Dielectric parameters and a.c. conductivity of pure and doped poly (methyl methacrylate) films at microwave frequencies

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Abstract. Dielectric properties of pure and doped poly (methyl methacrylate) (PMMA) films at microwave frequency, 8·92 GHz, have been studied at 35°C. Iodine, benzoic acid and $FeCl_3$ have been used as dopants. The losses in doped films are found to be larger than in pure PMMA films. The increased losses account for increased a.c. conductivity in doped films. The increase in conductivity is accounted due to creation of additional hopping sites for the charge carriers in doped samples. The dielectric data has also been used to evaluate optical constants, absorption index (K) and refractive index (n) of the films.

Keywords. Dielectric constant; a.c. conductivity; dielectric relaxation.

1. Introduction

In recent times polymers are finding an important place in different research laboratories for the study of their various properties. In view of the applications of insulation, isolation and passivation properties of polymers in microelectronics and optical waveguide systems, studies of the dielectric properties of polymers are of considerable interest. In polymeric materials, the polarization and depolarization behaviour are related to the dielectric relaxation process (Natarajan and Dube 1981).

The behaviour of polymeric films is of direct interest to both the basic studies of electrical conduction and their application in capacitors for microelectronics. Polymer films are being used as photoresist and electron beam resists for very large scale integration, photoconductors, printing and copying, liquid crystal displays, positive coatings and for surface modifications. Poly (methyl methacrylate) is one such potential polymer used in optical devices as adhesion promoters and lubricant.

Considerable work at low frequencies in polymeric materials has been reported in recent years (Srivastava and Shrivastava 1981; Aras and Baysal 1984; Frensch and Wendorff 1986; Chakraborty *et al* 1991; Wiibbenhorst *et al* 2003). But very little work has been done at microwave frequencies. Previously, we have done dielectric measurements at microwave frequencies in polymer blends (Tanwar *et al* 2006).

The present work describes the results of our investigations on dielectric properties of pure PMMA and doped by iodine, benzoic acid and $FeCl_3$ in the form of thin films at 8·92 GHz microwave frequency and at room temperature.

Iodine is a suitable acceptor dopant. Benzoic acid is a weak aromatic carboxylic acid. Its phenyl group functions as an electron withdrawing group. It is selected as a dopant material. $FeCl_3$ is also an acceptor dopant and selected for the dielectric studies.

2. Experimental

2.1 *Sample preparation*

Poly (methyl methacrylate) (PMMA) supplied by HiMedia Laboratories Pvt. Ltd, Mumbai (India) was used for the study. Iodine, benzoic acid and $FeCl_3$ were used as dopants.

Thin films of pure PMMA of thickness 60 μm, 100 μm, 150 μm, 200 μm, respectively were prepared by solution cast method, the solvents used were benzene and acetone. To prepare the iodine doped films of thickness, 100 μm, the iodine was taken in percentage weights viz. 2%, 4%, 6% and 8%. To prepare the benzoic acid doped films of thickness, 100 μm, the benzoic acid was taken in the percentage weights viz. 4%, 8%, 12%, 16% and 20% and in $FeCl_3$ doped films of thickness 200 μm, $FeCl_3$ was taken in the percentage weights viz. 2%, 4%, 6%, 8% and 10%. All the doped films were made by solution cast method by using suitable solvents i.e. benzene for iodine doped samples, acetone for $FeCl_3$ and benzoic acid doped samples.

