Optimization of Preparation Conditions on the Dielectric Properties of Polyaniline

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ABSTRACT: The dielectric response in the microwave field of polyaniline prepared at different temperatures and using different inorganic and organic dopants was studied. Chemical oxidative polymerization of aniline was done at low temperature (0–5°C), at room temperature, and at high (60°C) temperature using different inorganic dopants like HCl, HNO_3, H_2SO_4, $HClO_4$, etc. Polyaniline was also prepared with different organic dopants like camphor sulfonic acid, Toluene sulfonic acid, and Naphthalene sulfonic acid. All polymers formed were characterized using IR, TGA, DSC, and SEM, etc. The dielectric responses of all polymers are studied using cavity perturbation technique in the microwave field. The studies indicates that the polyaniline prepared with perchloric acid at room temperature shows higher conductivity and absorption coefficient compared with all other samples. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2676–2682, 2009

Key words: conducting composites; dielectric properties; cavity perturbation; dopants

INTRODUCTION

Polyaniline has been investigated extensively and attracted interest as a conducting material for several important reasons; the monomer is inexpensive, the polymerization reaction is straightforward and proceeds with high yield, and PAni has excellent stability. PAni exists in three well-defined oxidation states: leucoemeraldine, emeraldine, and pernigraniline. Leucoemeraldine and pernigraniline are the fully reduced (all the nitrogen atoms are amine) and the fully oxidized (all the nitrogen atoms are imine) forms, respectively, and in emeraldine the ratio is $\sim$ 0.5. As shown by Alan MacDiarmid and his collaborators in the mid-1980s, polyaniline can be rendered conducting through two independent routes: oxidation (either chemically or electrochemically) of the leucoemeraldine base or protonation of the emeraldine base through acid-base chemistry. Because the insertion of counterions is involved in both routes, conducting polyaniline may be regarded as a polycation with one anion per repeat unit. Thus, it is clear that starting from the electrically insulating leucoemeraldine, electrically conducting emeraldine can be obtained by standard chemical or electrochemical oxidation, as with other conducting polymers. But, upon further oxidation of emeraldine, a second redox process occurs, which yields a new insulating material, pernigraniline. Different oxidation states of polyaniline is shown below.

leuco emeraldine

emeraldine base

conducting emeraldine salt
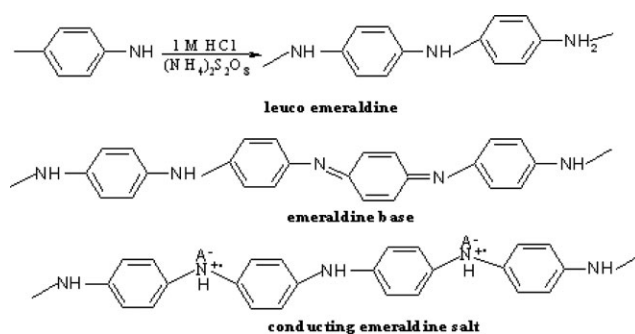
PAni and its analogues have generated tremendous interest among scientists and technologists because of their wide variety of desirable properties and potential technological applications. Effect of secondary doping of polyaniline (PAni) composites, prepared by *in situ* emulsion polymerization of aniline in the presence of chlorosulfonated polyethylene (CSPE) or styrene-butadiene-styrene triblock copolymer and dodecyl benzene sulfuric acid on conductivity were studied.[1] Secondary doping and dedoping process were characterized using UV-VIS spectrophotometry.

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It was found that the conductivity is increased on removal of secondary doping. The effect of chemical degradation on electrical properties were evaluated on undoped polyaniline.[2] The chemical degradation has been analyzed by several complements, FTIRS, XPS, and UV-VIS-IR spectroscopy.

The nano structures (e.g., Nano tubes or nano rods) of polyaniline with an average diameter of 150–340 nm and conductivity of 10^{-1}–10^0 S/cm, is prepared in the presence of self-assembly acids like HCl, H_2SO_4, H_3PO_4, and H_3F_4 as dopants.[3] It was found that the morphology, size, and electrical properties of nano structures depend on the dopant structures and the reaction conditions. It was characterized by FTIR, UV-VIS spectrum, XDS, and X-ray diffraction. The reliability and practicability of the self assembly method for synthesizing micro tubes or nano tubes of conducting polymers through changing polymer chains[4–6] and dopants[7–9] and using different polymerization methods are also reported.

