Microwave Properties of Selected Thermoplastic Conducting Composites

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ABSTRACT: Thermoplastic conducting composites of polyparaphenylene diazomethine (PPDA), polythiophene (PTH), poly-3,4-Ethylenedioxythiophene (PEDOT), and polyaniline (PANI) with polyvinylchloride (PVC) and polyurethane (PU) were prepared. Conducting composites were prepared by *in situ* polymerization of thiophene, ethylene dioxy thiophene, and aniline in the presence of polyvinyl chloride and polyurethane using $FeCl_3$ as the oxidizing agent. PPDA composites were prepared by dispersing PPDA powder in the polymer solution followed by casting. The microwave properties of all the composites were studied in the S band using Vector Network Analyzer and the best composite was selected based on the dielectric properties for microwave applications. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 5254–5259, 2012

Key words: thermoplastic conducting composites; microwave properties; dielectric properties

INTRODUCTION

Though various novel properties have been observed in conducting polymers, their practical applications have been rather limited, because of poor processability. To improve the processability of a conducting polymer, various methods to incorporate conducting polymer into processable insulating polymer have been reported.[1,2] Methods of the preparation of insulating polymer–conducting polymer composite in which electrical conductivity can be controlled by many orders of magnitude ranging from insulator to metal by changing the concentration of conducting polymer have been described.[3]

Conducting polymers show some specific characteristics in microwave frequencies that make them far more interesting than traditional dielectric materials. The intrinsic conductivity of conjugated polymers leads, in the field of their microwave properties to a dynamic conductivity leading to high levels of dielectric constant.[3–6] One of the inherent problems with conducting polymers is that they are typically intractable. To overcome the problems of processing some of the conducting polymers are made into emulsions and suspensions (PEDOT, PPY etc)

ready for coating.[7–9] Formation of composites with thermoplastic materials either by physical blending[10,11] or forming core- shell type of structures is another method.[12,13] Polypyrrole, has been polymerized on the surface of PVA, PVC and within it to form composites. Textile materials have been used as substrates for a number of materials and have been coated with conducting polymers by soaking them with oxidant and then exposing them to monomer. The use of polypyrrole coated fabrics (including glass fibers) enables the formation of structural RAM. The properties of the fabric-coated materials were modeled and made as Salisbury Screens and Jaumann layers.[14–16] It is now possible to design materials possessing permittivities, which have low variation with the frequency (ε'' ($\omega^{-0.3}$) i.e., dielectric loss directly proportional to [(angular frequency, $\omega)^{-0.3}$] or high ($\varepsilon'' \propto (\omega^{-0.7}$) i.e., dielectric loss is directly proportional to the [(angular frequency, $\omega)^{-0.7}$] directly correlated to the intrinsic conductivity of the polymer. To obtain the best performance (large bandwidth) these materials have to be associated in multilayer structures. Moreover, the use of structural laminates allows the integration of two functions, stealth and mechanical.[3]

Blending of conducting polymers with other insulating polymer matrices have been done to improve the processability, obtaining graded conductivity and tuned microwave absorption characteristics, EMI shielding, etc.[4,17–19] Blends formed by conducting

polymer as the guest and an insulating polymer host matrix constitute a novel class of conducting materials, which present attractive mechanical and processing performance imparted by the insulating polymer matrix with controlled levels of electrical conductivity. These blends are normally obtained by *in situ* polymerization of the monomer in the presence of the insulating polymer or blending of "soluble" or processable conducting polymer with another polymer in solution or melts.[20,21] Polyaniline (PANI) blends with EVA,[22] nylon-6, polyacrylamide, polyoxymethylene,[20] PET,[23] PMMA,[24] etc are reported. Polythiophene blends with polybutadiene,[25] PMMA, PS, PVC, etc[26] have been studied.

Recently many papers published on the studies on nanoconducting polymers and its composites. Polythiophene (PTh) nanoparticles with a narrow size distribution were successfully synthesized by a chemical oxidative polymerization. The highest conductivity of virgin PTh is 3.1×10^{-4} S cm^{-1} and can be dramatically enhanced to 50 S cm^{-1} by doping in iodine vapor.[27] Intrinsically self-stabilized nanoparticles of a copolymer from 4-sulfonic diphenylamine (SD) and pyrrole (PY) were facilely synthesized in HCl solution at 10°C by a chemically oxidative polymerization. The copolymers were partially soluble in concentrated H_2SO_4, demonstrating a new direction for synthesizing a soluble pyrrole copolymer.[28] Chemical oxidative polymerization at room temperature was reported to straightforwardly synthesize polyaniline (PANI) nanosticks with high yield, controllable size, intrinsic self-stability, high redispersibility, high purity, and optimizable conductivity.[29]

In this paper, the preparation of composites of PPDA, PTH, PEDOT and PANI with PVC and PU by *in situ* polymerization is reported. The microwave properties of all the composites are studied in the S band and the best combination with desirable properties is identified.

