Effect of Different Forms of Poly *o*-Toluidine/Poly Vinyl Chloride Composites on Dielectric Properties in the Microwave Field

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ABSTRACT: In this paper we report the preparation and dielectric properties of poly *o*-toluidine:poly vinyl chloride composites in pellet and film forms. The composites were prepared using ammonium persulfate initiator and HCl dopant. The characterization is done by TGA and DSC. The dielectric properties including dielectric loss, conductivity, dielectric constant, dielectric heating coefficient, absorption coefficient, and penetration depth were studied in the microwave field. An HP8510 vector network analyzer with rectangular cavity resonator was used for the study. S bands (2–4 GHz), C band (5–8 GHz), and X band (8–12 GHz) frequencies were used in the microwave field. Comparisons between the pellet and film forms of composites were also included. The result shows that the dielectric properties in the microwave field are dependent on the frequency and on the method of preparation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2253–2260, 2007

Key words: dielectric properties; cavity perturbation; composites; microwave

INTRODUCTION

Polyaniline (Pani) is reported to be the first conducting polymer synthesized[1] and Pani was described as existing in four different oxidation states,[2–5] each of which is an octamer. The main disadvantages of Pani are its insolubility in common organic solvents and infusibility. Incorporation of polar functional groups or long and flexible alkyl chains in the polymer backbone is a common technique to prepare Pani-type soluble polymer. For example poly *o*-toluidine (PoT) or methyl-substituted Pani are more soluble than the unsubstituted Pani.

Among the large variety of conducting polymers, Pani and its derivatives have received much attention because of its various technological applications,[6,7] reversible proton doping, high electrical conductivity, and ease of bulk preparation.[8] Green and Woodhead[2] achieved the first chemical synthesis of PoT as an analogue of Pani in 1910. PoT is generally prepared by the direct oxidation of toluidine using appropriate chemical oxidants or by electrochemical means using different electrode materials.[8,9] The synthetic strategies and reaction mechanisms for PoT are similar to those of Pani.

Leclerc et al.[10,11] have observed that the polymerization yield is strongly influenced by the bulkiness and position of the substituent. Since an ortho position is blocked in PoT, relatively fewer ortho couplings can be expected, leading to a more regular head to tail polymer structure and thereby higher polymerization yields. Moreover, higher molecular weights can be obtained by chemical synthesis than by electrochemical synthesis.

The conductivity of PoT is lower by two to three orders of magnitude compared with that of Pani. The conductivity of PoT base is less than 10^{-10} S/cm, which indicates that the acid part has been expelled from the polymer chain. The conductivity of PoT when it is doped with different dopants like HCl, HNO_3, H_2SO_4, I_2, $HClO_4$ were reported.[12,13] The decrease in conductivity in PoT can be attributed to their electronic structure. The observation of Pauli paramagnetism in PoT[12,13] reveals the existence of a degenerate electronic structure with a finite density of states at the fermi energy as in Pani.[14] MacDiarmid and coworkers[15–17] studied the electron localization in PoT, which leads to a reduced conductivity. It has been studied in depth for DC and microwave conductivity's, dielectric constant, AC conductivity and thermopower measurements. Wang et al.[18] have inferred from the much smaller DC conductivity, microwave conductivity, and dielectric constant of PoT–HCl salt at 6.5 GHz compared with that of Pani–emeraldine salt,[19] that the PoT–ES system is more localized. The PoT–HCl salt has the same electronic structure as that of Pani–HCl, but it shows a significantly decreased conductivity.[20] The origin of this divergent result is stated to be due to increased localization of conduc-

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tion electrons in POT as compared with Pani. And it is caused by the reduction in interchain interactions due to increased interchain separation.[21] To improve the solubility and hence the solution processing for various applications PoT is envisaged. The introduction of a substituent group (—CH_3 group in *o*-toluidine) would increase the torsion angle between the two adjacent phenylene rings and facilitates better solvation at the —NH group on the polymer backbone.[22] Conducting polymers, especially Pani and its analogues, find very good applications in industrial, scientific, and medical fields. But the main drawback of these conducting polymers is the difficulty in their processing. When PoT is prepared, the solubility of the conducting polymer is increased because of the presence of a substituent group. But the real fact is that it will contribute very little to the processing. So we have prepared PoT–Polyvinyl chloride semi-interpenetrating networks (PoT : PVC SIPN) to improve the processibility. In this paper we report the synthesis and characterization of PoT–PVC SIPN in pellet and film forms and its dielectric properties at microwave frequencies. Also, the degradation of SIPNs is presented.

