

Ultrasonic and Temperature Dependence on A.C. Conductivity of (PMMA)/Fe₂O₃ Nanocomposite Polymer Films

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Abstract: Ultrasonic and Dielectric characterization have been done by using Ultrasonic Pulse Echo method and LCR meter respectively. Temperature dependence of dielectric constant ϵ' and dielectric loss ϵ'' of PMMA and PMMA with composite of Fe₂O₃ polymer film are studied in the frequency range 50Hz-13 kHz and in the temperature range 40-120 °C. The experimental results show the PMMA polymer film and PMMA with composite with Fe₂O₃ polymer films the dielectric constant increases with increased the temperature as well as frequency, and is due to greater freedom of movement of the dipole molecular chains within the polymer film at high temperature. The dielectric loss of PMMA and composite film of Fe₂O₃ polymer film temperature increases dielectric loss decreases, which indicates that the major contribution to the polarization comes from orientation polarization. And the a.c.conductivity of PMMA film and its composite Fe₂O₃ polymer film shows that increases the temperature and frequency the a.c.conductivity increases anomaly at lower temperatures becomes more obvious with increasing the frequency and in composite film the Fe₂O₃ doping content, which probably corresponds to a transition from ferroelectric to anti-ferroelectric phases. The film is characterized by using X-Ray diffractometer and to measured lattice parameter of PMMA with composite of Fe₂O₃ polymer film it has a cubic and rhombohedra crystal structure of ferric oxide. The ultrasonic velocity is also found to be minimum in same film which may be attributed to maximum dissociation with least absorption in polymer matrix. Addition of Fe₂O₃ thermally stabilizes PMMA matrix.

Keywords: Polymer composites, Dielectric Constant, Dielectric loss, A.C.Conductivity.

1. Introduction

In recent years, the synthesis of polymeric nanocomposites has gained much interest in the scientific community thanks to their unique capability to combine the properties of the host polymer matrices, such as toughness, elasticity, processability, solubility, thermal stability, etc, with those of inorganic nanoparticles (NPs), such as hardness, chemical resistance, optical and electronic properties. Among a variety of nanofillers, semiconductor and metallic NPs are extensively studied and used, because of their unique properties especially in the nanoscale.[1-3] In this work we deal with polymeric nanocomposites incorporating various nanofillers,[4] each one of them having extremely attractive properties for technological applications. In particular we focus on iron oxide (Fe₂O₃) NPs due to their unique reversible wettability, due to their super paramagnetic nature[5,6] The dielectric properties of polymer/ceramic composites are influenced not only by the dielectric constant of the polymer and the ceramic, but also by the dispersion and loading of the ceramic in the polymer matrix.[7-8] Using higher dielectric constant particles and polymer matrix, and increasing the loading of particle fillers can increase the effective dielectric constant of a composite. As well, the morphological and structural optimization of particles will enhance their contribution to dielectric constant improvement [9]. Though lifting the filler content is a choice, however, too high loading of fillers would lead to poor quality of the composite. Polymers and polymer matrix composites are basically electrical insulators, due to their low concentration of free charge carriers. Thus their electrical response is, mainly, associated with relaxation phenomena occurring under the influence of ac field. The

observed relaxation processes are related to dipolar orientation effects or space charge migration [10, 11].

2. Experimental

Polymer substance of Polymethylmethacrylate (PMMA) and Fe₂O₃ are obtained from S.d. Fine Chem. Ltd, Mumbai, India. The 1N concentration of PMMA substances have been used for preparing the thin film. The film of PMMA and its composite with Fe₂O₃ are prepared by solution casting method. The polymer substance of PMMA is dissolved in acetone to get the PMMA film. The composite film of PMMA with Fe₂O₃ at weight percentages of 10 is obtained by mixing Fe₂O₃ with the PMMA 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 - 13 kHz at different temperature 40 °C to 120 °C using PC based LCR meter (Model: DPI-1100 N4L PSM 1735 Numetrig).