EXPERIMENTAL

Materials

Monomers

  i. *P*-phenylene diamine: Para phenylene diamine was obtained from S.D Fine-Chem Ltd, with minimum assay of 98% and melting point 139 to 143°C.
 ii. Glyoxal trimer dihydrate: Glyoxal Trimer Dihydrate having the following specifications was supplied by Fluka, with Minimum Assay of 98%, Molar Mass 210.14 g/mol and Bulk Density of 500 to 700 kg/m^3.
iii. Thiophene: Thiophene having the following specifications was obtained from Sigma-Aldrich Chemic Gmbh., with a boiling point of 84°C, refractive index 1.527, specific gravity 1.051.
 iv. EDOT: 3, 4-Ethylenedioxythiophene (EDOT) having the following specifications was supplied by Sigma-Aldrich Chemic Gmbh., with a boiling point >200°C, melting point 10.5°C and specific gravity 1.334.
  v. Aniline: Aniline having the following specifications was supplied by Merck, with minimum assay of 99% and specific gravity 1.020 to 1.022.

Polymers

  i. PVC: Polyvinyl chloride used in the study was a high-medium molecular weight dispersion resin grade 120 supplied by Chemplast Sanmar Limited, Chennai.
 ii. PU: Polyurethane used in this study is a polyether based TPU of grade KU2-8600 E supplied by Bayer Material Science Pvt. Ltd.

Preparation

First 1 : 1 composites of conducting polymer with polyvinyl chloride (PVC) and polyurethane (PU) were prepared with a FeCl$_3$: monomer ratio of 2.5. Monomer (thiophene, EDOT or aniline) was then added to the PVC or PU solution in THF to get a 10% 1 : 1 thermoplastic-monomer mixture. THF solution of FeCl$_3$ was added to the solution and the reaction was carried out for 24 h. Doping of PANI composites were done by adding camphor sulfonic acid to the composite solution in the ratio aniline : CSA (1 : 0.5). PTH and PEDOT gets *in situ* doped with FeCl$_3$.1 : 1 PPDA-PVC composite was prepared by dispersing PPDA powder in PVC solution to get a 10% solution.

About 10 mL of the composite solutions were cast in a petri dish and allowed to dry in vacuum oven at 40°C for 2 h. Thin strips of the films were cut and the dielectric properties in microwave frequencies (S band 2–4 GHz) were evaluated by Cavity Perturbation Technique.[30] The field perturbation inside the cavity is given by Kupfer et al.[31] The transmission type resonator used in this experiment was excited with TE$_{10P}$ mode by connecting it to an HP8510 C Network Analyzer.

The resonant frequency "f_0" and the corresponding quality factor "Q_0" of each resonant peak of the empty cavity are first determined. Now after selecting a particular resonant frequency, the dielectric sample is introduced into the cavity and the position is adjusted for maximum perturbation (i.e., maximum shift of resonant frequency toward the low frequency region, with minimum amplitude for the
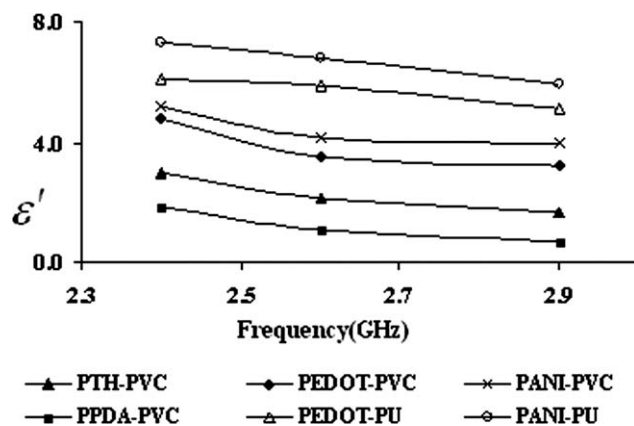
Figure 1 Variation of dielectric constant (ε') of conducting polymer–thermoplastic composites with frequency.

peak) and the corresponding change in the frequency of the resonant peak is observed. The new resonant frequency "f_s" the corresponding 3 dB bandwidth and the quality factor "Q" are determined. The procedure is repeated for other resonant frequencies and the measurements are carried out for all the samples. Knowing the volumes of the sample and the cavity resonator the dielectric parameters can be evaluated.

