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Conducting Polyaniline Composites as Microwave Absorbers

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Conducting polymers are excellent microwave absorbers and they show technological advantage when compared with inorganic electromagnetic absorbing materials, being light weight, easily processable, and the ability of changing the electromagnetic properties with nature and amount of dopants, synthesis conditions, etc. In this paper we report the synthesis, dielectric properties, and expected application of conducting composites based on polyaniline (PAN). Cyclohexanone soluble conducting PAN composites of microwave conductivity 12.5 S/m was synthesized by the in situ polymerization of aniline in the presence of emulsion grade polyvinyl chloride. The dielectric properties of the composites, especially the dielectric loss, conductivity, dielectric heating coefficient, absorption coefficient, and penetration depth, were studied using a HP8510 vector network analyzer. The microwave absorption of the composites were studied at different frequency bands i.e, S, C, and X bands (2–12 GHz). The absorption coefficient was found to be higher than 200 m^{-1} and it can be used for making microwave absorbers in space applications. POLYM. COMPOS., 28:588–592, 2007. © 2007 Society of Plastics Engineers

INTRODUCTION

Electrically conducting polymers have attracted a significant attention from all polymer branches with a growing interdisciplinary trend because of their various technological applications such as energy storage devices, sensors, and above all as a strong EMI [1, 2] material. With a large variety of conducting polymers, polyaniline (PAN) has emerged as one of the most promising conducting polymers because of its good environmental stability and adequate level of electrical conductivity [3–5].

However, to make PAN technologically viable, processability and thermal stability of polymer have to be improved. Copolymerization may be a simple and convenient method to accomplish this task. Incorporation of conducting polymer in to a host polymer substrate forming a blend, composite, or inter penetrated bulk network has been widely used as an approach to combine electrical conductivity with desirable physical properties of polymers [6, 7]. PAN is considered as one of the most promising candidate/s for the fabrication of conductive blends/composites with industrially important classical polymers [8].

Understanding of transport mechanisms in conducting polymers and the potential use of it as EMI shielding and absorbing materials have encouraged the study of dielectric behaviour at high frequencies. Nagai and Rendell [9] have summarized the theoretical and experimental aspects of a.c conductivity and dielectric relaxation of polymers. Some studies on dielectric behaviour of conducting polymers at microwave frequencies are also reported [10–14].

The dc and ac conductivity of PAN/polyvinyl-alcohol blends [15]and PAN and zinc sulfide composites were studied in the microwave field [16]. There are a number of papers dealing with this composite. Banerjee and Mandal [17, 18] have prepared blends of HCl doped PAN nanoparticles with polyvinyl chloride (PVC). PAN–PVC composite films prepared by solution blending in the presence of phosphoric acid and HCl as the dopants were also reported [19, 20]. A processable PAN/PVC composite was prepared by dispersing PAN in PVC matrix by mechanical mixing and then compression moulding in a hot press [21]. The electrochromic behaviour of PAN–PVC composite films with structural changes in PAN, using FTIR studies, were also reported [22]. Kaiser et al. [23] have recently reported the conductivity and thermopower data for PAN blends with PVC, which showed an increase in conductivity at lower temperature.

EXPERIMENTAL

Preparation of PAN in Pellet Form

Chemical oxidative polymerization [24] of aniline was carried out using ammonium per sulphate initiator in the presence of 1 M HCl at room temperature for 4 hr. The

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polymer formed was dried at 50–60°C for 6 hr and then it was pelletized. The dielectric properties and the conductivity of these samples were measured using cavity perturbation technique. PAN was dedoped to study the effect of different dopants. PAN was doped with different dopants such as H_2SO_4, HNO_3, toluene sulfonic acid, camphor sulfonic acid, $HClO_4$, etc. Also to study the effect of the amount of HCl dopant on the dielectric properties, PAN was doped with different molar concentrations of HCl.

Preparation of PAN–PVC Composite in Film Form

Chemical oxidative polymerization of aniline was carried out using ammonium per sulphate as initiator in the presence of emulsion grade PVC solution in cyclohexanone. The polymerization was carried out for about 4 hr at room temperature. It was then made in to film by solution casting and was doped with 1M HCl. The dielectric properties and conductivity of these composites were measured using cavity perturbation technique. Different compositions of PAN–PVC composites, say 1:0.5, 1:1, 1:1.5, 1:2, were prepared using the earlier procedure. Studies were conducted in S, C, and X bands of microwave frequencies.