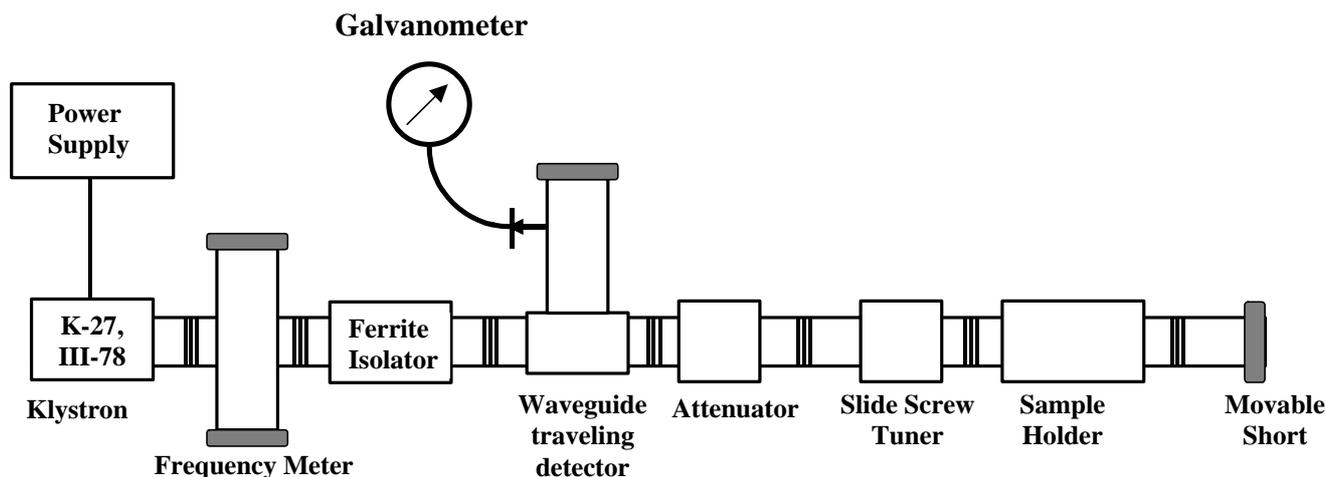*Author for correspondence (tanwar17msj@yahoo.com)

Galvanometer

Figure 1. Schematic diagram of the experimental set up.

Table 1. Dielectric parameters, absorption index and refractive index for pure PMMA at 8·92 GHz frequency and at 35°C temperature.

Thickness, C (μm)	Dielectric constant (e_r)	Dielectric loss (e_i)	Loss tangent (tan d)	Relaxation time ($t \times 10^{13}$ s)	Conductivity, s (mho/m)	Absorption index (K)	Refractive index (n)
60	2·67	0·036	$1·35 \times 10^{-2}$	2·4	$1·8 \times 10^{-2}$	$0·68 \times 10^{-2}$	1·63
100	2·52	0·057	$2·25 \times 10^{-2}$	4·0	$2·8 \times 10^{-2}$	$1·13 \times 10^{-2}$	1·58
150	2·53	0·071	$2·89 \times 10^{-2}$	5·1	$3·6 \times 10^{-2}$	$1·42 \times 10^{-2}$	1·59
200	2·47	0·091	$3·70 \times 10^{-2}$	6·6	$4·5 \times 10^{-2}$	$1·85 \times 10^{-2}$	1·57

2.2 *Dielectric measurements*

For microwave measurements of dielectric parameters of thin films, we have used the technique developed by Dube and Natarajan (1974). The experimental set up was as shown in figure 1. The sample is mounted along the axis of the waveguide. With this configuration, the electric field acts in the plane of the film. The advantage of this method is that the thin specimen is placed longitudinally at the centre of the broad side of a hollow rectangular waveguide excited in the TE_{10} mode so that the whole specimen remains in maximum electric field. Being an electrodeless technique, measurements at microwave frequencies are free from electrode polarization and associated problems and thus yield real material parameters. The accuracy for the measurement of e_r and e_i is about ±1% and ±5%, respectively.

3. Results and discussion

The dielectric constant (e_r), dielectric loss (e_i), loss tangent (tan d), relaxation time (t) and a.c. conductivity (s) were evaluated using the standard relations of these parameters (Dube 1984; Singh 1996).

Table 1 shows the experimentally observed values of dielectric constant (e_r), dielectric loss (e_i), loss tangent (tan d), relaxation time (t), conductivity (s), absorption index (K) and refractive index (n) for the PMMA films of varying thicknesses at 35°C. The value of e_r is in agreement with the value of 2·61 at 3 GHz frequency reported by Baker–Jarvis *et al* (2001). The values of e_i and tan d show that the PMMA films are of low loss, though these values increase with increasing film thickness.

The values of relaxation time are calculated by using the relation

$$t = e_i / w e_r,$$

which comes out of the order of 10^{-13} s. These values are close to the t values obtained by Khare *et al* (1993) with TSDC studies, although the measurement conditions are different. The decrease in t with the decrease in film thickness may be attributed to the decrease in number of dipoles in the sample.

The microwave conductivity (s) increases with the increase in thickness. Increase in s may be attributed to increase in e_i with film thickness, as $s = w e_0 e_i$.

The values of e_r, e_i, tan d, t, s, K and n for the PMMA films doped with iodine, benzoic acid and $FeCl_3$ are given in table 2. The concentration of iodine, benzoic acid and $FeCl_3$ in the samples varied up to 8%, 20% and 10%, respectively by weight. The variations of tan d and s with the doping percentage are shown in figures 2 and 3, respectively.

