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Synthesis, Ultrasonic and other characterization of PMMA / Fe_2O_3 films

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***Abstract*— Solid polymer metal oxide films containing Poly (methyl-methacrylates) PMMA/Ferric oxide Fe_2O_3 are synthesized following solution cast technique. Complexation and particle size are determined by XRD and SEM analysis. Ultrasonic and Dielectric characterization have been done by using Ultrasonic Pulse Echo method and LCR meter respectively. The dielectric behavior of PMMA/ Fe_2O_3 films has been studied as a function of concentration, and at lower frequencies over the range 100 Hz - 25 KHz. A 7:3 PMMA/Fe_2O_3 film have been found to posses optimal conducting and optical properties. 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 Fe_2O_3 thermally stabilizes PMMA matrix.**

***Index Terms*— Ultrasonic Pulse Echo, Dielectric, Optical, PMMA, Thin films.**

I. Introduction

Since organic/inorganic composites of polymers films exhibit enhanced properties than that of their constituent materials [1]-[2]. the polymer composite materials are important to the electronic industry for their dielectric properties in the use of capacitors and one of the most characteristic features is that of their dielectric properties can be widely changed by choice of shape, size, tacticity and conductivity of mixed constituents in the polymeric matrix[3]-[6]. Early studies on polymer-salt complexes have been focused on the exploitation of their viscoelasticity, flexibility, conductivity and chemical stability. Variation of composition of salt/metal oxide in Polymer composites is widely studied by Stephan, et al [7]-[8] and found that 7:3 organic/organic polymer blends posses optimal properties in terms of conductivity and mechanical strength.

The poly (methyl-methacrylate) is almost insulating in nature with high elastic strength and its conducting property can be enhanced by adding either metal oxide or supporting agent. Present study deals with the optimization of conductivity using inorganic oxide in PMMA films. They also provide substantial information on the processes involving polymer production and their uses [9]-[10].

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A. Theory

The electrical conductivity is strongly related to polarization and the total polarization P of a molecule in an electric field is given by

$$P = P_E + P_A + P_O \qquad (1)$$

Where P_E is the electronic polarization, P_A is the nuclear polarization (considered to be negligible) and P_O is the dipole or orientation polarization.

P is determined by *Claussious Mosotti* equation

$$P = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} \qquad (2)$$

Where D is the dielectric constant, M and ρ is molecular weight and density (average values in case of polymer composites)

The effect of the electron cloud displacement is known as electron polarization which can be determined as follows:

$$P_E = \left(\frac{n^2-1}{n^2+2}\right)\frac{M}{\rho} \qquad (3)$$

Where n is the refractive index.

In the case of symmetrical molecules such as carbon tetrachloride, benzene, polyethylene the only polarization effect is electronic and such materials have low dielectric constant. However in many of the polymers, groups attached to main chain are randomly oriented called as atactic, and induce dipole polarization along with electronic polarization where charge carrier is polaron possessing polarization history instead of electron and such effect is much less below the glass transition temperature. In case of PMMA and its composite films, there are two or more maxima present in the power factor- temperature curve for a given frequency which may be due to the different orientation times of the dipole with and without associated segmental motion of the main chain [11].

The ultrasonic velocity u_l and attenuation α reveals the weak interaction and is measured following equations

$$u_l = \frac{2d}{t} \qquad (4)$$

$$\alpha = \frac{2.303}{2d} log_{10}\left(\frac{A_1}{A_2}\right) \qquad (5)$$

Where d is the thickness of thin film, t is travel time of ultrasonic wave, A_1 and A_2 are first and second reflection decay peaks respectively.

II. Experimental Measurements

A. *Sample Preparation*

Poly(methyl methacrylate) PMMA (Molecular weight W_m = 1,20,000, purity 99.7%), Fe_2O_3, (general purpose) and acetone were obtained from S.D. Fine Chem. Ltd, Mumbai, India and are used as received without further purification. The films of PMMA and its composite with Fe_2O_3 are prepared following solution cast method. The composite films of 10, 20, 30, 40, 50 and 60 weight percent (Wt %) of Fe_2O_3 are obtained by mixing it with the PMMA solution in acetone. It were then dried at 40^0 C and kept under oven for 8 Hr before use. The solution were cast as films and allowed to evaporate at ambient temperature and at atmospheric pressure. After evaporation of acetone, the films were further dried in a temperature –controlled oven at 30^0C for 9 Hr to remove any remaining traces of acetone. Density ρ of all thin films was determined by employing the Pycknometric method using water as insoluble immersion liquid and applying the relation

$$\rho = \frac{W_1}{W_1 - W_2}\rho_W \qquad (6)$$

Where W_1 and W_2 are the weights of the thin films in air and in the immersion liquid respectively. ρ_W is the density of water at 303K.