3. Results and Discussion

The dielectric properties of Polymethylmethacrylate (PMMA) films and its composites with Fe₂O₃ are studied as a function of frequency at room temperature. The values of dielectric constants are obtained from the measured values of capacitances using the equation (1).

$$\epsilon' = \frac{C d}{\epsilon_0 A} \quad (1)$$

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

$$\epsilon^2 = \epsilon_0 \epsilon \quad (2)$$

$$s_{ac} = \frac{\epsilon_0 \epsilon \omega}{d} \quad (3)$$

A. Characterization using XRD

Figure.1, shows the crystalline or amorphous nature of PMMA and its composite films with Fe_2O_3 have been studied using powder X-ray diffractometer (XRD) at an angle 2θ (Regaku) taken at room temperature. The d spacing's deduced from the angular position 2θ of the observed peak, according to the Bragg formula

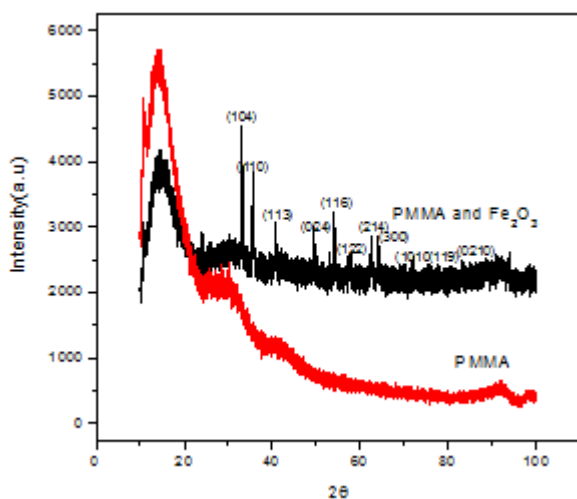


Figure 1: The XRD spectra of pure PMMA and its composite films

$$\lambda = 2d \sin \theta \quad (4)$$

are given in Table 1 (λ is the X-ray wavelength used). All the reflections peaks of the X-ray profiles were indexed in a rhombohedral cell and lattice parameters were determined using a least-squares method with the help of JCPDF data of hkl value. Good agreement between the observed and calculated interplanar spacing (d -value) suggests that the compounds are rhombohedral structure. X-ray diffraction confirms that specimen is single phase and matches with earlier report work. [12]

Table 1: X-ray diffraction data for PMMA with Composite of Fe_2O_3 films

2θ	d, Å	hkl
33.142	11.1359	1 0 4
35.597	3.5646	1 1 0
40.831	7.3242	1 1 3
49.427	8.2411	0 2 4
54.047	10.4519	1 1 6
57.393	4.8131	1 2 2
62.383	6.8012	2 1 4
63.934	4.3649	3 0 0
71.938	13.1809	1 0 10
72.258	11.8642	1 1 9
82.924	11.9022	0 2 10

B. Dielectric Properties

The dielectric constants of PMMA films are obtained from the measured values of capacitance as functions of temperature using equation (1), which are shown in Fig. 2. The dielectric

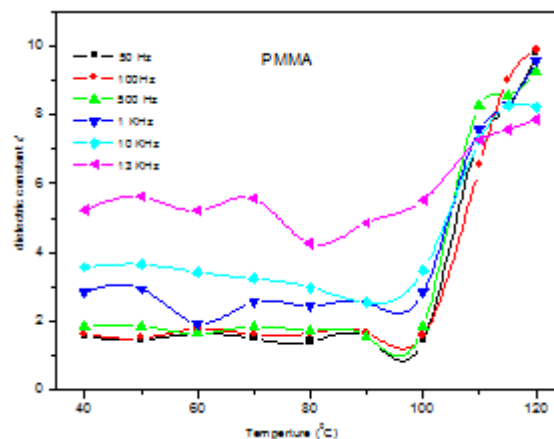


Figure 2: Plot of dielectric constant Vs temperature at different frequency of PMMA.

Constant of PMMA varies nonlinearly as the frequency increases and temperature increases up to around 100 °C for all samples. But where as at higher frequencies more than 1 KHz and higher Temp the dielectric constant is independent of the frequencies. A more dielectric dispersion is observed at the lower frequency region of 10 KHz and 13 KHz, and it remains almost independent of applied external field at high Temp side. Further we observed from Fig. 2 that as frequency of the PMMA samples increases the values of dielectric constant also increases appreciably with in the frequency range 100Hz-13 KHz, but where as at higher frequency. The peak of the nonlinear curves shifts towards the higher Temp as frequency of the sample increases.

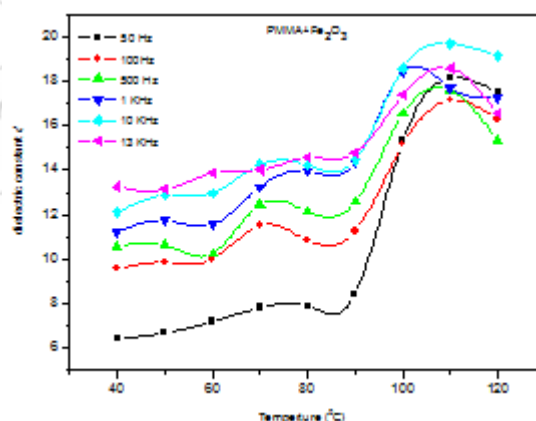


Figure 3: Temperature dependence of dielectric constant at different frequency of PMMA with Fe_2O_3 .