The parameters are calculated using the following formulae (1–7)[32,33]

$$\varepsilon' = 1 + \frac{f_0 - f_s}{2f_s}\left[\frac{V_c}{V_s}\right] \tag{1}$$

$$\varepsilon'' = \frac{V_c}{4V_s}\left[\frac{Q_0 - Q_s}{Q_0 . Q_s}\right] \tag{2}$$

$$J = \frac{1}{\varepsilon \tan \delta} \tag{3}$$

$$\alpha = \varepsilon_r'' f / n.c, \tag{4}$$

where $n = \sqrt{\varepsilon^*}$ and "c" is the velocity of light.

$$\sigma = 2\pi f \varepsilon_0 \varepsilon'' \tag{5}$$

$$\tan \delta = \varepsilon''/\varepsilon' \tag{6}$$

$$d = \frac{1}{\alpha} \tag{7}$$

where ε'' = dielectric constant, ε'' = dielectric loss, ε_0 = permittivitty of free space, α = absorption coefficient, d = penetration depth, σ = conductivity, J = efficiency of heating, c = velocity of light, V_c = volume of cavity, V_s = volume of sample.

RESULTS AND DISCUSSION

Comparison of dielectric constant (ε') of thermoplastic conducting composites

The variation of dielectric constant of conducting polymer–thermoplastic composites at S band fre-

quency is given in Figure 1. It can be observed that the dielectric constant decreases with frequency for all the composites. This is due to the orientation polarization in the microwave field. The polarization is caused by the alternating accumulation of charges at interfaces between different phases of the material. This dipole polarization may be related to the "frictional" losses caused by the rotational displacement of molecular dipoles under the influence of the alternating electrical field.[34,35] As the frequency of the applied field is increased the polarization has no time to reach its steady field value and the orientation polarization is the first that falls.[36] Due to the orientation polarization of the dipoles, the possibility of dielectric relaxation (so also dielectric loss) cannot be ruled out at higher frequencies. This might result in the decrease of "ε''" with frequency.[34,35] PANI-PU composite has highest dielectric constant followed by PEDOT-PU, PANI-PVC, PEDOT-PVC, PTH-PVC, and PPDA-PVC composite have the lowest dielectric constant.

Comparison of dielectric loss (ε'') of conducting polymer–thermoplastic composites

The variation of dielectric loss of conducting polymer–thermoplastic composites at S band frequency is given in Figure 2. In the microwave field the dielectric loss occurs due to the dipolar polarization. The dipolar polarization in an a.c. field leads to dielectric relaxation due to orientation polarization. Dielectric relaxation 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. It can be observed that the dielectric loss increases with frequency for all the composites. PANI-PU composite has highest dielectric loss followed by PEDOT-PU, PANI-PVC, PEDOT-PVC, PTH-PVC, and
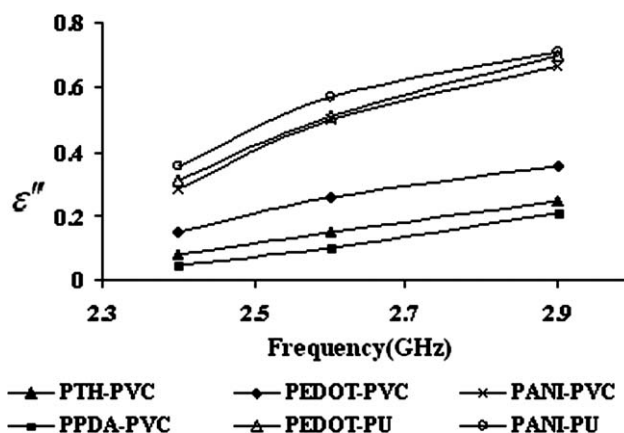

Figure 2 Variation of dielectric loss (ε'') of conducting polymer–thermoplastic composites at S band frequency.
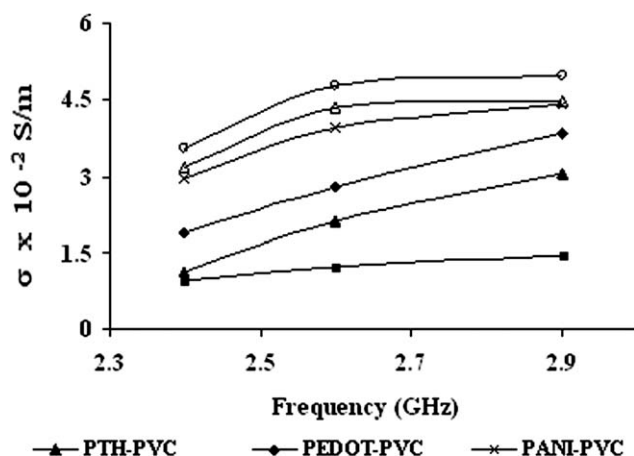
Figure 3 Variation of conductivity (σ) of conducting polymer–thermoplastic composites at S band frequency.