Table 2. Dielectric parameters, absorption index and refractive index for I_2 doped, benzoic acid doped and $FeCl_3$ doped PMMA films.

Doping (%)	Dielectric constant (e_r)	Dielectric loss (e_i)	Loss tangent (tan d)	Relaxation time ($t \times 10^{13}$ s)	Conductivity, s (mho/m)	Absorption index (K)	Refractive index (n)
PMMA + I_2 (film thickness = 100 μm)							
0	2·57	0·057	$2·25 \times 10^{-2}$	4·0	$2·8 \times 10^{-2}$	$1·13 \times 10^{-2}$	1·58
2	2·67	0·258	$9·66 \times 10^{-2}$	17·2	$12·8 \times 10^{-2}$	$4·82 \times 10^{-2}$	1·64
4	2·80	0·323	$11·52 \times 10^{-2}$	20·0	$16·0 \times 10^{-2}$	$5·74 \times 10^{-2}$	1·68
6	2·86	0·385	$13·46 \times 10^{-2}$	24·0	$19·1 \times 10^{-2}$	$6·70 \times 10^{-2}$	1·69
8	2·88	0·472	$16·38 \times 10^{-2}$	29·2	$23·4 \times 10^{-2}$	$8·13 \times 10^{-2}$	1·70
PMMA + benzoic acid (film thickness = 100 μm)							
0	2·52	0·057	$2·25 \times 10^{-2}$	4·0	$2·8 \times 10^{-2}$	$1·13 \times 10^{-2}$	1·58
4	2·54	0·377	$14·86 \times 10^{-2}$	26·5	$18·7 \times 10^{-2}$	$7·39 \times 10^{-2}$	1·60
8	2·65	0·478	$18·05 \times 10^{-2}$	32·2	$23·7 \times 10^{-2}$	$8·95 \times 10^{-2}$	1·64