Set Up and Theory

The dielectric properties of PAN and its composites were measured using cavity perturbation technique [25]. The experimental set up [26] consists of a HP8510 vector network analyzer, sweep oscillator, and rectangular cavity resonator. The measurements were done at 25°C in S band (2–4 GHz). In cavity perturbation technique for accuracy of results, the volume of the sample should be less than 1/1000th of the volume of the cavity. Because of this size limitation, the measurements on pellet samples were conducted in the S band only. 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 minimum. The field perturbation is given by Kupfer et al. [27].

The real and imaginary parts of the relative complex permittivity are given by $\varepsilon_r' = 1 + \frac{f_0 - f_s}{2f_s}\left(\frac{V_c}{V_s}\right)$, $\varepsilon_r'' = \frac{V_c}{4V_s}\left(\frac{Q_0 - Q_s}{Q_0 Q_s}\right)$. The real part of the complex permittivity (ε_r') is generally known as 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 $\tan\delta = \sigma + \omega\varepsilon_r''/\omega\varepsilon_r'$. Here, $\sigma + \omega\varepsilon_r''$ 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 $\sigma_e = \omega\varepsilon'' = 2_* \pi_* f_* \varepsilon_0 {}_* \varepsilon_r''$. The efficiency of heating is usually compared by means of a comparison Coefficient [28] J, which is defined as $J = 1/\varepsilon_r \tan\delta$. The absorption of electromagnetic waves when it passes through the medium is given by the absorption coefficient [29] (α_f), which is defined as, absorption coefficient (α_f) = $\varepsilon_r'' f/n\, c$, where $n = \sqrt{\varepsilon^*}$ 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 [30], skin depth (δ_f) = $1/\alpha_f$.

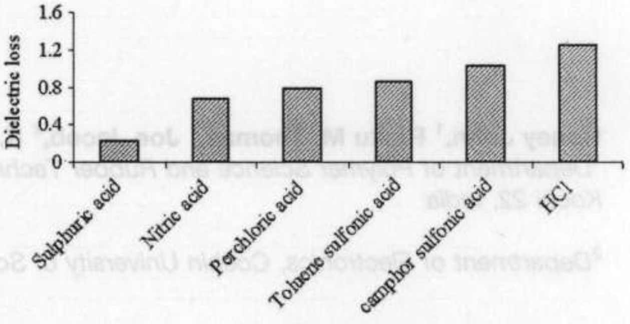

FIG. 1. Effect of different dopants on dielectric loss of PAN in pellet form.

The amplitude responses of S band cavity are shown in Fig. 1. Schematic diagram of the experimental set-up consisting of a transmission type cavity resonator, HP8510 C network analyzer and an interfacing computer and the S band cavity is shown in Fig. 2.

RESULTS AND DISCUSSION

Figures 1 and 2 show the effect of different dopants on dielectric loss and conductivity of the PAN in pellet form, respectively. It was clear from the figures that the dielectric loss and conductivity were greater for HCl doped PAN. When the polar group is large, or the viscosity of the medium is very high, the rotatory motion of the molecule is not sufficiently rapid for the attainment of equilibrium with the field [31]. In the case of HCl dopant, the size is less when compared to all other dopants and hence it shows better relaxation phenomenon, which increases dielectric

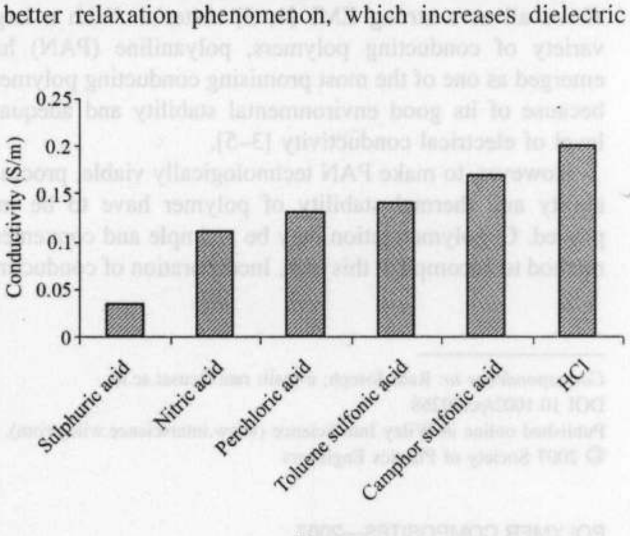

FIG. 2. Effect of different dopants on conductivity of PAN in pellet form.

