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Dielectric Properties of Polymethylmethacrylate and Its Composites with ZnO†

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The polymer films of polymethylmethacrylate at different thickness and its composites with ZnO at various weight percentages of same thickness have been studied for the determination of dielectric properties, dielectric loss, A.C. conductivity and dielectric modulus using measurements of capacitance of the above samples as a function of frequency over the range 50 Hz-5 MHz at room temperature. The films of polymethylmethacrylate and its composites have been characterized using X-ray diffractometer. The dielectric permittivity of films of polymethylmethacrylate behaves nonlinearly as frequency increases over the range 50-300 Hz, where as above 300 Hz the values of dielectric constant remain constant. But it is observed that the dielectric constant of polymethylmethacrylate increases as thickness of the film increases. In case of composite films of polymethylmethacrylate with ZnO the values of dielectric permittivity decreases gradually up to frequency of around 1 KHz and at higher frequencies it remains constant for all the weight percentages of ZnO. But it is observed that the properties of dielectric constant decrease as weight percentage of the compound increases. The complex form of dielectric modulus of polymethylmethacrylate is obtained from the experimentally measured data of dielectric constant and dielectric loss values. The relaxation time of the orientation of dipoles is obtained from the peak value of angular frequency through the plots of imaginary part of electrical modulus as function of frequency. The impedance of polymethylmethacrylate polymer increases as thickness of the films increases. The A.C. conductivity of polymethylmethacrylate film remains constant up to frequency of 1 MHz and above this it shows a nonlinear phenomena with peak values at frequency 4 MHz.

Key Words: Dielectric constant, Impedance, A.C. conductivity, Dielectric modulus, Relaxation time.

INTRODUCTION

It is well known that the composites of polymers films exhibit enhanced properties than that of the constituent materials[1,2]. The polymer composite films are combination of different polymers and or polymers with compound materials. The polymer composite material is important to the electronic industry for its dielectric properties in the use of capacitors[3]. One of the most characteristic features is that of their dielectric properties and that can be widely changed by choice of shape, size and conductivity of mixed constituents in the polymeric matrix[4]. The study of dielectric constant, dielectric loss, A.C. conductivity and electrical modulus as function of frequency is one of the most convenient and sensitive methods of studying the polymeric structure[5-8]. The physical structure is of great importance in determining the dielectric behaviour[9-10].

EXPERIMENTAL

Polymer substance of polymethylmethacrylate (PMMA) and ZnO are obtained from SD Fine Chem. Ltd., Mumbai, India. The different quantities of polymethylmethacrylate substances have been used for preparing the thin films of different thickness. The films of polymethylmethacrylate and its composite with ZnO are prepared by solution casting method. The different quantity of polymer substance of polymethylmethacrylate is dissolved in acetone to get the polymethylmethacrylate films of different thicknesses. The composite films of polymethylmethacrylate with ZnO at different weight percentages such as 10, 20, 30 and 40 are obtained by mixing of ZnO with the polymethylmethacrylate solution. The films are kept in between the parallel plate type sample holder to provide electrical connections. The measurements of capacitance, impedance, phase angle and dissipation factors are made as a function of frequency ranging from 50 Hz-5 MHz at room temperature using PC based LCR meter (Model: HIOKI 3552-50-LCR Hitester).

RESULTS AND DISCUSSION

The dielectric properties of polymethylmethacrylate films and its composites with ZnO are studied as a function of frequency at room temperature. The values of dielectric constants

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are obtained from the measured values of capacitances using the eqn. (1).

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \quad (1)$$

where, C is capacitance of the dielectric material, d is thickness of the sample, A is area of the sample and ε_0 is the permittivity of free space. Further, from the measured values of dielectric constants, dielectric loss and A.C. conductivities (σ_{ac}) are calculated using the eqns. (2) and (3) respectively, which are given below.

$$\varepsilon'' = \varepsilon' \tan \delta \quad (2)$$

$$\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta \quad (3)$$

X-Ray diffraction studies: The crystalline or amorphous nature of polymethylmethacrylate and its composite films with ZnO have been studied using powder X-ray diffractometer at an angle 2θ (Regaku) and the XRD spectra of polymethylmethacrylate and its composite films are given respectively in Figs. 1 and 2. In Fig. 2 it is observed that the diffused and broader peaks for polymethylmethacrylate film at 18º angle and strong intensive peaks for composite film at angles of 32º, 36º and 38º. This reveals that the polymethylmethacrylate composite films shown crystalline in nature.

The particle size could be easily estimate using the Debye Scherer formula given by:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (4)$$

where, D is the particle size (crystal size), β = FWHM of stronger peak (highest intensity peak) and λ is the wavelength of the X-ray.

