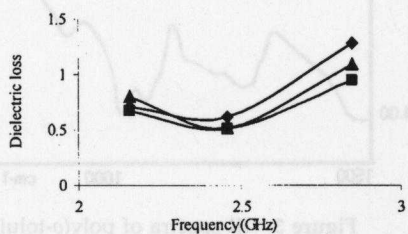


Figure 5 Variation of dielectric loss of (a) PoT alone and (b) copolymer, with frequency at different drying conditions (♦, room temperature dried; ■, vacuum dried; ▲, oven dried).

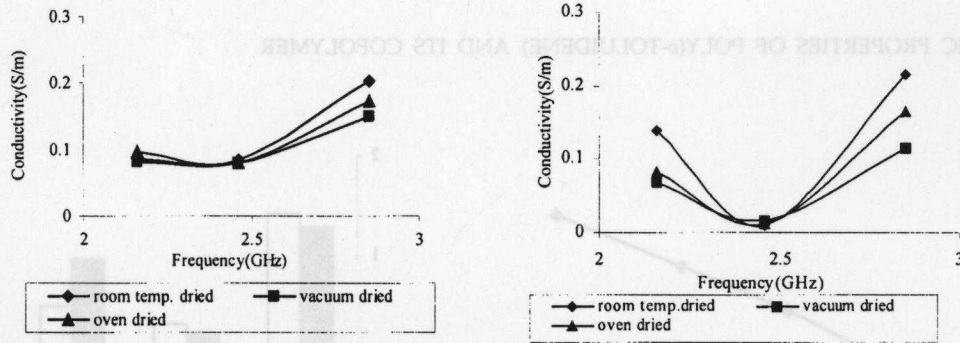


Figure 6 Variation of conductivity of (a) PoT alone and (b) copolymer, with frequency at different drying conditions (◆, room temperature dried; ■, vacuum dried; ▲, oven dried).

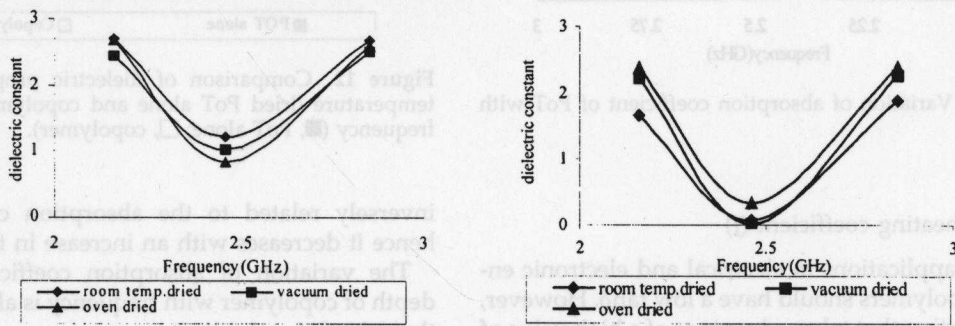


Figure 7 Variation of dielectric constant of (a) PoT alone and (b) copolymer, with frequency at different drying conditions (◆, room temperature dried; ■, vacuum dried; ▲, oven dried).

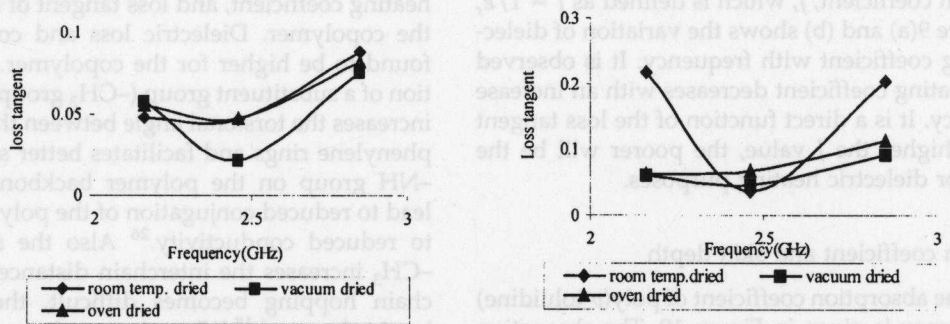


Figure 8 Variation of dielectric heating coefficient of (a) PoT alone and (b) copolymer, with frequency at different drying conditions (◆, room temperature dried; ■, vacuum dried; ▲, oven dried).