EXPERIMENTAL

Materials

1. *o*-Toluidine (reagent grade) is distilled prior to use.
2. Ammonium persulfate, emulsion grade Polyvinyl chloride (PVC) and cyclohexanone used are analar grade.

Preparation of PoT/PVC SIPN in pellet form

Chemical oxidative polymerization of *o*-toluidine was carried out using ammonium per sulfate as initiator in the presence of emulsion grade PVC and 1*M* HCl. The polymerization was carried out for 4 h. at room temperature. It was then filtered, washed, and dried in an oven at 50–60°C for 6 h and was pelletized. The dielectric properties of these composites were measured using cavity perturbation technique. Different compositions of PoT : PVC SIPNs (1 : 0.5, 1 : 1, 1 : 2, 1 : 3, 1:4) were prepared using the above procedure and the dielectric properties were measured.

Preparation of cyclohexanone-soluble PoT : PVC SIPN

Chemical oxidative polymerization of *o*-toluidine was carried out using ammonium persulfate as initiator in the presence of emulsion grade PVC solution in cyclohexanone. The polymer formed was then made into film by solution casting and was doped with 1*M* HCl. Different compositions of PoT–PVC SIPNs (2 : 1, 1 : 1, 1 : 2, 1 : 3, and 1 : 4) were prepared using the above procedure. Here the dielectric study was conducted in three bands, S, C, and X bands.

SET UP AND THEORY

The dielectric properties of Pani and its composites were measured using cavity perturbation technique.[23] The experimental set up[24] 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 powder and 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.[25] The real and imaginary parts of the relative complex permittivity are given by

$$\varepsilon_r' = 1 + \frac{f_0 - f_s}{2f_s}\left(\frac{V_c}{V_s}\right), \qquad \varepsilon_r'' = \frac{V_c}{4V_s}\left(\frac{Q_0 - Q_s}{Q_0 Q_s}\right)$$

The real part of the complex permittivity, ε_r', is generally known as dielectric constant and the imaginary part ε[dprime]$_r$, of the complex permittivity is related to the dielectric loss of the material.

The loss tangent is given by, tan δ = loss current/charging current = ε[dprime]/ε′, where ε′ is the measured dielectric constant of the dielectric material and ε[dprime] is the loss factor or loss index.

Here σ + ωε[dprime]$_r$ 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 σ_e = ωε[dprime]$_r$ = $2\pi f\varepsilon_0$ε[dprime]$_r$

The efficiency of heating is usually compared[26] by means of a comparison coefficient *J*, which is defined as $J = 1/\varepsilon_r$ tan δ. The absorption of electromagnetic waves when they pass through a medium is given by the absorption coefficient[26] (α_f), which is defined as, Absorption coefficient (α_f) = ε[dprime]$_r$ $f/n\,c$, 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,[27] Skin depth (δ_f) = $1/\alpha_f$ The amplitude responses of S band cavity are shown in Figure 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 Figure 2.

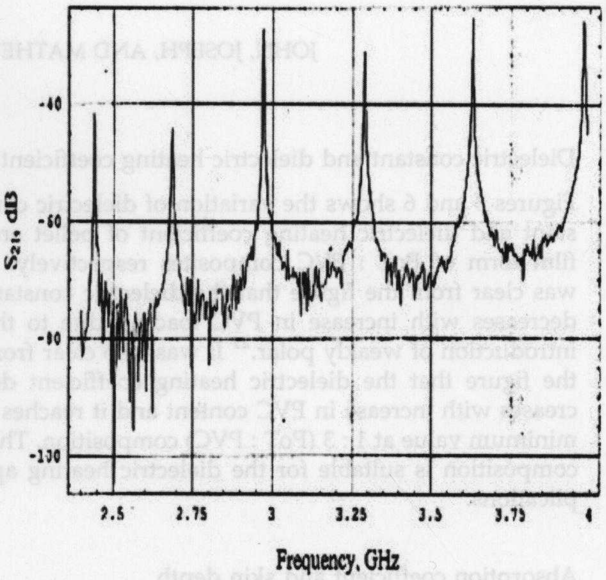

Figure 1 The amplitude responses of S band cavity.