Dielectric properties: The dielectric constants of polymethylmethacrylate films are obtained from the measured values of capacitance as functions of frequency at room temperature using eqn. (1), which are shown in Fig. 3. The dielectric constant of polymethylmethacrylate varies nonlinearly as the frequency increases up to around 1 KHz for all samples. But at higher frequencies more than 1 KHz the dielectric constant remains same and is independent of the frequencies. A more dielectric dispersion is observed at the lower frequency region and it remains almost independent of applied external field at high frequency side. Fig. 3 showed that as thickness of the polymethylmethacrylate samples increases the values of dielectric constant also increases appreciably within the frequency range 100 Hz-1 KHz. But at higher frequency, it remains constant. The peak of the non-linear curves shifts towards the lower frequency as thickness of the sample increases.

We have also studied the dielectric properties of the composite films of polymethylmethacrylate with 10, 20, 30 and 40 weight percentages of ZnO at thickness 0.525 mm as function of frequency and are given in Fig. 4. Here we have noticed that the values of dielectric constant of films of polymethylmethacrylate have been reduced by increase in weight percentage of ZnO. This implies that as dielectric constants of the composite films polymethylmethacrylate decrease as the weight per cent of ZnO increases. Hence we have seen the modifications in dielectric properties of the composite films. The dielectric permittivity of composite films decreases exponentially up to at lower frequency up to around 1 KHz. This may be attributed to the tendency of dipoles in polymeric composite films to orient themselves in the direction of the

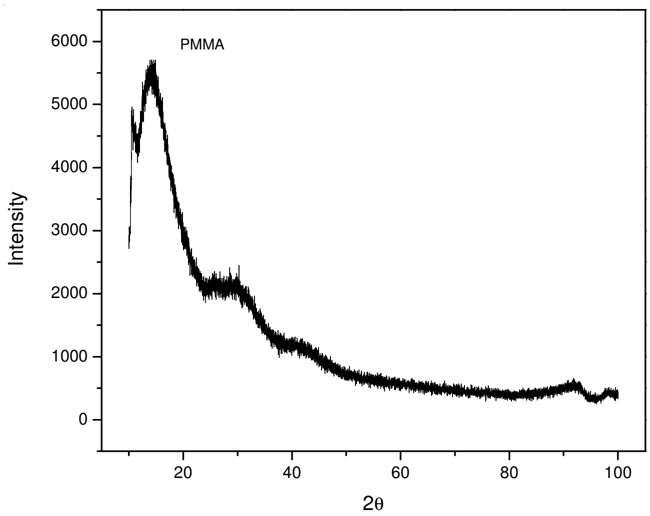

Fig. 1. XRD spectrum of pure polymethylmethacrylate

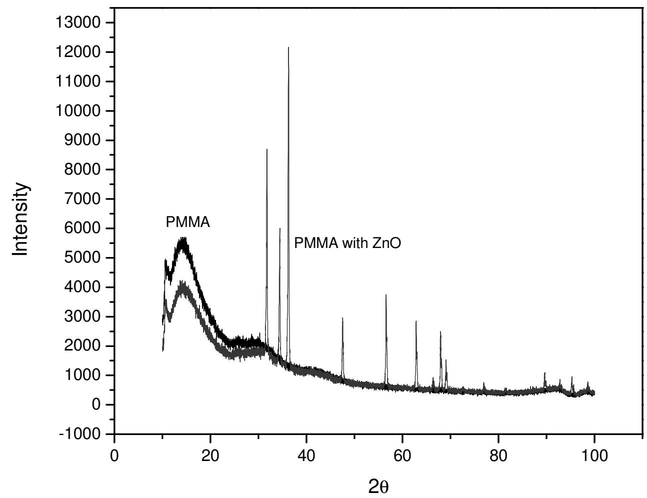

Fig. 2. XRD spectrum of the blend of polymethylmethacrylate with ZnO.