Of particular interest is the very large capacity of PAni to absorb and reflect electromagnetic radiation by changing its dielectric constant on interaction with energy of radiowave-microwave millimeter wave range.[10–12] This makes PAni an appropriate candidate to shield electromagnetic interference where PAni approaches the shielding efficiency of copper,[13–16] in the design of microwave absorbers for stealth purposes and in areas involving remote heating of materials and surfaces for example, joining of plastics.[17,18] Dependence of the electric behavior of PAni on the frequency of the electric field and temperature[19–21] allows designing PAni-based materials, which are effective in a defined temperature-frequency range both possible and attractive. In addition to this unusual behavior, a decrease of conductivity by 10 orders of magnitude is obtained just by treatment of the conducting emeraldine in neutral or alkaline media. Protonation induces an insulator-to-conductor transition, while the number of π-electrons in the chain remains constant. A lot of work has been devoted to unravel the mystery of this unusual transition.[22,23] The mechanism of oxidative polymerization of aniline, which always results in a conducting emeraldine PAni, appears also to be ambiguous.

In this article, we report the dielectric response of Polyaniline prepared at different temperatures with both organic and inorganic dopants, in the microwave field.

EXPERIMENTAL

Preparation of polyaniline (doped form-*in situ* polymerization)

With inorganic dopants: Chemical oxidative polymerization of aniline to give the conducting emeraldine salt was carried out using ammonium persulphate as initiator in the presence of $1M$ HCl room temperature (RT). The reaction was carried out for 4 h. The green precipitate formed was filtered washed with water, acetone, and methanol. The samples were then oven dried at 50–60°C for 6 h. The reaction was repeated with $1M$ solutions of different dopants like sulfuric acid, nitric acid, and perchloric acid, with a view to determine the best dopant. The consequence of variation in molar concentration of the best dopant was then evaluated. The dielectric parameters were measured for the pelletised samples (2.5 tonnage pressure) at high frequency using an Impedence analyzer and at microwave field using HP 8510 vector network analyzer. The polymer formed was characterized using IR spectroscopy, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Scanning Electron Microscopy (SEM).

With organic dopants, the polymerization reaction was repeated with $1M$ solutions of organic dopants like toluene sulfonic acid, naphthalene sulfonic acid, and camphor sulfonic acid.

Dielectric property measurement is done by cavity perturbation technique.[24,25] The measurements were done at 25°C in S band (2–4 GHz). The real and imaginary parts of the relative complex permittivity are given by:

$$\varepsilon_r' = 1 + \frac{f_o - f_s}{2f_s}\left(\frac{V_c}{V_s}\right), \quad \varepsilon_r'' = \frac{V_c}{4 V_s}\left(\frac{Q_o - Q_s}{Q_o Q_s}\right)$$

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 J,[26] 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[27] (α_f), which is defined as, Absorption coefficient $(\alpha_f) = \varepsilon_r'' f/nc$, 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,[28] Skin depth $(\delta_f) = 1/\alpha_f$.

RESULTS AND DISCUSSIONS

Effect of polymerization condition and inorganic dopants on the dielectric properties

Table I shows the effect of different dopants and the temperature of preparation at 0–5°C (Low

TABLE I
Effect of Dopants and Temperature of Preparation on the Dielectric Properties of Polyaniline at 2.97 GHz

Property	Dopant	LT (0–5°C)	RT (28°C)	HT (60°C)
Dielectric loss	$HClO_4$	0.1	**2.68**	0.4
	HCl	0.09	0.16	0.15
	HNO_3	0.09	0.13	0.18
	H_2SO_4	0.17	0.26	0.16
Conductivity (S/m)	$HClO_4$	0.02	**0.44**	0.07
	HCl	0.01	0.02	0.019
	HNO_3	0.02	0.025	0.03
	H_2SO_4	0.035	0.05	0.03
Dielectric constant	$HClO_4$	13.4	**11**	4.32
	HCl	18.54	16.35	18.83
	HNO_3	13.21	13.61	15.73
	H_2SO_4	14.78	19.45	18.43
Dielectric heating coefficient	$HClO_4$	105	**0.73**	14.44
	HCl	90.46	5.91	22.66
	HNO_3	151.2	105.25	29.43
	H_2SO_4	40.8	49.11	31.33
Loss tangent	$HClO_4$	0.018	**0.23**	0.08
	HCl	0.015	0.017	0.01
	HNO_3	0.015	0.01	0.018
	H_2SO_4	0.015	0.015	0.014

Temperature), RT 28°C, and at high temperature 60°C (HT) on the dielectric properties of polyaniline at 2.97 GHz.