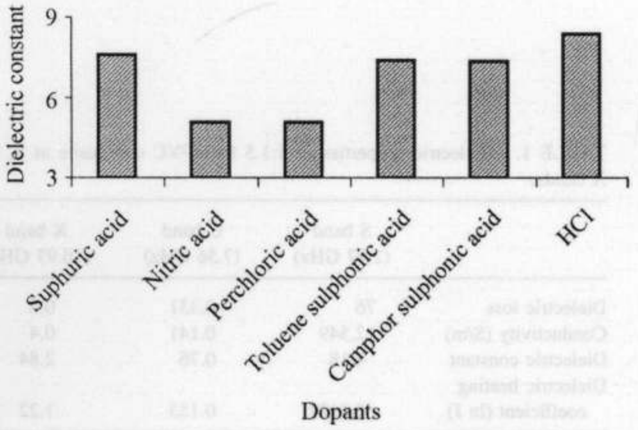

FIG. 3. Effect of different dopants on dielectric constant of PAN in pellet form.

loss. Since the conductivity is directly related to the dielectric loss factor the conductivity is also higher for HCl doped samples. Also in the case of HCl dopant, the doping is not diffusion limited and the counter anion (Cl^-) is homogeneously distributed in the material [32]. Figure 3 shows the variation of dielectric constant of different doped samples at 2.97 GHz. It was clear from the figure that the dielectric constant of HCl doped sample is high compared to other dopants. When the size of the dopants are high, the inter chain distance between the polymer chains increase, which result in a decreased capacitive couplings and hence the dielectric constant is low [33]. Figure 4 shows the effect of different dopants on the dielectric heating coefficient of PAN. It was clear from the figure that the dielectric heating coefficient was minimum for HCl doped sample. The dielectric heating coefficient is inversely related to the dielectric loss factor and hence the HCl doped samples shows the minimum value. The higher the heating coefficient the poorer is the heating property.

Figures 5 and 6 shows the variation of conductivity and dielectric heating coefficient of PAN doped with different molar concentrations of HCl, respectively. It indicates that the conductivity is not much influenced by the molarity of HCl i.e., the 1 M HCl is enough to produce the maximum conductivity.

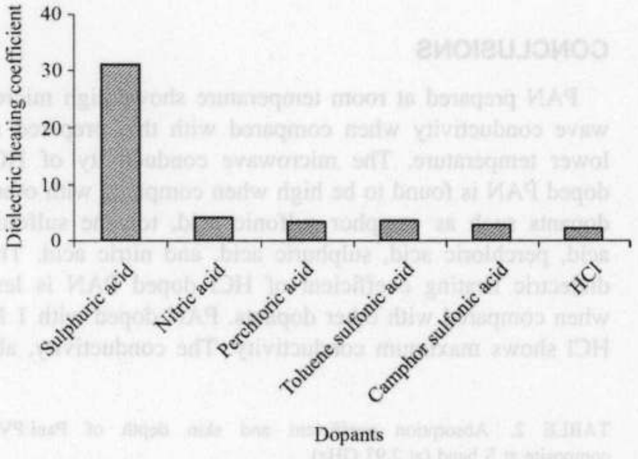

FIG. 4. Effect of different dopants on dielectric heating coefficient of PAN in pellet form.