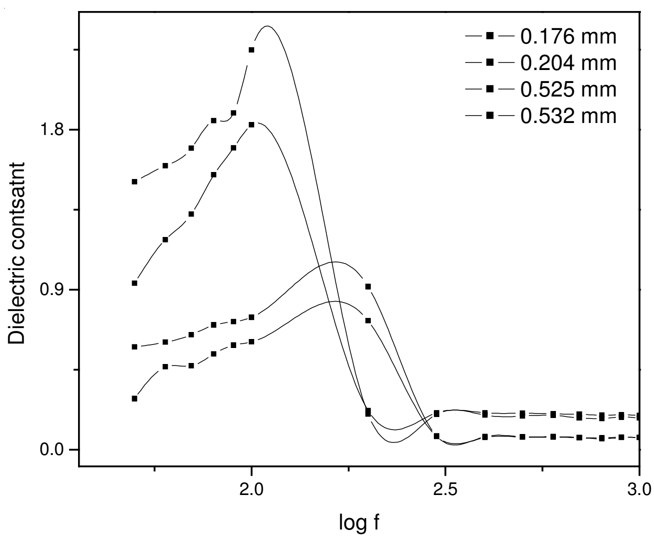

Fig. 3. Plot of dielectric constant *versus* frequency at different thickness of polymethylmethacrylate

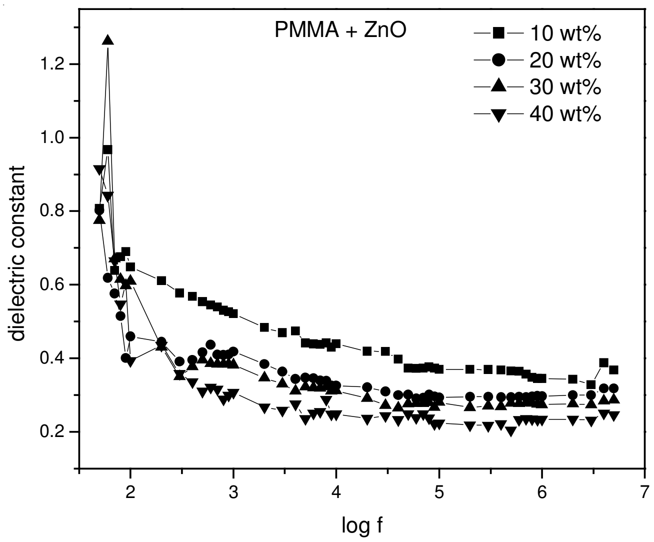

Fig. 4. Plot of dielectric constant *versus* frequency at different wt % of composite film

applied field. But at higher frequencies more than 1 KHz the dielectric constant remains same and is independent of the frequencies. It could be explained by dipoles orientation, which difficult to rotate at high frequency range. On the other hand, the high value of dielectric permittivity at lower frequency might be due to the electrode effect and interfacial effect of the sample[11].

Impedance measurements: The variation of impedances of films of polymethylmethacrylate as function of frequency at room temperature are measured (Fig. 5). The impedance of the polymethylmethacrylate film shown nonlinear behaviour at lower frequencies up to 1 KHz and onwards it remains almost constant over higher frequencies. Further we noticed in Fig. 5 that at lower frequency up to 1 KHz the impedance of the films of polymethylmethacrylate increases as thickness of the sample increases and it remains constant at higher frequency range.

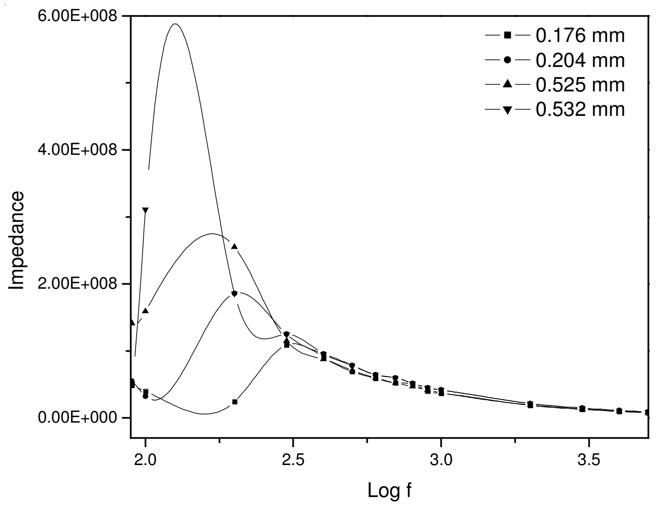

Fig. 5. Impedance of polymethylmethacrylate as function of frequency at different thickness

We have also studied the impedance of the composite films of polymethylmethacrylate with 10, 20, 30 and 40 weight percentages of ZnO at thickness 0.525 mm as function of frequency (Fig. 6). It is observed that the impedance of the composite film decreases exponentially at lower frequencies up to 10 KHz and onwards it remains constant for all composite films. Here we have noticed that the values of impedance of films of polymethylmethacrylate have been increased by increase in weight percentage of ZnO. This implies that as impedances of the composite films polymethylmethacrylate increases as the weight percent of ZnO increases.