It was clear from the table that Polyaniline prepared at RT shows higher conductivity in all cases. In the microwave field, the dielectric loss occurs due to the dipolar polarization. The dipolar polarization in an AC field leads to dielectric relaxation due to orientation polarization. Dielectric relaxation[29] 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, and thus, results in the generation of dielectric loss. When the polymerization temperature of aniline is increased, head to head (benzene to benzene) sequence of Polyaniline is greater compared with head to tail sequence (NH to benzene), which reduces the conjugation length of Polyaniline, and in turn reduces the intrachain conduction. Because the intrachain conduction is higher than the interchain conduction, samples prepared at high temperature shows less dielectric loss.[30] Because the conductivity in the microwave field is directly related to the dielectric loss factor, the conductivity is proportionately higher for Polyaniline prepared at RT. It is also clear from the table that the dielectric loss and conductivity is highest for $HClO_4$ doped polyaniline followed by HCl-doped sample.

The increase in the size of the counter ion leads to a material with conductive path having a higher doping level than small counter ions.[27] This will increase the intrachain conductivity and since the

intrachain conductivity contributes to an increase in dielectric loss than the interchain conductivity, the dielectric loss and conductivity of $HClO_4$ doped samples are higher than those of HCl and other inorganic acid doped samples.

Table I also shows the variation of dielectric constant of different doped samples at 2.97 GHz. Results indicate that the dielectric constant of $HClO_4$ doped sample was low compared with samples with other dopants. When a field is applied, the positive charges move with the electric field and an equal number of negative charge moves against it, resulting in no net charge within the polymer. However, there is a net positive charge at the surface where the positive direction of the field emerges and a negative charge at the surface where the field enters. Thus, a large field outside it produces the field within the polymer, and the normal components have the ratio given by the dielectric constant. 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.[31] In the case of $HClO_4$ doped polyaniline (ClO_4^- is large enough to act as the second phase), a charge build up can occur at the macroscopic interface as a result of the differences in the conductivity and dielectric constant of the matrices. This accumulation of charge then leads to field distortions and dielectric loss. This interfacial loss depends on the quantity of polar material present as well as on the geometrical shape.[32] The quantity and geometry of the ClO_4^- is more favorable for higher interfacial polarization leads to high dielectric loss and thereby less dielectric constant.

It was also clear from Table I that the dielectric heating coefficient is a minimum for $HClO_4$ doped sample prepared at RT. As the heat generation in polymers is due to relaxation loss, the efficiency of heating of a polymer is compared by means of a heating coefficient.[33]

The dielectric heating coefficient is inversely related to the dielectric loss factor, and hence, the $HClO_4$ doped samples shows the minimum value. The higher the heating coefficient the poorer is the heating property.

Loss tangent of Polyaniline doped with different dopants given in Table I indicates that the loss tangent also shows the same behavior as that of dielectric loss, because it is directly related to the dielectric loss. Loss tangent is the tangent of the angle δ between the vector for the amplitude of the total current and that for the amplitude of charging current.[34] Figures 1 and 2 show the absorption coefficient and penetration depth of Polyaniline samples, respectively. Absorption coefficient is derived from the complex permittivity and is a measure of
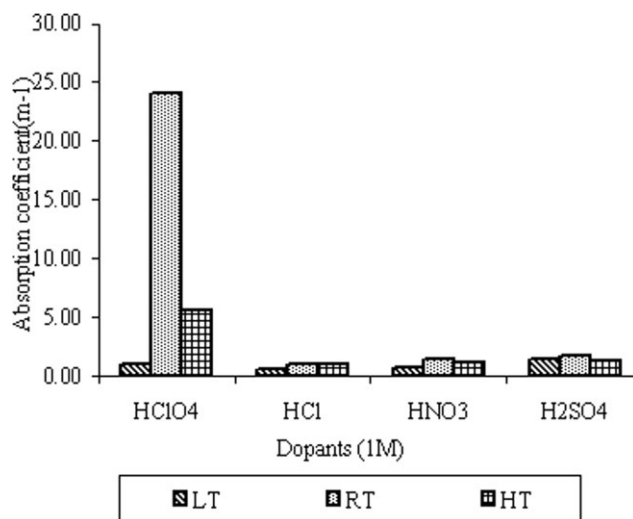
Figure 1 Effect of dopants and temperature on the Absorption coefficient at 2.97 GHz.