RESULTS AND DISCUSSION

Variations of dielectric properties with compositions

Dielectric loss and conductivity

Figures 3 and 4 shows the dielectric loss and conductivity of pellet and film forms of PoT : PVC composite respectively. It was clear from the figures that the dielectric loss and conductivity increases with PVC loading and reaches a maximum at 1 : 3 (POT : PVC) composition and then decreases. J. C. Maxwell[28] reported that 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. In the case of PoT : PVC composite, which consists of two phases, a charge build up can occur at the macroscopic interface as a result of the differences in the conductivity and dielectric constant of the materials. This accumulation of charge then leads to field distortions and dielectric loss. The interfacial loss depends on the quantity of weakly

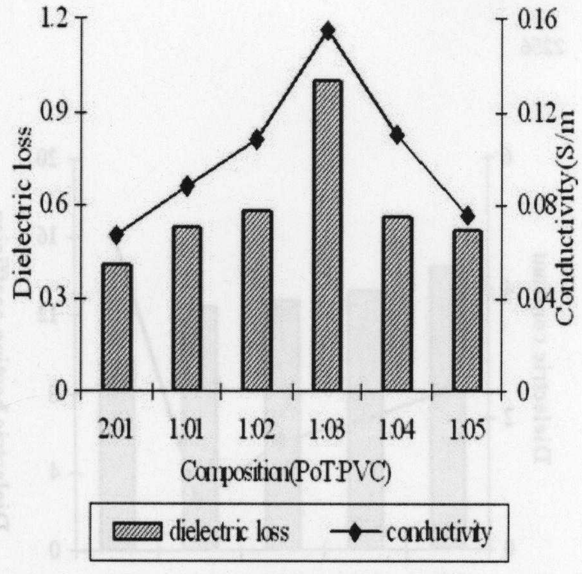

Figure 3 Variation of dielectric loss and conductivity of PoT : PVC composite in pellet form.

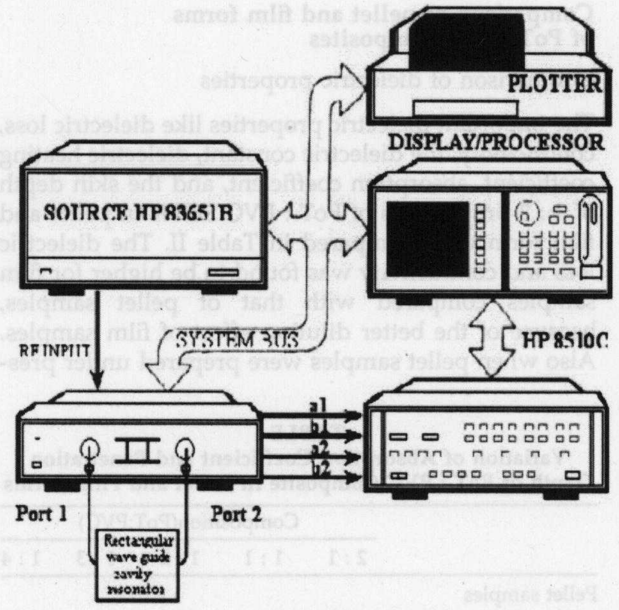

Figure 2 Experimental set up.