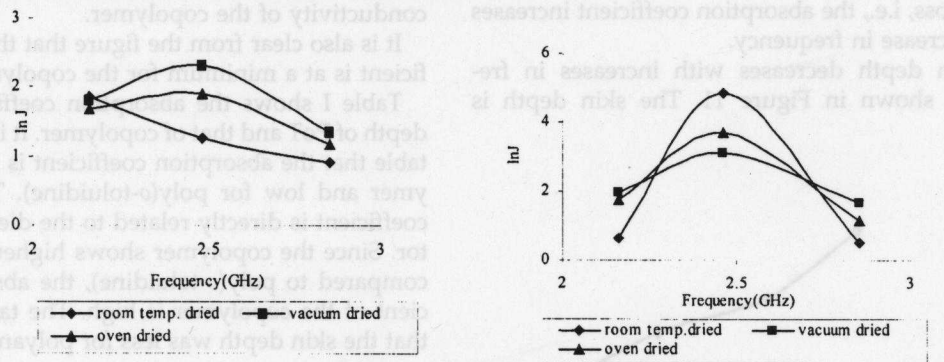


Figure 9 Variation of loss tangent of (a) PoT alone and (b) copolymer, with frequency at different drying conditions (◆, room temperature dried; ■, vacuum dried; ▲, oven dried).

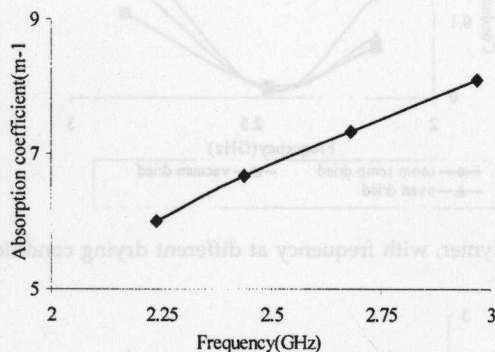


Figure 10 Variation of absorption coefficient of PoT with frequency.

Dielectric heating coefficient (J)

For many applications in electrical and electronic engineering polymers should have a low $\tan\delta$. However, one application that takes advantage of a high value of $\tan\delta$ is high frequency dielectric heating. The efficiency of heating is usually compared by means of a comparison coefficient, J , which is defined as $J = 1/\epsilon_r \tan\delta$. Figure 9(a) and (b) shows the variation of dielectric heating coefficient with frequency. It is observed that the heating coefficient decreases with an increase in frequency. It is a direct function of the loss tangent $\tan\delta$. The higher the J value, the poorer will be the polymer for dielectric heating purposes.

Absorption coefficient and skin depth

A plot of the absorption coefficient of poly(*o*-toluidene) with frequency is given in Figure 10. The absorption coefficient is directly related to the dielectric loss factor and therefore it shows the same behavior as that of dielectric loss, i.e., the absorption coefficient increases with an increase in frequency.

The skin depth decreases with increases in frequency as shown in Figure 11. The skin depth is

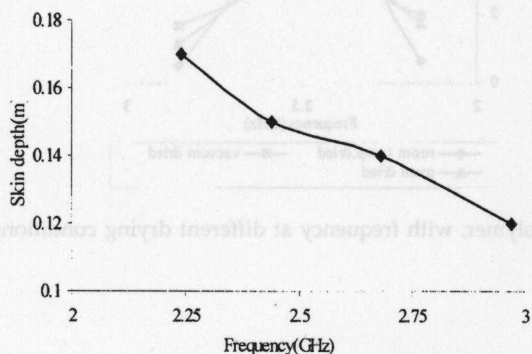


Figure 11 Variation of skin depth of PoT with frequency.