PPDA-PVC composite have the lowest dielectric loss.

Comparison of conductivity (σ) of conducting polymer–thermoplastic composites

The variation of conductivity of conducting polymer–thermoplastic composites at S band frequency is given in Figure 3. It is clear that the conductivity increases with frequency for all the composites. The microwave conductivity is a direct function of dielectric loss and so it shows a similar variation with frequency as the dielectric loss factor. PANI-PU composite has highest conductivity followed by PEDOT-PU, PANI-PVC, PEDOT-PVC, PTH-PVC, and PPDA-PVC composite have the lowest conductivity.

In the low frequency range, "σ" is constant and equal to "σ_{dc}" and beyond a frequency called relaxation frequency, f_r, the ac conductivity appears. It has been reported that f_r ($\sigma_{dc} \times 10^{10}$. In heterogeneous systems, the relaxation frequency is given by $f_r = \frac{\sigma_2}{2\pi\varepsilon_0(2\varepsilon_1+\varepsilon_2)}$, where (1) represents matrix and (2) represents the inclusion.[37] This model predicts that the conductivity is proportional to "ω^2" from low frequencies until the relaxation frequency and that beyond this frequency conductivity is constant.[38,39] So it seems that the relaxation frequencies of these blends are above 2.9 GHz.

Comparison of absorption coefficient (α) of conducting polymer–thermoplastic composites

The variation of absorption coefficient of conducting polymer–thermoplastic composites at S band frequency is given in Figure 4.

It can be observed that the absorption coefficient increases with frequency for all the composites. Absorption coefficient is directly related to the dielectric loss factor and therefore it shows the same
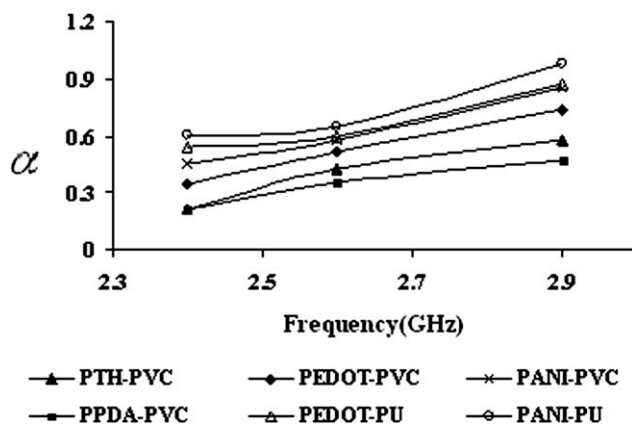

Figure 4 Variation of absorption coefficient (α) of conducting polymer–thermoplastic composites S band frequency.

behavior as dielectric loss. PANI-PU composite has highest absorption coefficient followed by PEDOT-PU, PANI-PVC, PEDOT-PVC, PTH-PVC, and PPDA-PVC composite have the lowest absorption coefficient. 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.[39]

Comparison of loss tangent (tan δ) of conducting polymer–thermoplastic composites

The variation of loss tangent of conducting polymer–thermoplastic composites at S band frequency is given in Figure 5. It can be observed that the loss tangent increases with frequency for all the composites. Since it is directly related to the dielectric loss it shows the same behavior as that of dielectric loss.
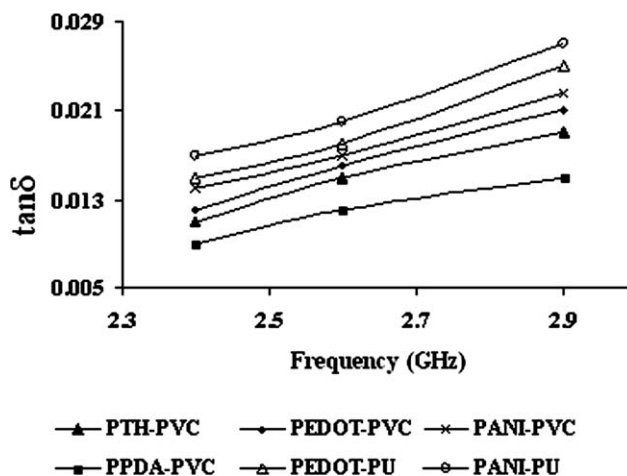

Figure 5 Variation of loss tangent (tan δ) of conducting polymer–thermoplastic composites at S band with frequency

PANI-PU composite has highest loss tangent followed by PEDOT-PU, PANI-PVC, PEDOT-PVC, PTH-PVC, and PPDA-PVC composite have the lowest loss tangent.