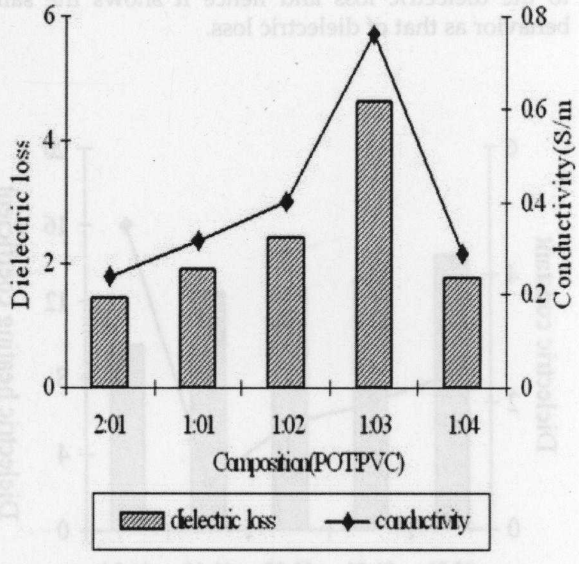

Figure 4 Variation of dielectric loss and conductivity of PoT : PVC composite in film form.

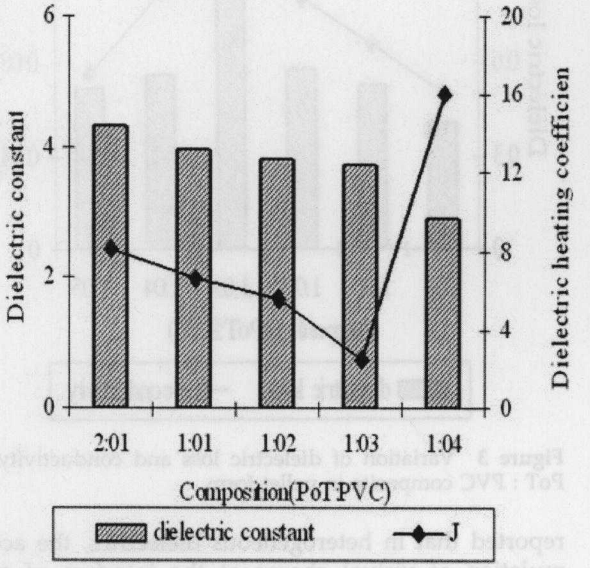

Figure 5 Variation of dielectric constant and dielectric heating coefficient of PoT : PVC composite in pellet form.

polar material present as well as on the geometrical shape of its dispersion.[29] The quantity and geometry of the PVC at 1 : 3 proportion was more favorable for higher interfacial polarization. This may be the reason why maximum dielectric loss was shown by the 1 : 3 composition of PoT : PVC composite. The conductivity in the microwave frequencies was directly related to the dielectric loss and hence it shows the same behavior as that of dielectric loss.

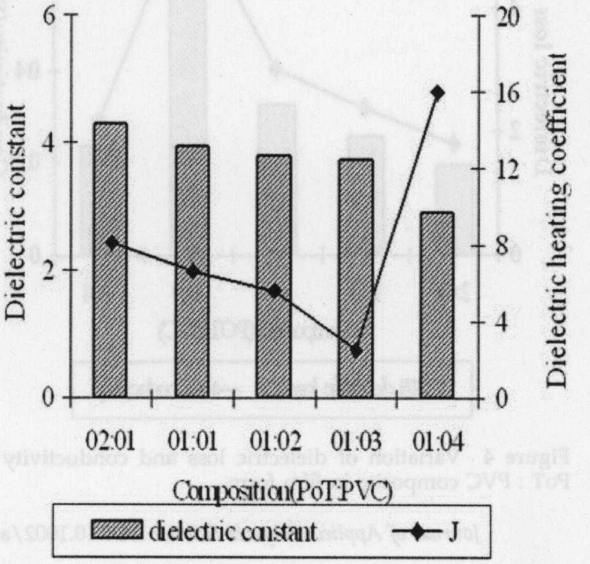

Figure 6 Variation of dielectric constant and dielectric heating coefficient of PoT : PVC composite in film form.

Dielectric constant and dielectric heating coefficient

Figures 5 and 6 shows the variation of dielectric constant and dielectric heating coefficient of pellet and film form of PoT : PVC composites respectively. It was clear from the figure that the dielectric constant decreases with increase in PVC loading due to the introduction of weakly polar.[21] It was also clear from the figure that the dielectric heating coefficient decreases with increase in PVC content and it reaches a minimum value at 1 : 3 (PoT : PVC) composition. This composition is suitable for the dielectric heating applications.