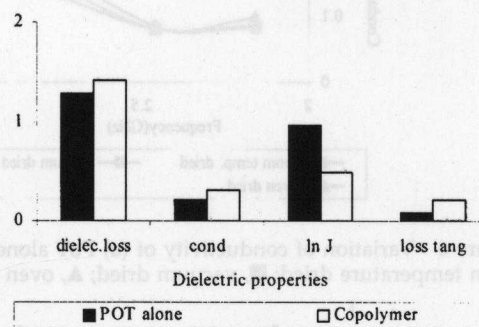


Figure 12 Comparison of dielectric properties of room temperature dried PoT alone and copolymer at 2.85 GHz frequency (■, PoT alone; □, copolymer).

inversely related to the absorption coefficient and hence it decreases with an increase in frequency.

The variation of absorption coefficient and skin depth of copolymer with frequency is also the same as that of poly(*o*-toluidene).

Figure 12 shows the variation of dielectric properties, such as dielectric loss, conductivity, dielectric heating coefficient, and loss tangent of PoT alone, and the copolymer. Dielectric loss and conductivity are found to be higher for the copolymer. The introduction of a substituent group ($-\text{CH}_3$ group in *o*-toluidene) increases the torsional angle between the two adjacent phenylene rings and facilitates better solvation at the $-\text{NH}$ group on the polymer backbone. This would lead to reduced conjugation of the polymer and hence to reduced conductivity.²⁶ Also the steric effect of $-\text{CH}_3$ increases the interchain distance and, as interchain hopping becomes difficult, the conductivity level is lowered.¹⁸ When the copolymer is prepared, a part of the poly(*o*-toluidene) is replaced with highly conducting polyaniline, which, in turn, increases the conductivity of the copolymer.

It is also clear from the figure that the heating coefficient is at a minimum for the copolymer.

Table I shows the absorption coefficient and skin depth of PoT and that of copolymer. It is clear from the table that the absorption coefficient is high for copolymer and low for poly(*o*-toluidene). The absorption coefficient is directly related to the dielectric loss factor. Since the copolymer shows higher dielectric loss compared to poly(*o*-toluidene), the absorption coefficient of the copolymer is high. The table also shows that the skin depth was less for polyaniline alone and

TABLE I
Absorption Coefficient and Skin Depth at 2.97 GHz

	POT alone	Copolymer
Absorption coefficient(m^{-1})	8.1	14.72
Skin depth(m)	0.12	0.07

TABLE II
Dielectric Properties of Base Form of the Copolymer

Frequency (GHz)	Dielectric loss	Conductivity (S/m)	Dielectric heating coefficient	Absorption coefficient (m^{-1})
2.17	0.386	0.05	2.37	0.42
2.46	0.373	0.049	5.88	0.17
2.86	0.74	2.9	12.43	0.08

copolymer. Therefore the copolymer is more opaque to electromagnetic radiation compared to poly(*o*-toluidine).

Table II shows the dielectric properties of the base form of copolymer. The dielectric loss, conductivity, and absorption coefficients are less and the dielectric heating coefficient is high for the base form of the copolymer.

CONCLUSION

The dielectric properties of poly(*o*-toluidine) and poly(*o*-toluidine *co* aniline) are found to be related to the frequency. The microwave conductivity of poly(*o*-toluidine) and poly(*o*-toluidine *co* aniline) are found to be related to the dopant concentration, and the conductivity is decreased when the amount of dopant molecules is decreased. Also the conductivity of the poly(*o*-toluidine *co* aniline) copolymer is found to be higher than the conductivity of poly(*o*-toluidine) alone. The dielectric heating coefficient is found to be at a minimum for the copolymer and the copolymer can be used for dielectric heating applications. The absorption coefficient of poly(*o*-toluidine) is found to be less compared to the copolymer. The penetration depth of the copolymer is found to be less and the copolymer can be used in EMI shielding applications.