12	2·78	0·635	$22·90 \times 10^{-2}$	40·9	$31·6 \times 10^{-2}$	$11·31 \times 10^{-2}$	1·68
16	2·60	0·433	$16·65 \times 10^{-2}$	29·7	$21·5 \times 10^{-2}$	$8·27 \times 10^{-2}$	1·62
20	3·00	0·706	$23·50 \times 10^{-2}$	41·9	$35·0 \times 10^{-2}$	$11·60 \times 10^{-2}$	1·74
PMMA + $FeCl_3$ (film thickness = 200 μm)							
0	2·47	0·091	$3·70 \times 10^{-2}$	6·6	$4·5 \times 10^{-2}$	$1·85 \times 10^{-2}$	1·57
2	2·51	0·173	$6·91 \times 10^{-2}$	12·3	$8·6 \times 10^{-2}$	$3·45 \times 10^{-2}$	1·58
4	2·53	0·194	$7·69 \times 10^{-2}$	13·7	$9·6 \times 10^{-2}$	$3·84 \times 10^{-2}$	1·59
6	2·49	0·112	$4·51 \times 10^{-2}$	8·0	$5·6 \times 10^{-2}$	$2·25 \times 10^{-2}$	1·58
8	2·48	0·099	$3·98 \times 10^{-2}$	7·1	$4·9 \times 10^{-2}$	$1·99 \times 10^{-2}$	1·58
10	2·50	0·194	$7·76 \times 10^{-2}$	13·9	$9·6 \times 10^{-2}$	$3·88 \times 10^{-2}$	1·58
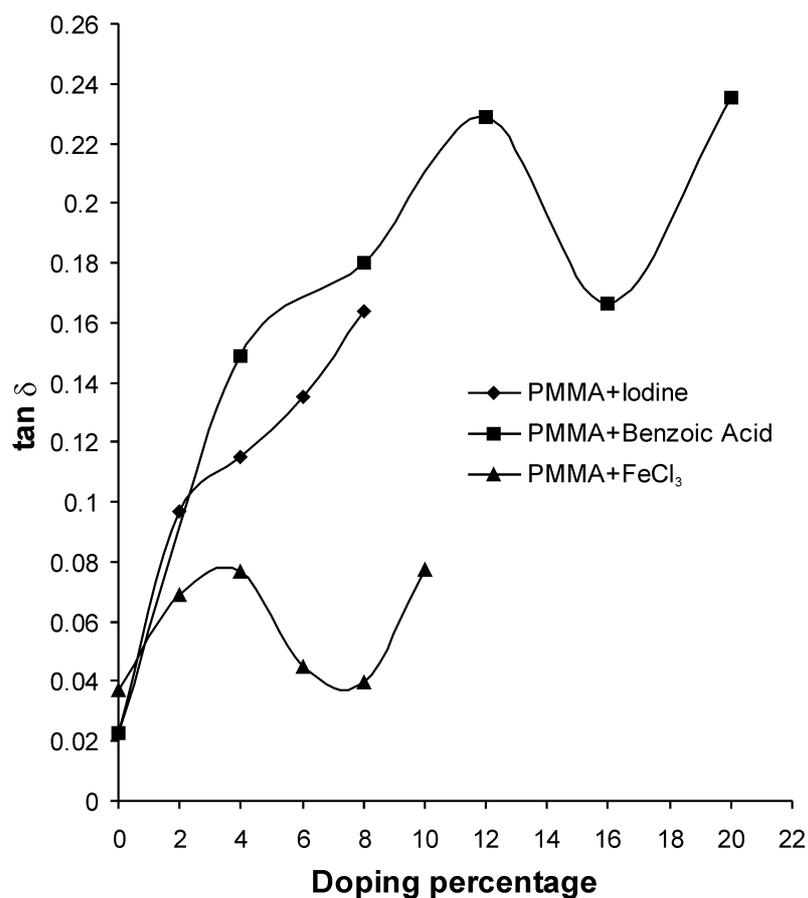
Figure 2. Variation of loss tangent with doping percentage at 8·92 GHz and at 35°C temperature.
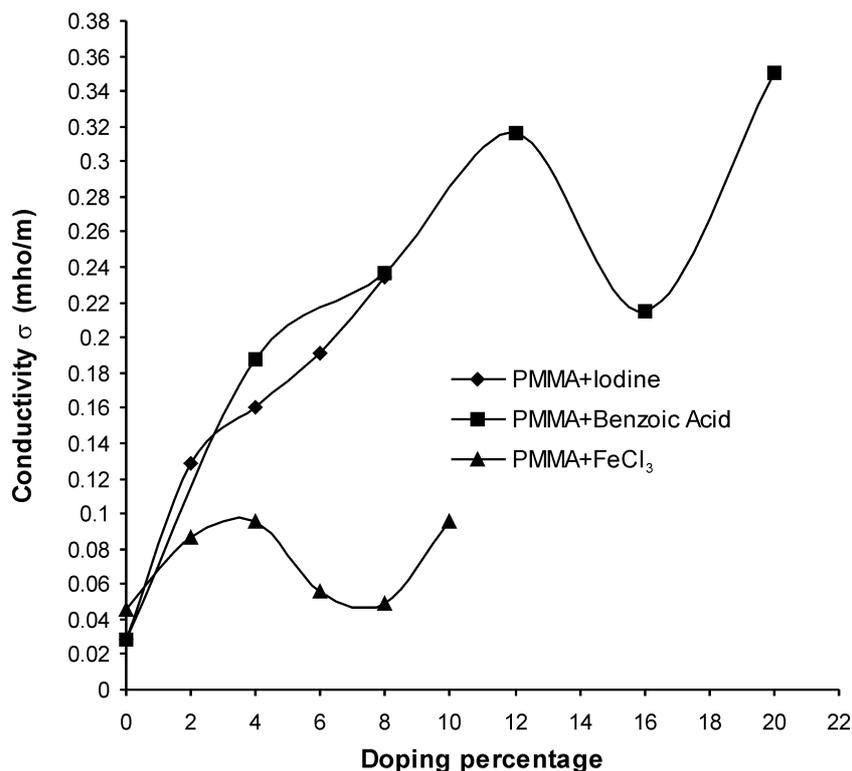
Figure 3. Variation of a.c. conductivity with doping percentage at 8·92 GHz and at 35°C temperature.