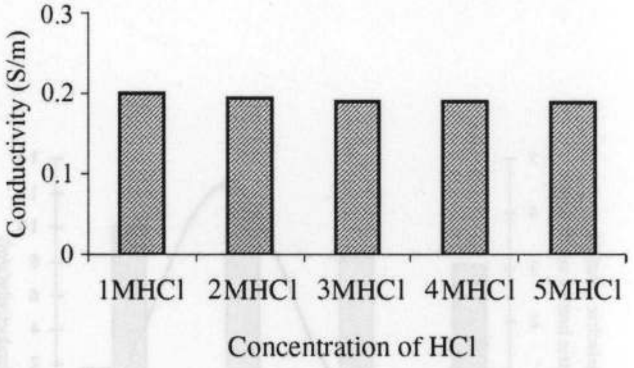

FIG. 5. Effect of concentration of HCl on conductivity of PAN in pellet form.

Variation of Dielectric Properties of Composites with Compositions

Figures 7, 8, and 9 show the variation of conductivity, dielectric constant, and dielectric heating coefficient of dif-

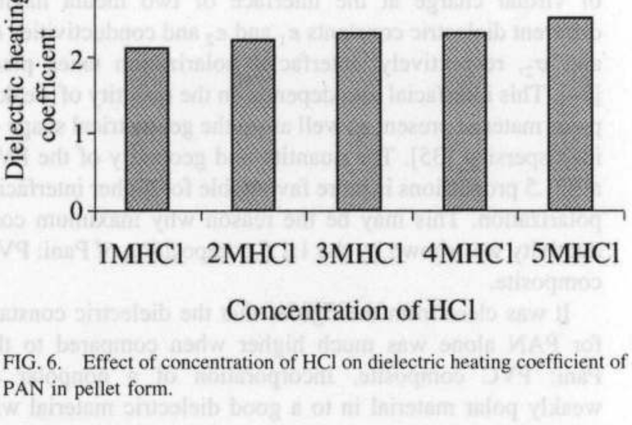

FIG. 6. Effect of concentration of HCl on dielectric heating coefficient of PAN in pellet form.

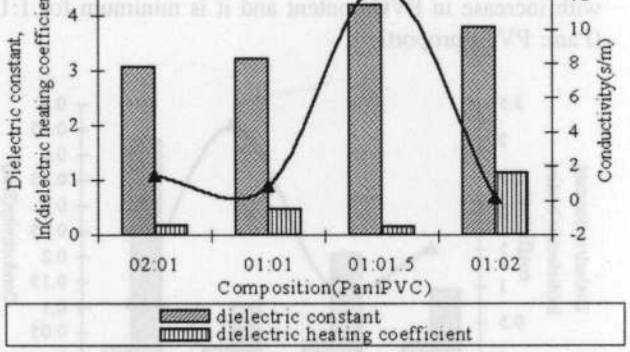

FIG. 7. Dielectric properties of Pani: PVC composite in film form at S band.

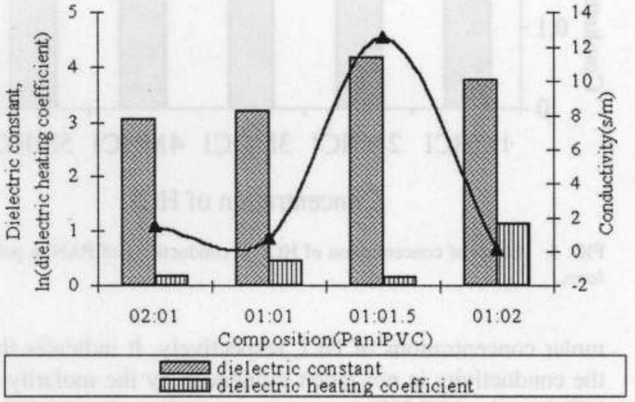

FIG. 8. Dielectric properties of Pani: PVC composite in film form at C band.

ferent proportions of Pani: PVC composites in S, C, and X bands, respectively. Eventhough, basically PVC is an insulator, the conductivity of the base conducting polymer (PAN) increases on adding PVC and it reaches a maximum for 1:1.5 proportion, irrespective of the bands as shown in the figures. In heterogeneous dielectrics, the accumulation of virtual charge at the interface of two media having different dielectric constants ε_1 and ε_2 and conductivities σ_1 and σ_2, respectively, interfacial polarization takes place [34]. This interfacial loss depends on the quantity of weakly polar material present as well as on the geometrical shape of its dispersion [35]. The quantity and geometry of the PVC at 1:1.5 proportions is more favourable for higher interfacial polarization. This may be the reason why maximum conductivity was shown by the 1:1.5 composition of Pani: PVC composite.