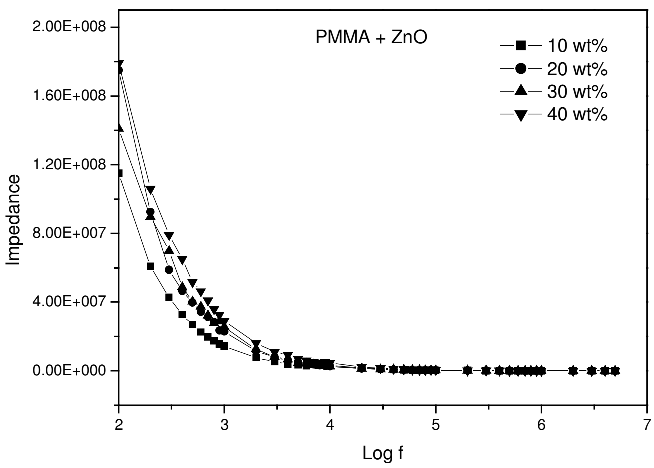

Fig. 6. Variation of impedance of composite films as function of frequency

Further, using the calculated data of dielectric constant (ε') and dielectric loss (ε''), given in eqns. (1) and (2), we find out the dielectric modulus. The complex form of dielectric modulus[6] is given by:

$$M^* = \frac{1}{\varepsilon^*} = M' + iM'' \quad (5)$$

where M' and M'' are the real and imaginary part of dielectric modulus. The formula to calculate dielectric modulus are given by:

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \quad (6)$$

$$M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \quad (7)$$

From the imaginary part of electrical modulus, M'', the relaxation time of the orientation of dipole can be obtained. The peak of the angular frequency (ω_p) can be obtained from the graphs M'', *versus* log frequency.

$$\tau = \frac{1}{\omega_p} \quad (8)$$

The variation of M' and M'' as function of frequency for polymethylmethacrylate films are given in Figs. 7 and 8 respectively. From the graphs M'', *versus* log frequency, the relaxation time of the orientation of dipole is obtained from the peak of the angular frequency (ω_p) and are given in Table-1. It is observed that magnitude of the relaxation time is increased as thickness of the polymethylmethacrylate film increases.

A.C. conductivity: The A.C. conductivity of polymethylmethacrylate films are obtained as functions of frequency from the measured values of dielectric permittivity and dielectric

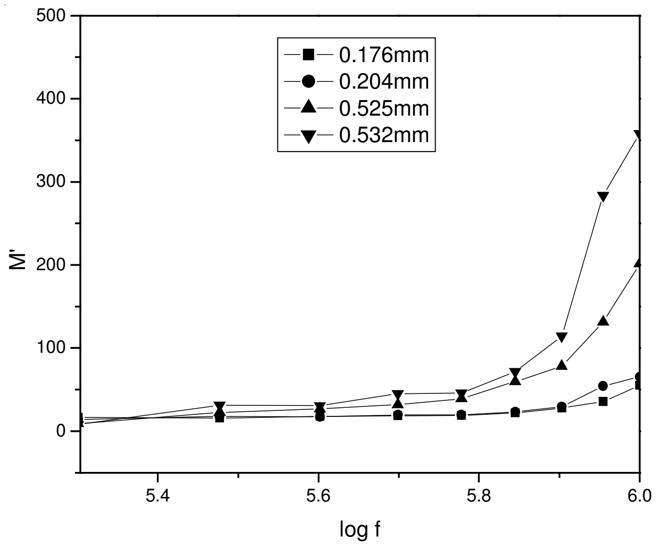

Fig. 7. Plots of dielectric modulus (M') of polymethylmethacrylate as function of frequency at different thicknesses

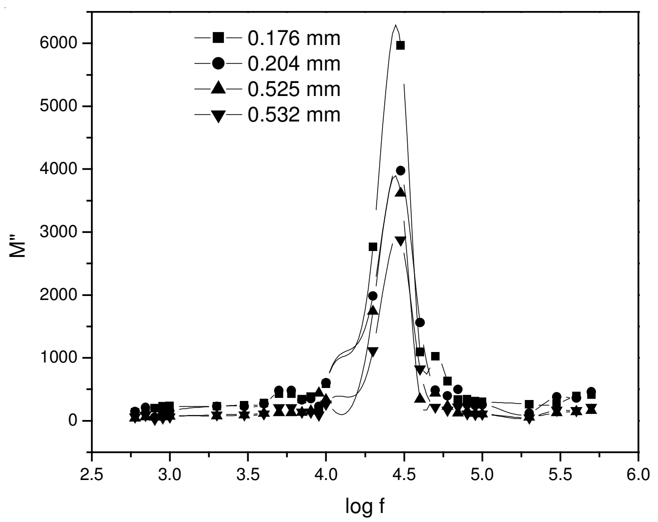

Fig. 8. Plots of dielectric modulus (M") of polymethylmethacrylate as function of different thicknesses