For the iodine doped PMMA films, the e_r values increase as the iodine content in the sample increases and this may be attributed to the presence of highly polarizable molecular iodine. The increase in e_i, tan d and t with increase in iodine concentration shows that on increasing the doping, the number of dipoles participating in the orientation process increases, while the frequency of orientation remains unchanged. The iodine doping changes the effective polarization so to say.

The conductivity values also increase as the iodine concentration for doping increases. The increase in s may be correlated with the increase in e_i and this may be attributed to the doping of acceptor iodine into the polymer, which increases the dielectric constant and loss factor due to the formation of newer complexes. The addition of I_2 reduces the insulating capacity (by increasing conductivity) due to introduction of localized states. When I_2 is mixed with PMMA in a common non-polar solvent like benzene, due to its high electron affinity, it may interact with carbon (carrying unsaturation) to form electrostatic linkage. During the process of evaporation and also during outgassing at high temperature when benzene is completely evaporated, I_2 may form a strong bond with carbonyl carbon ($-\overset{\text{C}}{\underset{\text{O}}{\Vert}}-$) of ester group (–COOCH$_3$) of PMMA. The addition of I_2 to PMMA enhances the polar character of PMMA, making it electrically more conductive. It is known that I_2 diffuses preferentially in the amorphous regions of the

molecular chain. I_2 goes either as single molecules or as molecular aggregate. Iodine ($r = 1·35$ Å) owing to its smaller size has an ability to diffuse vigorously in the polymer structure. When PMMA is doped with iodine, it may reside at various sights. It may undergo substitution into polymer chain at the amorphous or crystalline boundaries and preferentially into amorphous regions of the polymer.

Furthermore, it is asserted that addition of I_2 creates additional hopping sites for the charge carriers and hence increase in its concentration increases the conductivity. Conductivity of *a*-AgI at microwave frequencies was also explained by Saraswat and Dube (1990) by using the ion hopping models (Dietrich *et al* 1980).

Table 2 also shows various dielectric parameters for the benzoic acid doped PMMA films. All the evaluated dielectric parameters first increase with the increase in doping percentage and becomes maximum at 12% doping and then decreases at 16% concentration and after that again increases with the increase in the doping concentration of benzoic acid in the PMMA film.

The benzoic acid is a weak aromatic carboxylic acid (Sangawar and Adgaonkar 1998). Its phenyl group functions as an electron withdrawing group. The decrease in the various dielectric and conductivity values at 16% concentration of benzoic acid may be attributed to the formation of charge transfer complexes. The side group (ester) of PMMA may form CTC by donating electron to the dopant.

The TSDC studies carried out by Sangawar and Adgaonkar (1998) for the BA doped PMMA films at different polarizing fields, show that the d.c. conductivity increases with increasing polarizing field and they have observed two peaks in the conductivity data. In the present studies for the BA doped PMMA films we have observed enhancement in the a.c. conductivity values at microwave frequencies. The anomalous variation in s suggests that the random coiling of PMMA molecules in PMMA matrix marks the effect of CT complexes and also the additional trapping sites generated are responsible for increase in conductivity with increase in dopant level of benzoic acid.

The dielectric data for the PMMA films doped by 2–10% $FeCl_3$ have also been reported in table 2. The values of the various parameters first increase up to 4% doping concentration and after that decreases with increasing doping percentage of $FeCl_3$ in the films and attains a minimum value at 8% and after that again goes on increasing.

The polymer or macromolecule has large number of monomers. The doping of $FeCl_3$ in the polymer affects its chemical as well as physical properties e.g. density, composition, stability, conductivity etc. The doping in polymer clearly showed the presence of Fe ions by change in colour i.e. transparent to yellowish. It is expected that Fe ions were well dispersed in the PMMA.

The peak values in conductivity at 4% and again towards 10% and also minimum at 8% doping concentration give indication of the formation of another bond. It is expected that the Fe ions were either residing in the voids between the chain or got attached to the functional group in the side chain. This may also be attributed by the C–Fe clusters that increase the crosslinking between the polymer chains. The formation of C–Fe clusters have also been confirmed by the Mössbauer spectroscopy studies of $FeCl_3$ doped PMMA by Somayajulu *et al* (2001).

Absorption index (K) and refractive index (n) are calculated using the following relation (Vankrevelen and Hoftyzer 1976)

$$\tan \boldsymbol{d} = \frac{2K}{1 - K^2} \quad \text{and} \quad \boldsymbol{e}_i = 2n^2 K.$$

Comparison of K values in table 2 shows that the absorption increases in the doped PMMA films. Higher K values are obtained for benzoic acid doped PMMA films as compared with iodine or $FeCl_3$ doped films. The refractive index values (n) are found to be almost constant for $FeCl_3$ doped films, while for benzoic acid doped and iodine doped films, 'n' value increases with the increase of doping in PMMA films.

4. Conclusions

(I) The conductivity of PMMA can be increased by using a suitable dopant material. All the doped films show better conductivity as compared to pure PMMA films.
(II) The increase in conductivity is accounted due to creation of additional hopping sites for the charge carriers in doped samples.
(III) Hopping process is the probable mechanism of conduction phenomenon.

Acknowledgements

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