Absorption coefficient and skin depth

Table shows the absorption coefficient and skin depth of different compositions of PoT : PVC SIPNs at 2.97 GHz of pellet forms. It was clear that the absorption coefficient was found to be high for 1 : 3 PoT : PVC composition and the skin depth was found to be low for that composition. The absorption coefficient was directly related to the dielectric loss and the skin depth or penetration depth was inversely related to the loss factor.

The DC conductivity of 1 : 3 PoT : PVC SIPN is found to be 4.49 × 10^{-5}(S/m), which is much less than microwave conductivity(0.155 S/m), since the non conducting PVC decreases the conductivity of PoT.

Comparison of pellet and film forms of PoT : PVC composites

Comparison of dielectric properties

The important dielectric properties like dielectric loss, conductivity, the dielectric constant, dielectric heating coefficient, absorption coefficient, and the skin depth of 1 : 3 proportions of PoT : PVC SIPNs in pellet and film form were compared in Table II. The dielectric loss and conductivity was found to be higher for film samples compared with that of pellet samples, because of the better dilution effect of film samples. Also when pellet samples were prepared under pres-

TABLE I
Variation of Absorption Coefficient and Penetration Depth of PoT : PVC Composite in Pellet and Film Forms

	Composition(PoT:PVC)				
	2 : 1	1 : 1	1 : 2	1 : 3	1 : 4
Pellet samples					
Absorption coefficient (m^{-1})	6.02	7	7.82	8	3.88
Skin depth (m)	0.17	0.14	0.13	0.12	0.26
Film samples					
Absorption coefficient (m^{-1})	21.67	31.19	38.66	40.45	7.56
Skin depth (m)	0.046	0.032	0.025	.024	.13

TABLE II
Comparison of Dielectric Properties of Pellet and Film Forms of PoT : PVC (1 : 3 Composition) Composite at 2.97 GHz

Property	PoT : PVC pellet form	PoT : PVC film form
Dielectric loss	1	4.62
Conductivity (S/m)	0.155	0.762
Dielectric constant	6.8	11.32
Dielectric heating coefficient (J)	2.5	0.34
Absorption coefficient (m^{-1})	8	40.45
Penetration depth (m)	0.12	0.024

sure there is a loss of dopant molecules[30] and it will reduce the dielectric properties. The film samples were able to produce more dipolar polarization under the influence of an AC field and hence the dielectric constant was higher for film as indicated in the table. The film samples also show minimum heating coefficient.

It was clear from the table that the absorption coefficient was higher and the skin depth was lower for the film sample. Therefore the film samples are better for shielding applications.

TGA and DSC studies

Figure 7 shows the TGA thermogram of pellet and film samples of 1 : 3 composition. It was clear from the figure that an initial loss of about 6% at a temperature of 100–220°C was observed for both samples. The second loss of about 44% in the case of pellet sample and 48% for film sample was observed at a temperature of 360°C. Also a third loss of 28% in the case of pellet sample is seen at 550°C, but in the case of film samples there was a sharp reduction in the weight observed from 360°C. The higher percentage of weight loss in the case of film samples indicates the more closeness of PVC to the PoT chain.

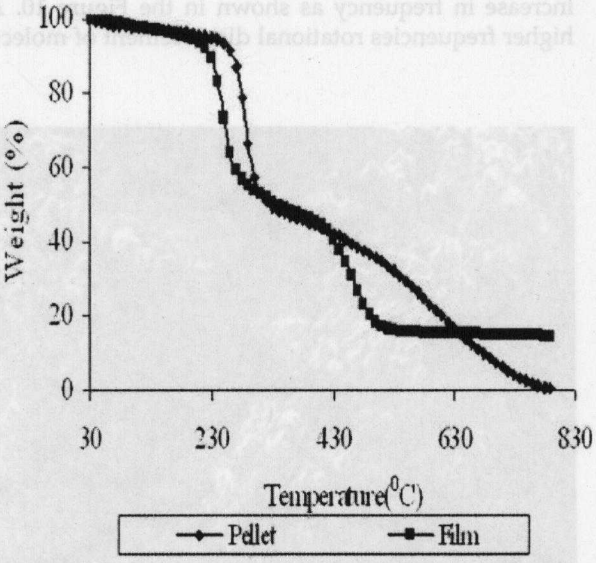

Figure 7 TGA thermogram of PoT : PVC composite in pellet and film form.