TABLE-1
RELAXATION TIME OF THE POLYMETHYLMETHACRYLATE FILMS AT DIFFERENT THICKNESSES

Thickness (mm)	Relaxation time, τ (μ sec)
0.176	40.9
0.204	40.8
0.525	40.7
0.532	40.7

loss using eqn. (3) at room temperature (Fig. 9). The A.C. conductivity of polymethylmethacrylate re mains constant over the frequency range 50 Hz to 2 MHz and afterwards it varies nonlinearly at higher frequencies. Further, it is observed that as thickness of the films of polymethylmethacrylate samples increases the values of A.C. conductivity also increases at higher frequency range 2-5 MHz.

The A.C. conductivity of composite films of polymethylmethacrylate with 10, 20, 30 and 40 weight percentages of ZnO are obtained as functions of frequency using eqn. (3) (Fig. 10). The A.C. conductivity of these composite films

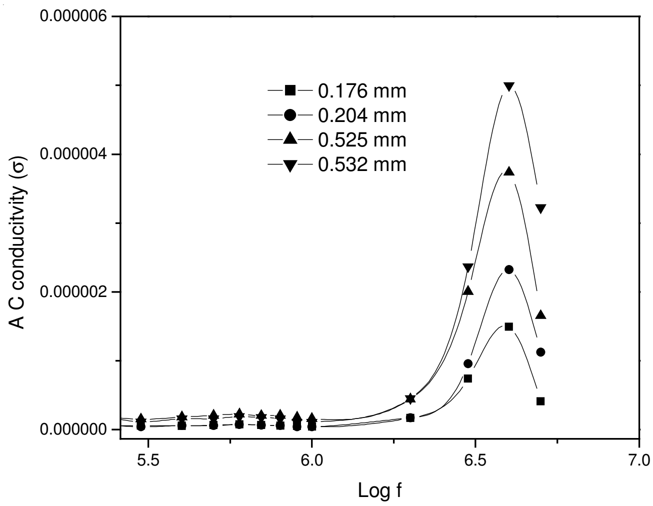

Fig. 9. Plot of A.C. conductivity as function of frequency at different thickness

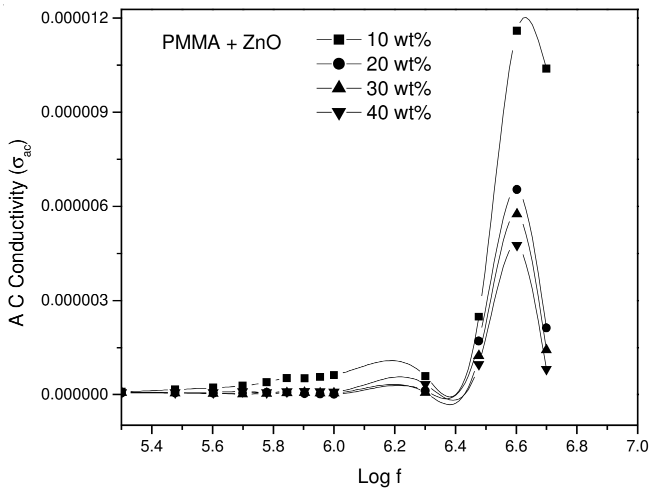

Fig. 10. Plots of A.C. conductivity as function of frequency at different weight percentage

remains constant over the frequency range 50 Hz to 2 MHz and afterwards it varies nonlinearly at higher frequencies over the range 2-5 MHz. Further, it is observed that as weight percentage of ZnO increases A.C. conductivity of composite films of polymethylmethacrylate decreased. Hence we observed the modification in A.C. conducting properties of the polymethylmethacrylate composite films.

Conclusion

The XRD characterization reveals that the polymethylmethacrylate composite films shown more crystalline in nature. In case of dielectric measurements as thickness of the polymethylmethacrylate samples increases the values of dielectric permittivity also increases appreciably within the frequency range 100 Hz-1 KHz. The values of dielectric permittivity of films of polymethylmethacrylate have been reduced by increase in weight percentage of ZnO. Hence we have seen the modifications in dielectric properties of the composite films. It is observed that magnitude of the relaxation time is increased not much as thickness of the polymethylmethacrylate film increases. Further we observed that as thickness of the films of polymethylmethacrylate increases the values of A.C. conductivity also increases at higher frequency range 2-5 MHz. But as weight percentage of ZnO increases A.C. conductivity of composite films of polymethylmethacrylate decreases.

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