We have also studied the dielectric properties of the composite films of PMMA with Fe_2O_3 at thickness 0.525 mm as function of Temp and are given in Fig. 3. The dielectric Constant of PMMA with Fe_2O_3 varies nonlinearly as the frequency increases and temperature increases up to around 90 °C for all frequencies. But where as at higher Temp more than 90 °C of all frequency range the dielectric constant is independent of the Temp. A more dielectric

dispersion is observed at the higher frequency region of 1 KHz and 13 KHz, and it remains almost independent of applied external field at high Temp side. Further we observed from Fig. 3, that as frequency of the PMMA with Fe₂O₃ polymer film increases the values of dielectric constant also increases appreciably with in the frequency range 50Hz-13 KHz, But where as at higher Temp. The peak of the nonlinear curves shifts towards the higher Temp at 110 °C as frequency of the polymer film increases.

C. Dielectric loss

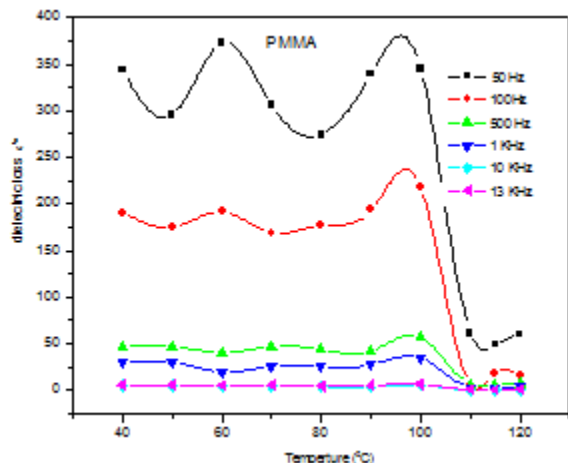


Figure 4: Temperature dependence of dielectric loss at different frequency of PMMA.

The dielectric loss of PMMA film is obtained as functions of Temp at different frequency using Equation (2) and is given in Fig 4. The Dielectric loss of these composite films at higher frequency range 500 Hz to 13 KHz it remains constant but in lower frequency 50 Hz and 100 Hz it shows nonlinearly at the temperature 40 °C to 100 °C afterwards it remains same at higher Temp range. The PMMA film frequency increases the dielectric loss of film of PMMA decreases. Hence we observed the modification in dielectric loss of the PMMA composite films.

The dielectric loss of composite film of PMMA with Fe₂O₃ is obtained as functions of Temp at different frequency using Equation (2) and is given in Fig 4. The Dielectric loss of these composite films at higher frequency range 500 Hz to 13 KHz it remains constant but in lower frequency 50 Hz and 100 Hz it shows nonlinearly at the temperature 40 °C to 120 °C. The PMMA with Fe₂O₃ composite film frequency increases the dielectric loss of composite film of PMMA decreases. Hence we observed the modification in dielectric loss of the PMMA composite films

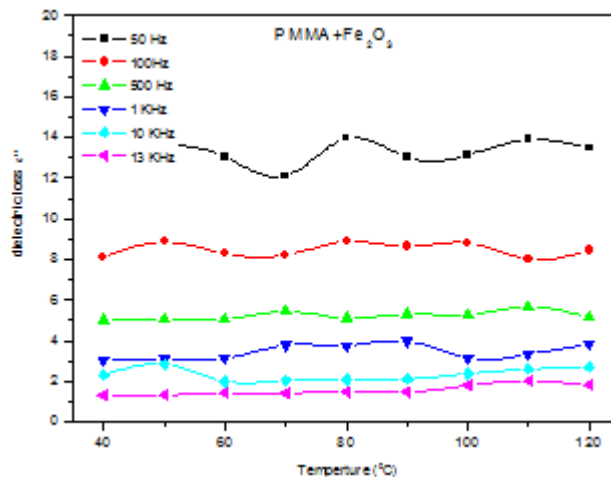


Figure 5: Temperature dependence of dielectric loss at different frequency of PMMA with Fe₂O₃.