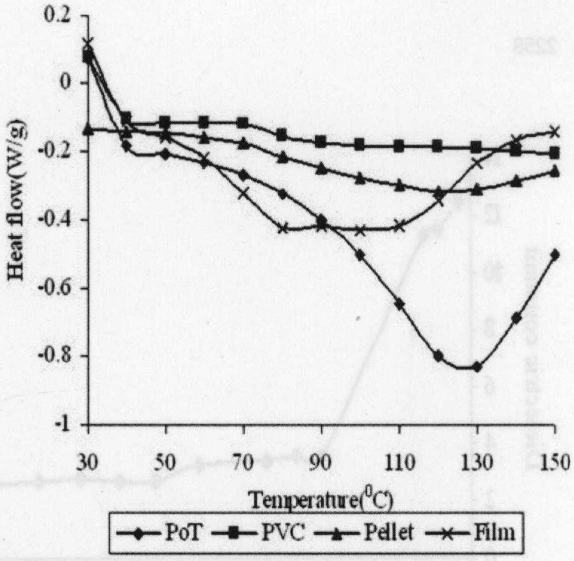

Figure 8 DSC thermogram of PoT : PVC composite in pellet and film form.

Figure 8 shows the DSC of PoT : PVC and SIPN of 1 : 3 composition in pellet and film forms. It was clear from the figure that the T_g of PoT (130°C) was shifted to 117°C in the case of pellet form and to 95°C in film form. The lower T_g of film sample is an indication of higher flexibility because of the plasticizing action of

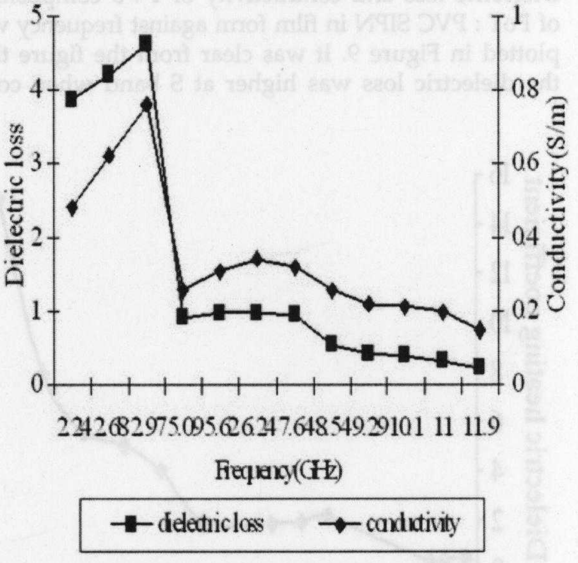

Figure 9 Variation of dielectric loss and conductivity of film form of PoT : PVC with frequency.

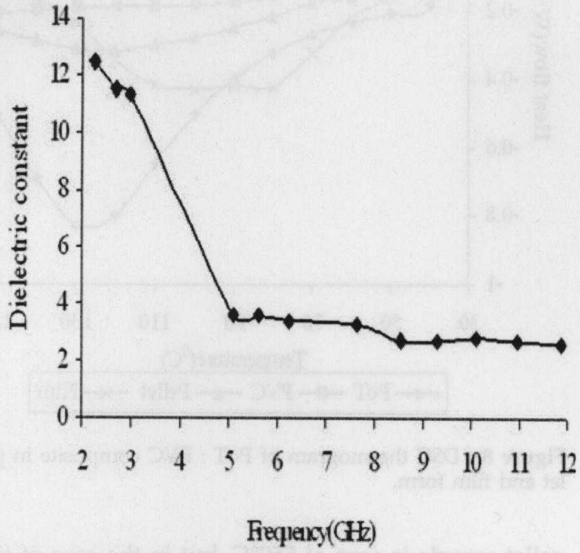

Figure 10 Variation of dielectric constant of film form of PoT : PVC with frequency.

PVC. This result also proves the higher dielectric properties of film form compared with that of the pellet form.