Comparison of heating coefficient (J) of conducting polymer–thermoplastic composites

The variation of heating coefficient of conducting polymer–thermoplastic composites at S band frequency is given in Figure 6. It can be observed that the heating coefficient decreases with frequency for all the blends. The heating coefficient is inversely related to the loss tangent and hence it decreases with increase in frequency. PANI-PU composite has the lowest heating coefficient followed by PEDOT-PU, PANI-PVC, PEDOT-PVC, PTH-PVC, and PPDA-PVC composite in the ascending order. Higher the J value, poorer will be the polymer for dielectric heating purposes. The heat generated in the polymeric material comes from the loss tangent, but that loss may not come entirely from the relaxation loss. Rather, conductivity of the polymeric material may also contribute to the tan δ. This situation may be compared with ohmic heating of metals.[40]

Comparison of skin depth (d) of conducting polymer–thermoplastic composites

The variation of skin depth of conducting polymer–thermoplastic composites at S band frequency is given in Figure 7. It can be observed that the skin depth decreases with frequency for all the composites. The self-inductance of the conductor effectively limits the conduction of the signal to its outer shell and the shell thickness is the skin depth, which decreases with increase in frequency. PANI-PU composite has lowest skin depth followed by PEDOT-PU and PPDA-PVC composite shows the highest skin depth.
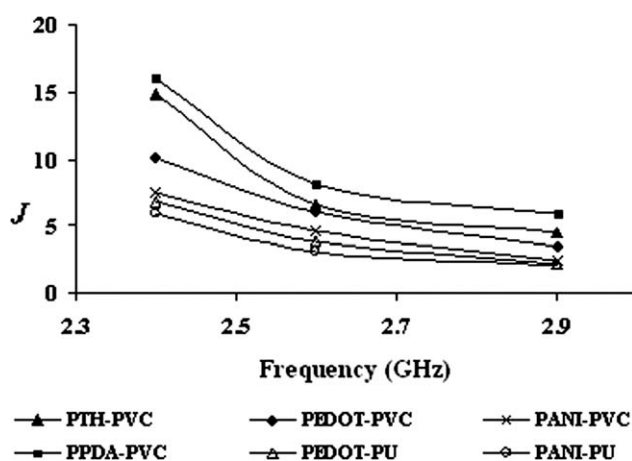
Figure 6 Variation of heating coefficient (J) of conducting polymer–thermoplastic composites at S band with frequency.
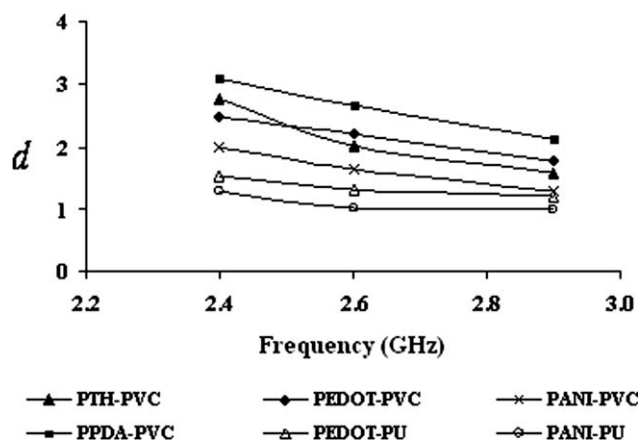
Figure 7 Variation of skin depth (d) of conducting polymer–thermoplastic composites at S band with frequency.

CONCLUSIONS

Microwave properties of PEDOT-PU, PANI-PU, PEDOT-PVC, PTH-PVC, PANI-PVC, and PPDA-PVC composites were studied. Comparing the different blends, better microwave properties are shown by PANI-PU and PEDOT-PU composites. For all the composites, dielectric constant tends to decrease with frequency but dielectric loss, conductivity, loss tangent, and absorption coefficient increases with frequency in S band. The dielectric heating coefficient and skin depth were decreases with increase in frequency.

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