Dielectric Properties of Potassium permanganate (KMnO₄)-PMMA Composite Films

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Abstract - Authors have developed films of pure Poly-methylmethacrylate (PMMA) and (0.5%, 1%,

2% and 5%) Potassium permanganate (KMnO4) doped PMMA composite films of thickness (~100 \square m) using the solution cast technique using dichloromethane as a solvent. Dielectric behavior of these composite films have been investigated using an impedance analyzer at room temperature and frequencies in the range 100 Hz to 100 KHz. Results show that the dielectric parameters like dielectric constant (\square '), dielectric loss (\square ''), loss tangent (tan \square) and a.c. conductivity (\square) of these composite films change with frequency and change in concentration of KMnO4. The dielectric constant and dielectric loss decrease with increase in frequency whereas decreases with increase in concentration of potassium permanganate. From the results we can conclude that KMnO4PMMA nano composite films can be used as a potential dielectric for charge separation as well as for timing, filtering etc.

Keywords — dielectric constants, ac conductivity. Electrical properties, PMMA-KMnO₄Composite films.

1. INTRODUCTION

The desire for high performance combined with reductions in size, weight, and manufacturing cost and the amenability for moulding into various desirable shapes suggests that polymers are promising potential materials to develop things of desired properties. One significant aspect is that there properties can be tailor made for specific applications by use of filler/doped material. A careful literature survey reveals that the addition of small quantity of dopant filler significantly changes the optical, electrical, mechanical and thermal properties of polymeric materials, which assists in development of novel materials with high end applications for device industry. These changes in physical properties depend on the chemical nature of the dopant and on the interaction mechanism between the dopant and the host polymer. Recently, in their pursuit to develop suitable electrically conductive polymer composite materials for use within the electronics industry as suitable shielding for electromagnetic interference applications, the authors have developed Potassium permanganate (KMnO4) doped Poly methyl methacyralate (PMMA) composite films as explained in reference. The addition of small quantity of metal nano-particles into an insulating polymer matrix are of great interest to a material scientist as this leads to creation of novel materials with enhanced properties catering wide range of applications. Basically, the introduction of nanoparticles leads to variation in aspect ratio resulting in varied performance of the nanocomposites from traditional composites. A careful literature survey [1-7] reveals that the polymer nanocomposite (PNC) depicts a significant variation in the physical properties which are highly dependent on the chemical nature of the dopant and on the interaction mechanism between the dopant and the host polymer.

The electrical properties of these composites developed by dispersing a conductive phase in an insulating matrix significantly

depends on the type and concentration of the filler added. For small concentration of filler nanoparticles, as the the average distance between the filler particles is generally more than their size the electrical conductivity of the composite material is more likely to that of the pure insulating matrix.[8-9]. On an addition of adequate amount of filler, a "percolation" path of is formed connecting the filler particles which allows charge transport through its surface leading to a change in the charge storage capacity. Such composites materials find varied applications in electromagnetic shielding purpose, as electrostatic discharge coatings, or as transparent conductors.[10-11].

Recently, the authors have taken efforts to develop electrically conductive polymer composite materials for EMI shielding applications, as explained in reference [11-13]. In this paper we have analyzed the dielectric properties of developed Potassium Permanganate (KMnO₄) doped Poly methyl methacyralate (PMMA) composite films. The study of variation in dielectric properties with frequency provides an understanding of the capacitive or conductive nature of the material. The values of impedance parameters *viz.*. resistance, capacitance, inductance, dissipation factor (tan \square), phase angles and impedance were measured by WAYNE KERR 6500B impedance analyser and from the data obtained the dielectric parameters *viz.*, the real part \square ' and imaginary part \square ' of dielectric constant and ac conductivity (\square) has been calculated in the frequency range (100 Hz – 100 kHz) at room temperature.

2. EXPERIMENTAL DETAILS

- **2.1. Materials**: The host polymer matrix made of granular Polymethylmethacrylate (PMMA) of molecular weight 119.14 gm/mol has been purchased from M/s Gadra Chemicals, Bharuch whereas potassium Permanganate used as filler, of analytical reagent grade in dehydrated purified form of about 10–30 nm in diameter and of 1–2 nm in length has been procured from Merck Specialities Private Limited Mumbai. The solvent dichloromethane (purity of 99.8%) was purchased from Merck Specialties Private Limited, Mumbai.
- **2.2 Synthesis Process:** Films of pure PMMA and its potassium permanganate filled composites of thickness 100 □m were synthesized using solution casting technique using dichloromethane as a solvent. For this purpose a predetermined amount of granular PMMA was dissolved in dichloromethane by stirring it uniformly on a magnetic stirrer. Different concentration of KMnO₄ (0.5%, 1%, 2% and 5% by weight) were made to disperse completely to this solution by using an ultrasonicator (220 W, 20 kHz) for 1 h to yield a clear solution. The solution was then poured into a glass petri dish of diameter 6 cm floating over mercury and is kept for almost twenty four hours so that the solvent evaporates gradually and the films are casted which were peeled off by tweezers clamp. Transparent flexible nano composite polymer films were obtained.

2.3. Characterization of Dielectric Properties: The study of variation in dielectric properties with frequency provides an understanding of the capacitive or conductive nature of the material. The values of impedance parameters viz.. resistance (R), capacitance (C), inductance (L), dissipation factor (tan \square), phase angles (\square) and impedance (Z) were measured by WAYNE KERR 6500B impedance analyser in the frequency range (100 Hz - 100 kHz) at room temperature. From these data for any film of thickness t , surface area A and value of capacitance C, the real part of dielectric constant \square ' at given frequency is calculated from the familiar expression

$$\Box' = C t / (\Box_0 A) \qquad \dots (1)$$

where \Box_0 is the dielectric constant in vacuum with the standard value equal to 8.854×10^{-12} F/m.