Variation of dielectric properties of PoT : PVC SIPN in film form with frequency

TABLE III
Variation of Absorption Coefficient and Skin Depth of Film Form of PoT : PVC with Frequency

	Frequency (GHz)	Absorption coefficient (m^{-1})	Skin depth (m)
S band	2.24	25.17	0.04
	2.68	33.17	0.03
	2.97	40.45	0.02
C band	5.09	25.3	0.04
	5.62	29.8	0.031
	6.24	34	0.03
	7.64	35	0.0278
X band	8.54	29.4	3
	9.29	25.4	4
	10.1	26	3
	10.96	26.3	3
	11.86	26.3	3.17

Dielectric loss and conductivity of 1 : 3 composition of PoT : PVC SIPN in film form against frequency was plotted in Figure 9. It was clear from the figure that the dielectric loss was higher at S band when compared with that of the C and X bands. When the frequency increases (C and X bands) the dielectric loss decreases because of the rapid rotational displacement of polar molecules under the influence of an AC field. At higher frequencies the molecules will not get enough time to get aligned with the field.[31] But within the S band the dielectric loss and conductivity were increased. When the frequency is increased, the inertia of the molecule and the binding forces become dominant and it is the basis for dielectric heating or dielectric loss at higher frequencies of S band.[30]

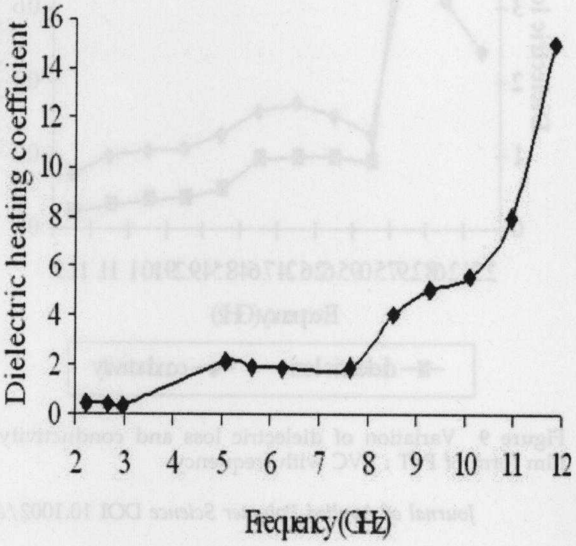

Figure 11 Variation of dielectric heating coefficient of film form of PoT : PVC with frequency.

The dielectric constant was found to decrease with increase in frequency as shown in the Figure 10. At higher frequencies rotational displacement of molecu-

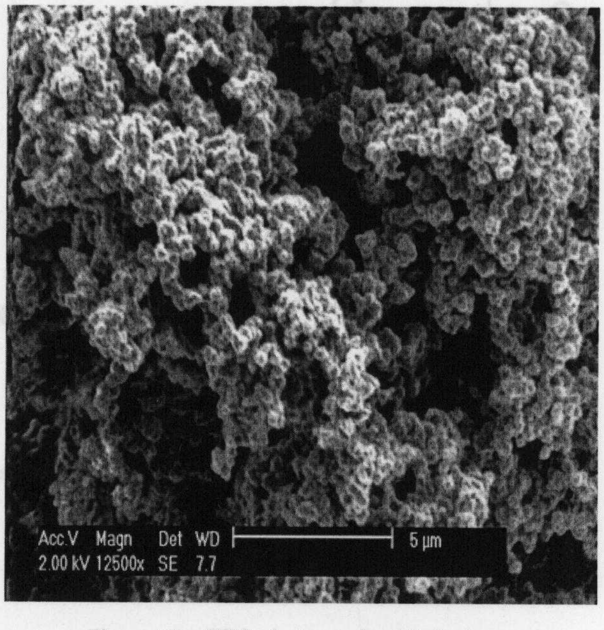

Figure 12 SEM photograph of PoT alone.

lar dipoles under the influence of alternating field may lead to dielectric relaxation and this leads to a decrease in dielectric constant.[32] It was observed in Figure 11 that the SIPN shows very good dielectric heating property, i.e., the dielectric heating coefficient was low, in the S band and it was higher for C and X bands. The dielectric heating coefficient is inversely related to the loss tangent and therefore the heating coefficient was higher at C and X bands.