D. A C Conductivity

Fig. 6. Shows the variation of a. c. conductivity with frequency at different temperatures for PMMA polymer film. The measured values of dielectric permittivity and dielectric loss using Equation (3) at different temperature. The plot of A C conductivity and frequency at different Temp is given in Fig. 6. The A C conductivity of PMMA remains constant over the frequency range 50 Hz and 100 Hz and afterwards it varies nonlinearly at higher frequencies. Further it is also observed that at Temp increases the values of a. c. conductivity also increases at higher degree Temp at 110 0C it is suddenly decreases frequency range of 500Hz- 13 KHz due to greater freedom of movement of the dipole molecular chains within the polymer at high temperature.

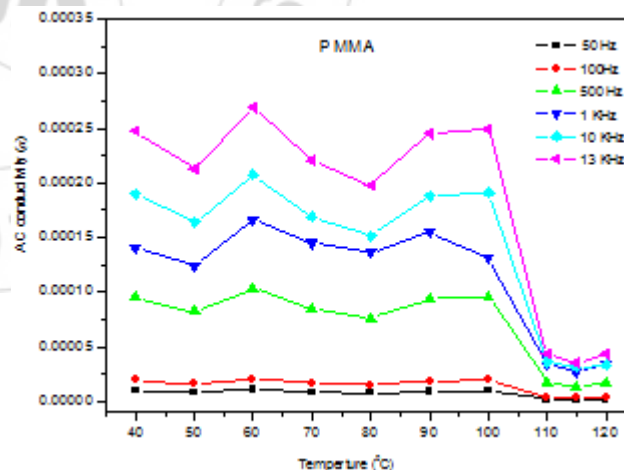


Figure 6: Plot of A.C. conductivity Vs temperature PMMA with composite films.

The A C conductivity of composite films of PMMA with Fe₂O₃ with frequency at different temperatures is obtained Equation (3) and is given in Fig. 7. Shows for PMMA with Fe₂O₃ polymer film. The measured values of dielectric permittivity and dielectric loss using Equation (3) at different temperature. The plot of A C conductivity and frequency at different Temp is given in Fig. 7. The A C conductivity of PMMA with Fe₂O₃ remains constant over the frequency range 50 Hz and 100 Hz and afterwards it

varies nonlinearly at higher frequencies at different Temp. Further it is also observed that at Temp increases the values of a. c. conductivity also increases at lower degree Temp at 60 °C it is suddenly decreases frequency range of 50 Hz- 13 KHz it remains constant.

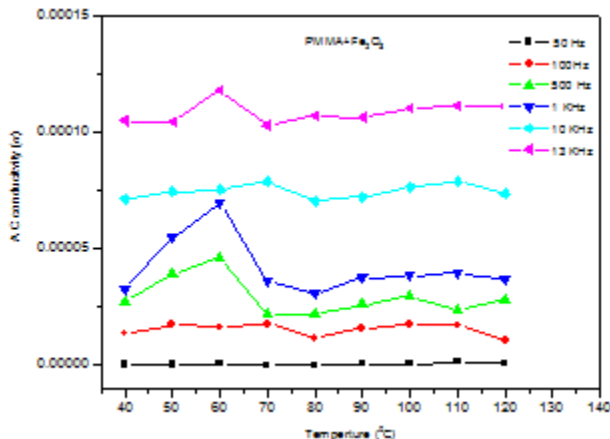


Figure 7: Plot of A.C. conductivity Vs temperature PMMA with composite films

4. Conclusions

The XRD spectra reveals that the PMMA composite films shown the crystalline in nature calculated interplanar spacing (d -value) suggests that the compounds are rhombohedral structure. The PMMA polymer film higher frequencies more than 1 KHz and higher Temp the dielectric constant is independent of the frequencies. A more dielectric dispersion is observed at the lower frequency region of 10 KHz and 13 KHz, and it remains almost independent of applied external field at high Temp side. In case of composites we have noticed that the values of dielectric constant of film as at higher Temp more than 90 °C of all frequency range the dielectric constant is independent of the Temp. A more dielectric dispersion is observed at the higher frequency region of 1 KHz and 13 KHz, Hence we have seen the modifications in dielectric properties of the composite films. The a. c. Conductivity of PMMA remains constant over the frequency range 50 Hz and 100 Hz and afterwards it varies nonlinearly at higher frequencies. Further it is also observed that at Temp increases the values of a. c. conductivity also increases at higher degree Temp at 110 °C it is suddenly decreases frequency range of 500Hz- 13 KHz. Further we observed that The A C conductivity of PMMA with Fe_2O_3 remains constant over the frequency range 50 Hz and 100 Hz and afterwards it varies nonlinearly at higher frequencies at different Temp. Hence we observed the modification in A C conductivity of the PMMA composite films.

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