B. *Characterization*

a) *XRD Characterization*

The Complexation of PMMA/ Fe_2O_3 has been studied using powder X-ray Diffractometer (XRD) at an angle 2θ (Regaku). And the XRD spectrum of composite films is given in Figure 1. It is observed that the diffused and broader peaks for PMMA film at 18^0 angle and strong intensive peaks for composite film at angles of 32^0, 36^0 and 52^0. This reveals that the PMMA/Fe_2O_3 Complexation is done successfully.

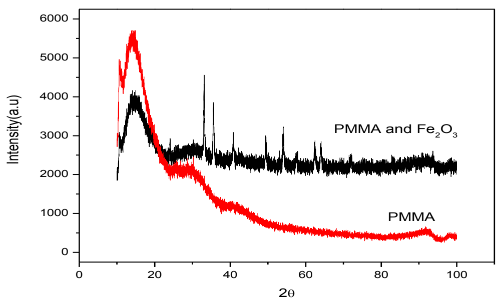

Figure 1. The XRD spectrum of 7:3 Wt% of PMMA/Fe_2O_3 composite film.

b) *SEM Characterization*

The morphology and size of the synthesized particles were studied by scanning electron microscopy- SEM. SEM micrographs of PMMA/Fe_2O_3 films were taken on a ZEISS Supra 35 VP field emission electron microscope.

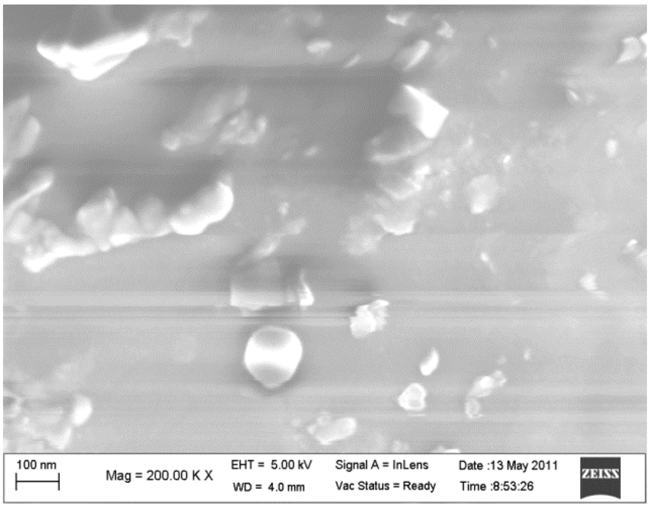

Figure 2 SEM micrographs of 7:3 PMMA/Fe_2O_3.

The SEM micrographs show that in PMMA/Fe_2O_3 particles are predominately crystallites with size between 80-100 nm

c) *Dielectric Characterization*

The thickness of films lies between 0.19-0.29 $\pm$ 0.01 mm is measured by micrometer screw. Extra portion of films is completely removed as per electrode dimensions and then coated by silver for ohmic contact. Conductivity measurements were performed by sandwiching the film between silver electrodes of diameter 3.47$\pm$0.01mm. Using PC based LCR meter (Model: Scientific LCR Meter SM6020 India) over a frequency range of 100Hz -25KHz at Constant Temperature 26^0C using Plasto Crafts Thermostat (accuracy $\pm$0.1^0C).

d) *Optical Characterization*

The optical properties of PMMA/Fe_2O_3 have been studied using PC based WAY-2S Digital Abbe Refractometer (accuracy$\pm$0.0002) at 26^0C.

e) *Thermal Characterization*

The thermophysical properties of PMMA/Fe_2O_3 and its composites were studied by TGA and DSC. The weight loss (%) was recorded as function of temperature for both PMMA and its composite films with Fe_2O_3 using TGA (SDT Q600 V20.9 Build 20). The samples weighing about 6.0 mg were scanned in the temperature range of 0-600^0C under nitrogen atmosphere at a heating rate of 20 ^{0}C/min

f) *Ultrasonic characterization*

Ultrasonic measurements were performed at 2MHz by pulse echo method. Transmission and detection of pulsed sound wave were made by an apparatus MHF-400 Pulser Receiver system from Roop Telsonic Ultrasonix ltd. The ultrasonic velocity & attenuation are measured using TDS 2022B, 200 MHz Two channel dual trace CRO, Tektronix.