Table III shows the variation of absorption coefficient and skin depth of 1 : 3 PoT : PVC composite with frequency. The absorption coefficient was higher at S band when compared to C and X bands. Also the skin depth was lower at S band, makes it useful for shielding applications. But within each band the absorption coefficient increases and the skin depth decreases with increase in frequency.

SEM analysis

Figures 12, 13, and 14 show the scanning electron micrographs of PoT, PVC, and its SIPN of 1 : 3 PoT : PVC composition. The SEM photograph of PoT shows that the chains were loosely packed. In the case of PVC, it shows a globular shape and was thickly packed (Fig. 13). Figure 14 shows that the PoT was uniformly distributed in the PVC matrix and there were no separate domains for PVC and PoT. It was also clear from this figure that the PoT chains were interpenetrated in PVC matrix and it forms semi-interpenetrating networks with PVC.

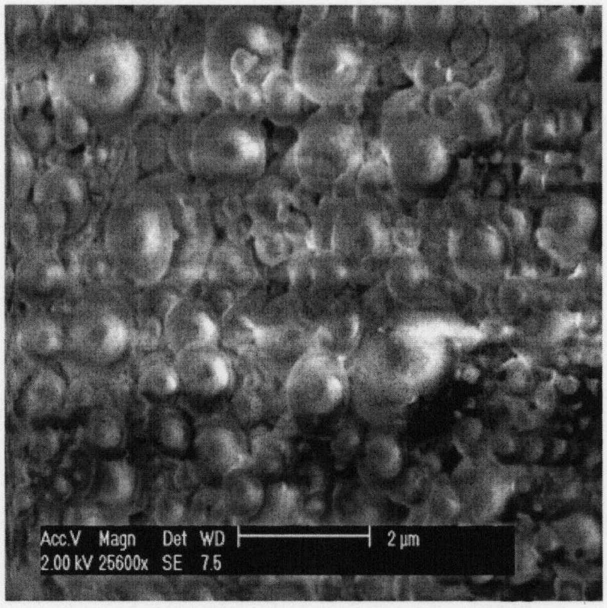

Figure 13 SEM photograph of PVC alone.

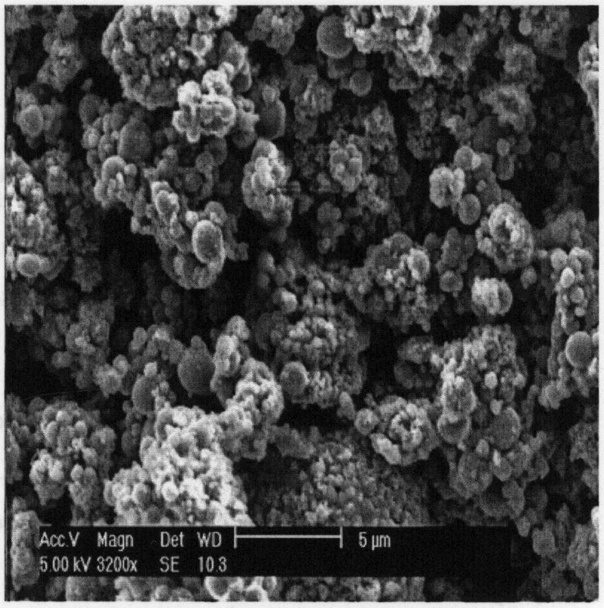

Figure 14 SEM photograph of PoT: PVC 1:3 composition.

CONCLUSIONS

The conductivity and the dielectric loss of PoT increases with increase in PVC loading and it reaches a maximum at 1:3 (POT : PVC) proportion in both pellet and film forms. The dielectric heating coefficient is found to be minimum for 1 : 3 composition. The absorption coefficient is found to be high for 1 : 3 composition and the skin depth minimum for that composition. The dielectric properties are higher at S band when compared to C and X bands for film samples. The film samples show higher conductivity and absorption coefficient values than do pellet samples. The dielectric heating coefficient and penetration depth are lower for film samples. The dielectric constant is found to be higher for the film samples. The difficulty in processing can be overcome by preparing the film sample.

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