The imaginary part of dielectric constant i.e. dielectric loss factor is calculated using the expression

where $\tan \Box$ is loss tangent. Further the a.c. conductivity \Box of the sample films has been evaluated using the relation

$$\Box = t/(RA) \qquad \dots (3)$$

Since R is resistance and A is area of sample

3. RESULT AND DISCUSSION

3.1. Analysis of dielectric parameters: The study of dielectric parameters offers an understanding of the electrical characteristics of the material in two ways: (i) the capacitive behavior indicates the ability of material in charge storage and (ii) the conductive behavior indicates the ability of electronic charge transfer. The variation of dielectric parameters (\square ', \square '', $\tan\square$, \square) with frequency and composition have been of different Potassium permanganate concentration as function of frequency at room temperature is shown in Figure 1.

It is observed for pure PMMA and for all weight fractions of PMMA/KMnO₄ nano composites that (i) in the frequency region < 10 KHz, the dielectric constant \Box ' decreases with increase in frequency and (ii) it remains almost constant in frequency range 100-100 Khz. This behavior is typical characteristics of dielectric materials. At low frequencies (here <10 KHz) the dipoles have sufficient time to align themselves with the electric field resulting in a higher value of dielectric constant. Contrary to it in the high frequency region, due to rapid periodical reversal of the electric field the dipoles are unable to orient themselves along the electric field so that there is no excess ion diffusion in the electric field direction leading to observed decrease in the value of dielectric constant.

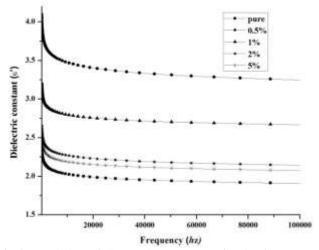


Fig.1 : Variation of di electric constant (\square ') with frequency of PMMA- KMnO₄ composites

In figure 1 it is also observed that the dielectric constant decreases with increasing $KMnO_4$ concentration; which can be attributed to the fact that the host and the filler material are electrically heterogeneous in nature (i.e. they differ from each other in their capacitive and conductive behavior) so that the randomly mobile charge carriers are confined at the interface of such multi phase material with different conductivity thus increasing the amount of charge at the interface. The increase of $KMnO_4$ concentration in polymer matrix increases the number of interfaces, culminating it as an increase in interfacial polarization so as to increase the value of dielectric constant.

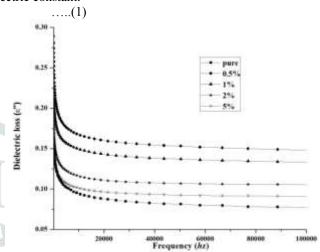


Fig.2. Variation of di electric loss (□")□with frequency

Figure 2 which depicts the variation of the dielectric loss of PMMA/KMnO₄ composites as a function of frequency at room temperature indicates that \square ' obeys the same trend as \square '. As the value of dielectric loss at low frequencies is due to motion of free charges it is higher as compared to that at higher frequencies where due to ion hopping the conduction losses and ion polarization losses come into existence. The vibration of ions may be yet another source of loss in this range of frequencies. On increasing the concentration of filler nanoparticles there is an enhancement in the amount of charge carriers so the dielectric loss value also increases.

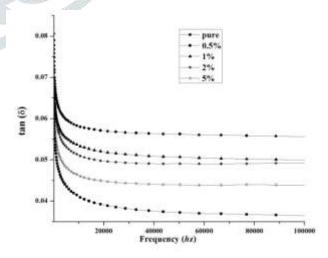


Fig.3. Variation of loss tangent $(\tan \square)$ with frequency

The relaxation phenomena given by $\square \square = 1$ gives the condition of resonance, where the electron hopping probability $f = \square \square \square \square$ is equal to the frequency of applied electrical field, which appears in form of a peak in the plots of loss tangent vs frequency. Here \square

represents the relaxation time. The variation of the loss tangent with frequency shown in Figure 3 do not exhibit any dielectric relaxation peak (a maxima at a particular frequency) which suggest that there does not exist any dynamical process in these composites.

3.2. A.C. Conductivity: Figure 4 depict the variation of a.c. electrical conductivity of PMMA and its composites containing varying concentrations of potassium permanganate. From the figure it is obvious that the conductivity increases with increase in frequency as well as $KMnO_4$ concentration. This increase is attributed to the formation of excess charge carriers developed in the polymer matrix. The higher conductivity of $PMMA/KMnO_4$ is due to the uniform dispersion and the spatial arrangement of metal particles within the polymer matrix.

4. CONCLUSION

In this work, composite sample films have been synthesized by adding potassium permanganate to PMMA using the solution casting technique. From the measured values of impedance parameters viz.. resistance, capacitance, inductance, dissipation factor (tan \square), phase angles and

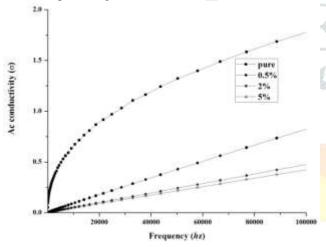


Fig.4. Variation of a.c conductivity (\Box) with frequency

impedance, the dielectric parameters were evaluated in the frequency range (100 Hz - 100 kHz) at room temperature. The dielectric constant is observed to decrease with increase in frequency and concentration of KMnO4. The dielectric loss also depicts the same trend of decreasing with increase in frequency and increase with increase of KMnO4 wt. % content. The a.c. conductivity of PMMA/ KMnO4 nanocomposites is observed to increase with increase in frequency and concentration of KMnO4. Thus it can be concluded that by dispersion of KMnO4 in polymer matrix brings out an improvement in the charge transport property and electrical conduction.

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