III. RESULTS AND DISCUSSION

A. Electrical Conductivity

The dielectric properties of (PMMA) / Fe_2O_3 composite films are studied as a function of frequency at 26^0C. The values of dielectric constant ε' and loss of tangent tanδ, dielectric loss ε" and a.c. conductivity (σ_{ac}) are obtained from the measured values of capacitance C and dissipation factor D using following equations

$$\varepsilon' = \frac{C\,d}{\varepsilon_0 A} \tag{7}$$

$$tan\delta = D \tag{8}$$

$$\varepsilon'' = \varepsilon' \tan\delta \tag{9}$$

$$\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan\delta \tag{10}$$

The dielectric properties PMMA/Fe_2O_3 films as function of Wt% of Fe_2O_3 and frequency are determined and it is found that dielectric Constant decreases as the frequency increases up to around 1 KHz for all samples where as at higher frequencies the dielectric constant remains same and is independent of the frequencies and is given in Figure3, 4. Here we have noticed that the values of dielectric constant of films of PMMA have been found to be slowly increasing with Wt% of Fe_2O_3 and has peek at 70:30 and 50:50 Wt% and matched with the Stephan's observations [9] Hence we have seen the modifications in dielectric properties of the composite films as given in figure 3.

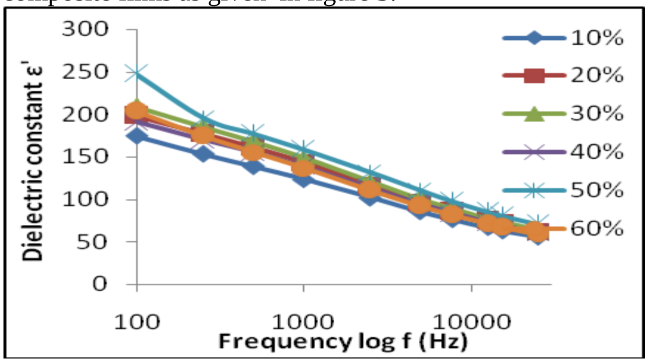

Figure **3**. Frequency dependent of dielectric constant ε' at different Fe_2O_3 Wt%

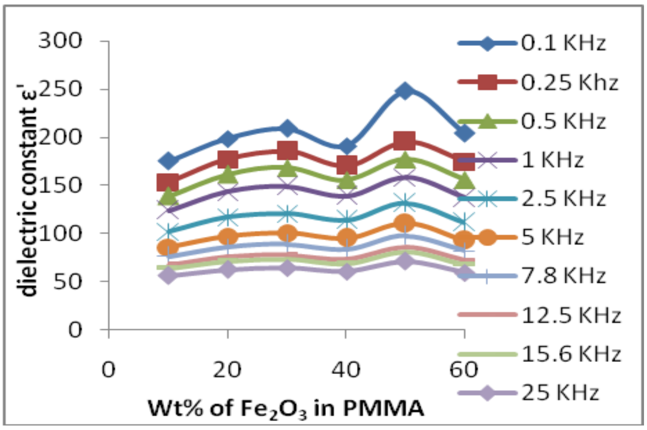

Figure **4.** Concentration dependent of ε' at different frequencies.

This may be attributed to the tendency of dipoles in polymeric composite films to orient themselves in the direction of the applied field. whereas 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 is 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 effects of the sample

B. Dielectric loss

The dielectric loss tan δ of composite films of PMMA/Fe_2O_3 is obtained as functions of Wt% o Fe_2O_3 at different frequencies given in Figure 5. The Dielectric loss of these composite films maintains upto 40Wt% and increases thereafter in the frequency range 100Hz - 25 KHz. Therefore the dielectric loss is minimum at 30 Wt % with high dielectric constant. Hence we observed the modification in dielectric loss of the PMMA composite films.