the propagation and absorption of electromagnetic waves when it passes through a medium. The dielectric materials can be classified in terms of this parameter indicating the transparency of waves passing through it. The absorption coefficient is directly related to the dielectric loss factor and therefore it shows the same behavior as dielectric loss. It was clear from Figure 2 that the skin depth was low for $HClO_4$ doped Polyaniline prepared at RT. As the skin depth, also called penetration depth, is basically the effective distance of penetration of an electromagnetic wave into the material,[35] it is inversely related to the absorption coefficient.

Characterization of $HClO_4$ doped samples

IR spectroscopy

The IR spectrum of $HClO_4$ doped Polyaniline is presented in Figure 3. The peak at 3449/cm indicates
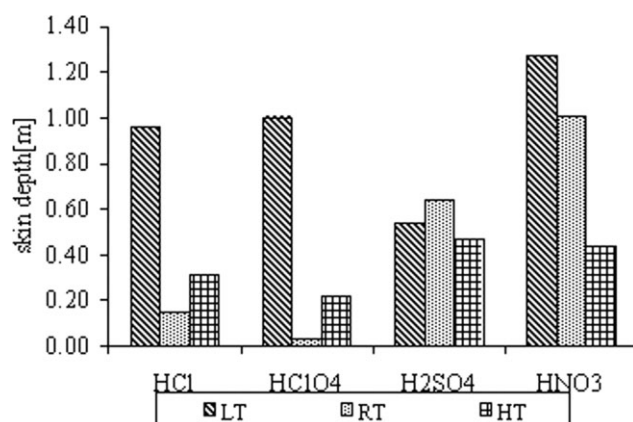
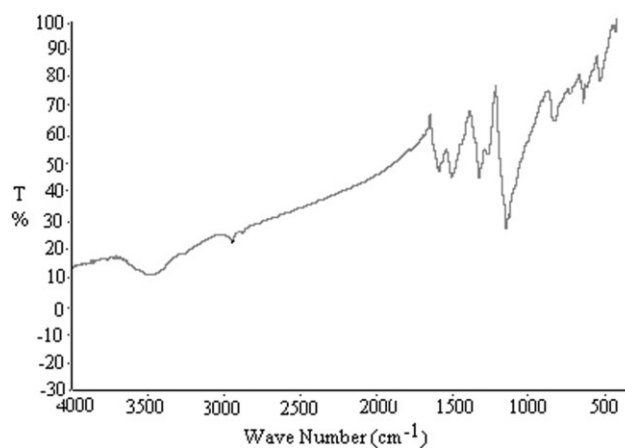**Figure 2** Effect of dopants and temperature on the skin depth at 2.97 GHz.

Figure 3 IR spectrum of $HClO_4$ doped Polyaniline.

the presence of —NH stretching vibration and the peaks at 1238/cm, 1117/cm, 1108/cm, and 882/cm are the characteristic frequencies of Polyaniline samples.[36] The peak at 1556/cm indicates the presence of quinoid ring stretching vibration and the band at 1298/cm indicates the presence of CN stretching vibration in polyaniline. All these findings confirm the formation of doped polyaniline samples in the presence of $HClO_4$.

Thermal studies

Figures 4 and 5 show the TGA and DSC thermogram of $HClO_4$ doped Polyaniline samples. The TG curve indicates that there is a weight loss of 20% for polyaniline because of the evolution of $HClO_4$ dopant at 240°C. About 41% of weight loss at 550°C indicate the degradation of polyaniline chain. The DSC curve shows that the glass transition temperature (T_g) of polyaniline is 110°C.
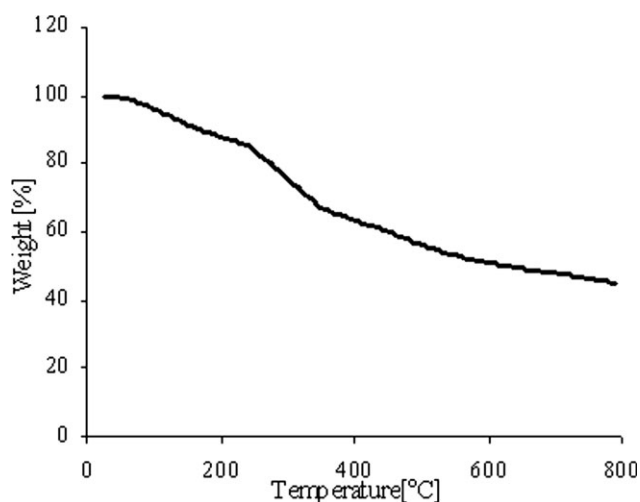