It was clear from the figures that the dielectric constant for PAN alone was much higher when compared to the Pani: PVC composite. Incorporation of a nonpolar or weakly polar material in to a good dielectric material will decrease the dielectric constant. It was also clear from the figures that the dielectric heating coefficient is decreased with increase in PVC content and it is minimum for 1:1.5 (Pani: PVC) proportion.

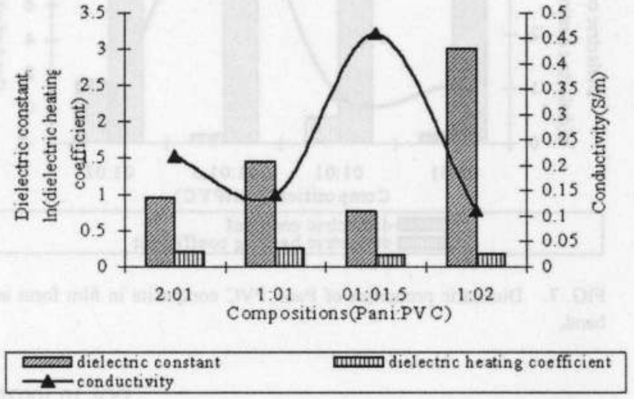

FIG. 9. Dielectric properties of Pani: PVC composite in film form at X band.

TABLE 1. Dielectric properties of 1:1.5 Pani:PVC composite at S, C, X bands.

	S band (2.97 GHz)	C band (7.56 GHz)	X band (10.97 GHz)
Dielectric loss	76	0.331	0.6
Conductivity (S/m)	12.549	0.141	0.4
Dielectric constant	4.18	0.76	2.84
Dielectric heating coefficient (ln J)	0.0122	0.153	1.22

Table 1 shows the variation of conductivity, dielectric loss, dielectric constant, and dielectric heating coefficient for 1:1.5 proportion at different bands. It was clear from the table that the S band shows very high dielectric loss, high conductivity, high dielectric constant, and low dielectric heating coefficient when compared with C and X bands. The X band shows better properties compared to C band.

Table 2 shows the absorption coefficient and penetration depth Pani: PVC composite at S band. As the absorption coefficient is derived from the complex permittivity and is a measure of propagation and absorption of electromagnetic waves when it passes through the medium, the dielectric materials can be classified in terms of this parameter indicating transparency of waves passing through it [29]. The skin depth, also called penetration depth, is basically the effective distance of penetration of an electromagnetic wave into the material [30], and it can be applied to a conductor carrying high frequency signals. When the skin depth or the penetration depth is decreased, the material becomes more opaque to electro magnetic radiation. It was clear that the absorption coefficient is very high for 1:1.5 proportions and the skin depth is very low, since the absorption coefficient is a direct function of dielectric loss and skin depth is inversely related to the dielectric loss.

CONCLUSIONS

PAN prepared at room temperature shows high microwave conductivity when compared with that prepared at lower temperature. The microwave conductivity of HCl doped PAN is found to be high when compared with other dopants such as camphor sulfonic acid, toluene sulfonic acid, perchloric acid, sulphuric acid, and nitric acid. The dielectric heating coefficient of HCl doped PAN is less when compared with other dopants. PAN doped with 1 M HCl shows maximum conductivity. The conductivity, ab-

TABLE 2. Absorption coefficient and skin depth of Pani:PVC composite at S band (at 2.97 GHz).

	Composition (Pani:PVC)			
Property	2:1	1:1	1:1.5	1:2
Absorption coefficient (m^{-1})	29.9	57.6	235	30
Skin depth (m)	0.03	0.02	0.004	0.031

sorption coefficient, etc. are found to increase with increase in PVC loading up to 1:1.5 composition. The dielectric heating coefficient and penetration depth or skin depth are found to decrease with increase in PVC loading, and it shows a minimum value for 1:1.5 Pani: PVC composition.

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