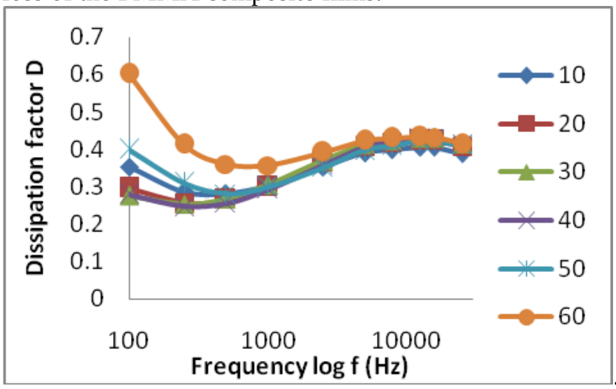

Figure **5** variation of loss tangent of PMMA/ Fe_2O_3 films at different frequencies

C. a. c. Conductivity

The a. c. conductivity of composite films is obtained as functions of frequency from the measured values of dielectric permittivity and dielectric loss using Equation (10) at 26^0C. The plot of a. c. conductivity σ_{ac} as a function of Wt% of Fe_2O_3 at different frequencies is given in Figure 5. It is observed that of PMMA/ Fe_2O_3 films has high ac conductivity σ_{ac} at 70:30 and 50:50 Wt% in given frequency range. Hence we observed the modification in a.c. conductivity of the PMMA composite films.

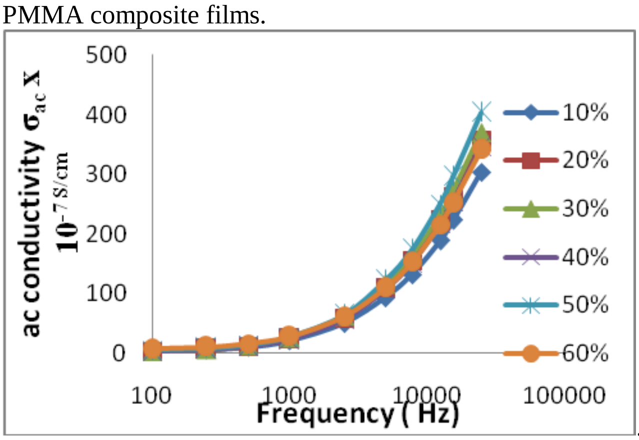

Figure **6.** a. c. conductivity as function of wt%. of Fe_2O_3 in PMMA composites films at different frequencies.

D. Optical properties

The refractive index of films shows linear decrease with increase in Wt% of Fe_2O_3 except at 70:30 ratio related to higher transparency with maximum dissociation of molecules from ultrasonic velocity data which promotes the 70:30 composition is quite good for stabilized energy conductor as shown in figure 7.

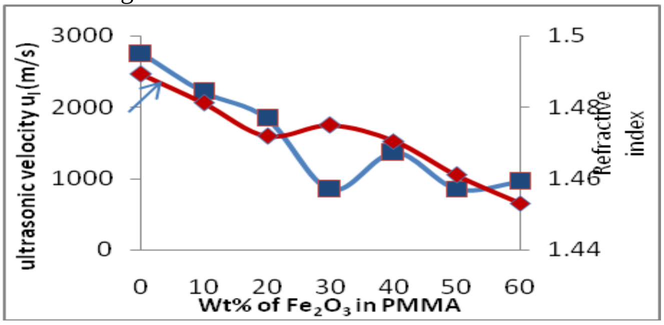

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Figure 7: Variation of ultrasonic velocity and refractive index as a function of Wt% of Fe_2O_3 in PMMA

E. Ultrasonic Properties

The ultrasonic velocity and attenuation are measured following pulse echo technique with an accuracy of $\pm$1m/s. Ultrasonic velocity is found to be decreased with increase in Fe_2O_3 Wt% with abrupt dip at 70:30 ratio corresponds to maximum dissociation of atoms and minimum attenuation corresponds to reduction in loss of energy as shown in figure 8.