References

- Lee, N. L.; Ong, L. H. *J Appl Electrochem* 1992, 22, 512.
- Trinidad, F.; Montemayer, M. C.; Falas, E. *J Electrochem Soc* 1991, 138, 3186.
- Peltola, J.; Cao, Y.; Smith, P. *Adhesives Age* 1995, 39, 18.
- Kathirgamanathan, P.; Adams, P. N.; Quill, K.; Underhill, E. *J Mater Chem* 1991, 1, 141.
- Wei, Y.; Hariharan, A.; Patel, S. A. *Macromolecules* 1990, 23, 758.
- Dhawan, S. K.; Trivedi, D. C. *Synth Met* 1993, 60, 63.
- Bergeron, J. Y.; Dao, L. H. *Macromolecules* 1992, 25, 3332.
- Ye, S.; Besner, S.; Dao, L. H.; Vijh, A. K. *J Electroanal Chem* 1995, 381, 71.
- Nagai, K. L.; Rendell, R. W. *Handbook of conducting polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.
- Feldblum, A.; Park, Y. W.; Heeger, A. J.; MacDiarmid, A. G.; Wnek, G.; Karasz, F.; Chien, J. C. W. *J Polym Sci: Polym Phys Edn* 1981, 19, 173.
- Phillips, G.; Suresh, R.; Waldman, J.; Kumar, J.; Chen, J. I.; Tripathy, S.; Huang, J. C. *J Appl Phys* 1991, 69, 899.
- Unsworth, J.; Kaynak, A.; Lunn, B. A.; Beard, G. E. J. *Mater Sci* 1993, 28, 3307.
- Buckley, L. J.; Dudeck, K. E. *Synth Met* 1992, 52, 353.
- Javadi, H. H. S.; Cromack, K. R.; MacDiarmid, A. G.; Epstein, A. *J Phys Rev (B)* 1989, 39, 3579.
- Mathew, K. T.; Raveendranath, U. *Microwave Optical Technol Lett* 1993, 6, 104-106.
- Kupfer, K.; Kraszewski, A.; Knochel, R. *Sensors Update Vol 7 and Microwave Sensing of Moist Materials Food and Other Dielectrics*; Wiley-VCH: Germany, 2000; pp. 186-209.
- Chen, C. K.; Liepens, R. *Electrical Properties of Polymers: Chemical Principles*; Hanser Publishers: Munich, 1987.
- Bradford, L. S.; Carpentier, M. H. *The Microwave Engineering Handbook*; Chapman and Hall: London, 1993.
- Stephen, C. W.; Frederic, H. L. *Microwaves Made Simple: Principles and Applications*; United States Bookcrafters, Chelsea, 1985.
- Debye, P. *Polar Molecules*; Chemical Catalog Co.: New York, 1929.
- Olmedo, L.; Hourquebie, P.; Jousse, F. *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley: New York, 1997; Vol. 3, Chapter 8.
- Anand, J.; Rao, P. S.; Palaniappan, S.; Sathyanarayana, D. N. *Macromolecules New Front* 1998, 1, 374.
- Maccallum, R. J.; Vincent, C. A. *Polymer Electrolyte Reviews II*; Elsevier Applied Science Publishers Ltd: London and New York, 1987; Chapter 2.
- Kyritsis, A.; Pissis, P.; Grammatikakis, J. *J Polym Sci Part B: Polym Phys* 1995, 33, 1737.
- John, H.; Bijukumar, S.; Mathew, K. T.; Joseph, R. *J Appl Polym Sci* 2002, 83, 2008.
- Maruthamuthu, M.; Harichandran, G.; Jeyakumar, D. *Macromolecules New Front* 1998, 1, 359.