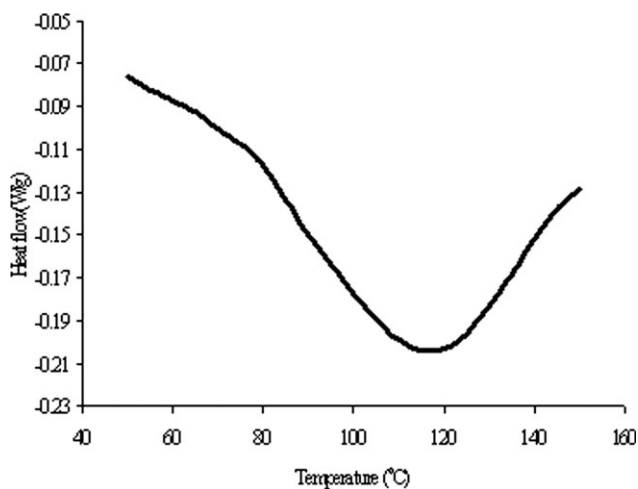**Figure 4** TGA thermogram of PAni [$HClO_4$].

Figure 5 DSC thermogram of PAni [HClO$_4$].

Scanning electron microscopy

The SEM photograph (Fig. 6) of polyaniline shows that the chains are loosely packed and has a grain size of 1 μm.

Effect of organic dopants

Dielectric loss (ε″) and conductivity (σ)

Figure 7 shows the dielectric loss and conductivity of Polyaniline *in situ* doped with organic sulfonic acids. The dielectric loss and conductivity of camphor sulfonic acid doped samples shows higher values compared to toluene sulfonic acid and naphthalene sulfonic acid doped samples. When a microwave field is applied to a polar material, the dipoles orient themselves with the field called dipolar polarization, leading to dielectric loss and conductivity. When the size of the chain is reduced, the movement of molecular chain is easier and therefore the
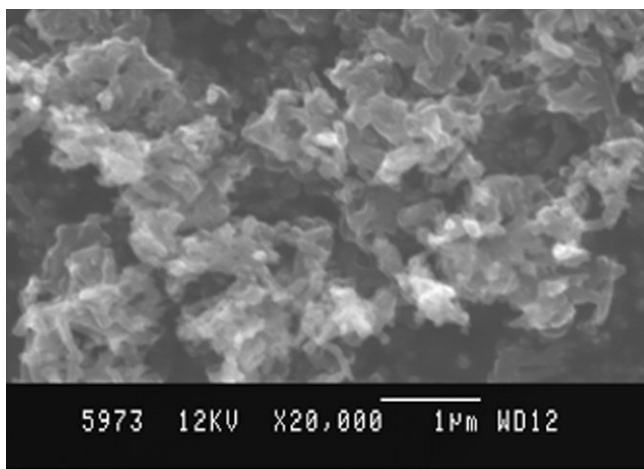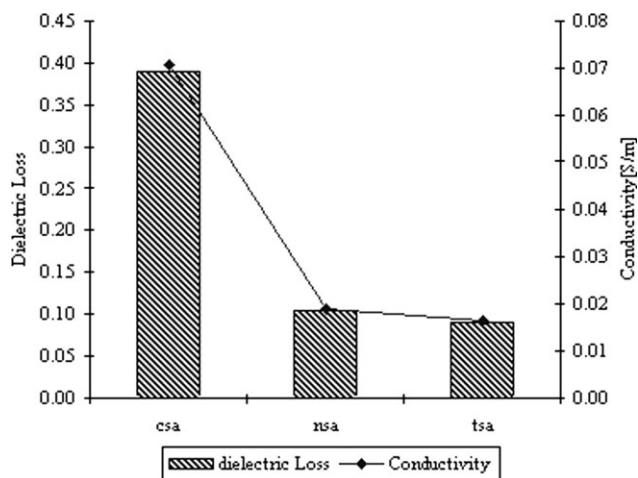