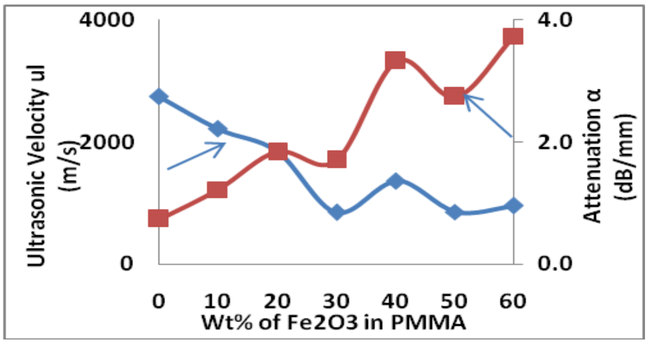

Figure 8: Variation of ultrasonic velocity and attenuation verses against Wt% of Fe_2O_3 in PMMA

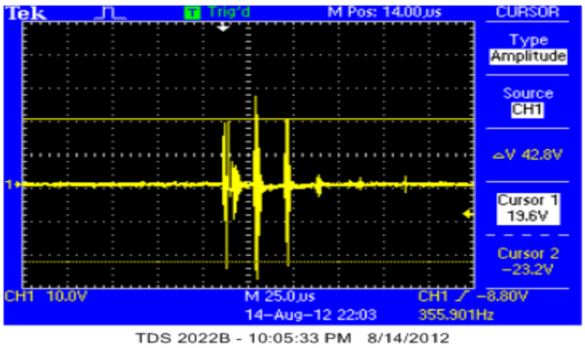

Figure 9: Ultrasonic pulse echo of 70:30 PMMA/Fe_2O_3 thin film.

The cumulative data of ultrasonic and optical parameters is given in Table 1

Table 1Ultrasonic and optical data of PMMA/Fe_2O_3 film.

Sr. No	Sample	Density r(g/cm^3)	Ultrasonic velocity u_l (m/s)	Attenuation α (dB/mm)	Refractive index n
1	PMMA	1.18	2747	0.74	1.4892
2	PMFe10	1.457	2210	1.22	1.4811
3	PMFe20	1.734	1840	1.84	1.4719
4	PMFe30	2.011	843	1.70	1.4749
5	PMFe40	2.288	1362	3.33	1.4705
6	PMFe50	2.565	854	2.74	1.461
7	PMFe60	2.842	953	3.74	1.453

F. Thermal Properties

. The weight loss (%) was recorded as function of temperature for PMMA and 70:30 PMMA/ Fe_2O_3 films using TGA (SDT Q600 V20.9 Build 20). The samples weighing 6.0 mg were scanned in the temperature range of 0-600 ^{0}C under nitrogen atmosphere at a heating rate of 20 ^{0}C/min and is given in Figure 10.

PMMA lost its weight 4.052% (0.247 mg) at temperature of 150.28 ^{0}C and 97.79% (5.962 mg) at 359.32 ^{0}C and the composite lost its weight 73.13% (3.900 mg) at temperature of 357.61^{0}C. These indicate that addition of Fe_2O_3 reduces the weight loss of the PMMA as heated and improves thermal stability.

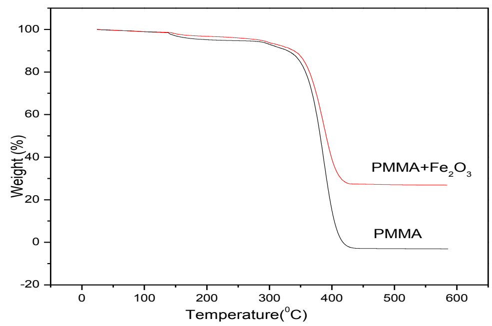

Figure10 TGA of films

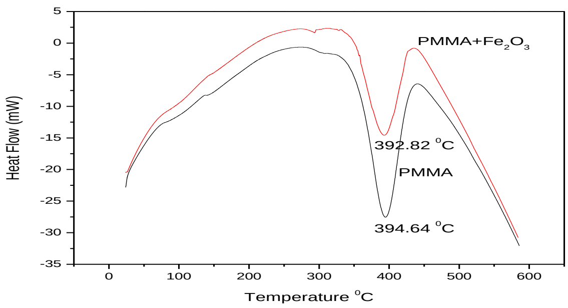

Figure 11 **DSC** of composite film

The DSC is also measured for these samples at same weight and temperature range and is given in Figure 11.
It is seen that melting peak is occurred at temperature 394.64^0C for PMMA and at 392.85^0C for its composite. The observed two peaks may be attributed to the different orientation times of the dipole with and without associated segmental motion of the main chain.

IV. CONCLUSIONS

The crystallite size of PMMA/Fe_2O_3 is found to be in between 80-100 nm. The organic/inorganic composite film having 70:30 have highest compatibility for optimal electrical conductivity with maximum dissociation and reduction in loss of energy. Addition of inorganic Fe_2O_3 thermally stabilizes PMMA.

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