Figure 7 Effect of different organic sulphonic acids on the dielectric loss and conductivity of Polyaniline at 2.97 GHz.

dipole alignment on the application of a field becomes more rapid compared with longer chains.[37]

The scanning electron micrographs of CSA (Fig. 8) and NSA (Fig. 9) doped samples show that CSA gives shorter chains of average grain size 1 μm compared with 10 μm of NSA doped samples. This may be the reason why CSA give higher values of dielectric loss and conductivity than NSA, even though the sizes of counter ions are comparable. Another factor is that the CSA doped Polyaniline is the more solubilized form compared with the other dopants, which also contribute to higher dielectric loss for CSA doped Polyaniline owing to the greater flexibility of the chains.

Dielectric constant (ε′) and dielectric heating coefficient (J)

Figure 10 shows that the dielectric constant of CSA doped sample are higher compared with the other dopants. The shorter chain length of CSA doped
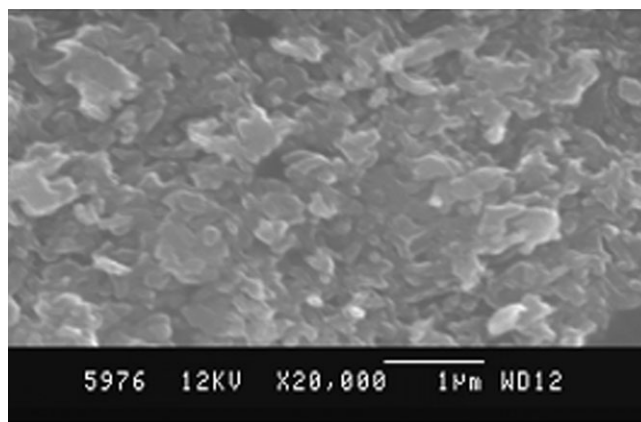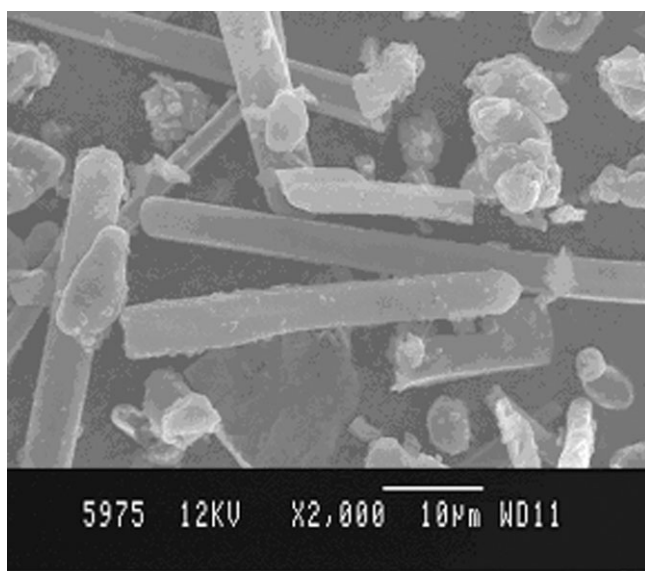

Figure 6 Scanning electron micrograph of PAni [HClO$_4$].

Figure 8 Scanning electron micrograph of PAni [CSA].

Figure 9 Scanning electron micrograph of PAni [NSA].

Figure 11 Effect of different organic sulphonic acids on the Loss tangent and absorption coefficient of Polyaniline at 2.97 GHz.

polyaniline increases free charge motion that in turn increasing the capacitive coupling between the chains and thus increases the dielectric constant.[38] It is also clear from the figure that the dielectric heating coefficient is minimum for CSA doped samples as expected.

Loss tangent (tan δ) and absorption coefficient

Figure 11 shows the variation of loss tangent and absorption coefficient of Polyaniline samples. Because the loss tangent and the absorption coefficient are directly related to the dielectric loss, they show a proportional behavior.

Comparison of the dielectric properties of PAni (HClO₄) and PAni (CSA)

The dielectric parameters of PAni (HClO₄) and PAni (CSA) are compared in Table II. It is clear from the
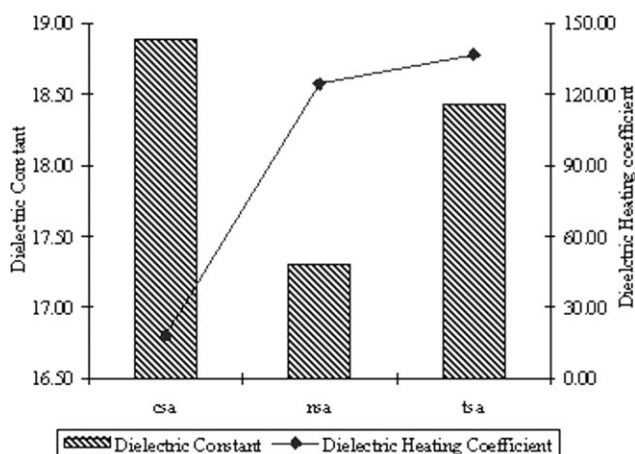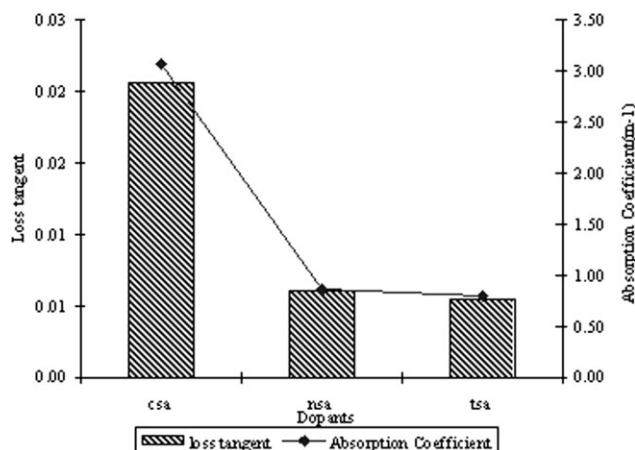
table that the dielectric properties of $HClO_4$ doped Polyaniline is superior than CSA doped and in the case of $HClO_4$ dopant, the size is less and the doping is not diffusion limited, when compared with CSA dopant and hence the former shows better relaxation leading to high dielectric loss. Because the conductivity is directly related to the dielectric loss factor, the conductivity is also higher for $HClO_4$ doped samples compared with CSA samples. When the size of the dopants are high, the interchain distance between the polymer chains increases, which results in a decreased capacitive couplings and hence the low values of dielectric constant as noted earlier[38] for CSA doped Polyaniline samples.

The dielectric heating coefficient is inversely related to the dielectric loss factor and hence the $HClO_4$ doped samples show the minimum value. The loss tangent and absorption coefficient are higher for $HClO_4$ doped polyaniline and penetration depth or skin depth is low for $HClO_4$ doped polyaniline, as expected.

CONCLUSIONS

The polyaniline prepared at RT shows better microwave response compared with those prepared at low and high temperatures. The microwave response of

Figure 10 Effect of different organic sulphonic acids on the dielectric constant of Polyaniline at 2.97 GHz.

TABLE II
Comparison of Dielectric Properties of PAni (HClO₄) and PAni (CSA)

Dielectric property	PAni (HClO₄)	PAni (CSA)
Dielectric loss (ε_r'')	2.68	0.3
Conductivity (σ S/m)	0.44	0.05
Dielectric constant (ε_r')	11.60	18
Dielectric heating coefficient (J)	0.78	26.03
Loss tangent (tan δ)	0.23	0.02
Absorption coefficient (m^{-1})	24.02	2.18
Skin depth (m)	0.04	0.46

$HClO_4$ doped PAni is better when compared with other inorganic dopants like HCl, HNO_3, and H_2SO_4. The dielectric heating coefficient is a minimum for $HClO_4$ doped PAni and the conductivity is a maximum. The dielectric parameters such as loss, conductivity, loss tangent, and absorption coefficient, all show a strong frequency dependence. Among the organic dopants, sulfonic acids like CSA, NSA, and TSA were efficient for *in situ* doping reaction. CSA doped samples showed better properties. NSA imparted a tubular morphology to the PAni formed. This effect was not prevalent with the other acids used.

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