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RESEARCH ARTICLE

Conductivity and Dielectric Studies of PMMA Composites†

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Abstract: Poly(methyl methacrylate) (PMMA) / ZrO_2 composites were prepared by sol gel method. The structural, micro structural and the dielectric properties of the composites were studied using X- ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Hioki 3522-50 LCR Meter respectively. The electrical conductivity of composites has been investigated at different temperatures at frequency ranging from 50 Hz to 1MHz. The dielectric loss, dielectric constant and conductivity were changed with change in the concentration of ZrO_2 and frequency of applied field. The electrical conductivities of the composites were found to increase with increasing temperature.

Keywords: PMMA, ZrO_2, Electrical conductivity, Polymer composite

Introduction

Composites, the wonder materials are becoming an essential part of today's materials due to the advantages such as low weight, corrosion resistance, high fatigue strength and faster assembly. They are extensively used as materials in making aircraft structures, electronic packaging to medical equipment and space vehicle to home building. There is much interest in the development of inexpensive composite polymers with an appropriate weight, appropriate electric conductivity and/or appropriate impact value for use with practical articles[1-3]. Polymer composites have steadily gained growing importance during the past decade. A vigorous development of polymer composite and extensive utilization of polymer materials in technology has led to the polymer composites[4]. The importance of polymers is mainly because polymers are still regarded as a cheap alternative material that is manufactured easily. The intensive use of polymer in broad use has led to the development of materials for specific applications namely composites[5]. Ceramic materials are typically brittle, possess low dielectric strength and in many cases are difficult to be processed requiring high temperature. On the other hand, polymers are flexible, can be easily processed at low temperatures and exhibit high dielectric break down fields[6]. A good amount of work has been reported on the conduction mechanism in polymeric materials. The electrical conduction in polymer film has much importance due to the discovery of the memory phenomenon and has wide applications now-a-days in thin film devices[7].

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The electrical conduction in iodine doped polystyrene (PS) and poly(methyl methacrylate) (PMMA) has already been reported. Belasare *et al.*[8] measured the electrical conductivity of iodine doped polyblend films of polystyrene (PS) and poly(methyl methacrylate) (PMMA). Electrical conduction in semiconducting PVC–PMMA thin film has been reported[9].

Experimental

The monomer MMA, ZrO_2, benzoyl peroxide, chloroform and petroleum ether were obtained from SD Fine Chemicals Limited, Mumbai, India and used as such.

Preparation of PMMA

The purified monomer MMA (10 mL) was taken in a polymerization tube and 50 mg of benzoyl peroxide which acts as a catalyst was added to accelerate polymerization, in the polymerization reaction. The polymerization tube was then kept in a water bath at 60-70 ^{o}C with periodical shaking. A hard viscous polymer was obtained after 90 minutes of heat treatment. The polymerized mass was dissolved in chloroform and then transferred into a beaker. The viscous polymer solution was precipitated by the addition of petroleum ether. The precipitated polymer was then filtered and oven dried at 60 ^{o}C. The polymer formed was found to be syndiotactic[10].

Preparation of PMZr composites

A definite quantity of PMMA was dissolved in chloroform followed by the addition of a known quantity of ZrO_2 and then it was made into a paste in an agate mortar then it was subjected to heat at 80 °C for 30 minutes in a Muffle furnace and made into a powder. PMZr composites were prepared in the following proportions of PMMA and ZrO_2: PMZr 1 – 9:1, PMZr 2 – 8:2, PMZr 3 - 7:3, PMZr 4 -6:4, PMZr 5 – 5:5 and PMZr 6 – 4:6.

PXRD

In order to understand the properties of composite material, it is essential to know about the details of its structure. The X-ray diffraction pattern (XRD) technique was used for characterization. The PXRD of PMMA, ZrO_2 and PMZr composites were recorded using Philips X'PERT PRO diffractometer with Cu Kα (λ= 1.54060 Å) incident radiation. The XRD peaks were recorded in the 2θ range of 20°–80°.

SEM

The Scanning electron microscopy produces detailed photographs that provide important information about the surface structure. The morphology of PMMA, ZrO_2 and PMZr are recorded using Philips XL30. The samples were gold plated before SEM observation.

Dielectric properties and conductivity measurements

The electrical conductivity of composites were measured using Hioki 3522-50 LCR Meter. Testing temperature ranged from 40 to 60 °C at frequency ranging from 50 Hz to 5MHz.

Results and Discussion

PXRD

Pure PMMA shows a predominant and broad peak with a maximum at 2 θ 13.89° along with broad but low-intensity peaks at 30° and 34°. These broad peaks indicate the amorphous nature of the polymer (Figure 1). Peaks appear at 2 θ: 30.02, 35.0, 50.41 and 60.0 corresponding to the diffraction patterns of (1 1 1), (0 0 2), (1 1 2) and (2 1 1), respectively, of the pure tetragonal phase of ZrO_2 (Figure 2). From the XRD pattern of PMZr 6 (Figure 3) composite, it was observed that there is no broad peaks and the sharp peaks between 28 to 59 with a maximum at 2 θ 28.05° along with low-intensity peaks at 8.5°, 13.8°, 14.2°, 18.6° and 34°, 35°, 38°. The peak at 35.10°, 50.24°, 59.48° is due to tetragonal phases of ZrO_2. The peak at 38.36°, 48.97° due to anatase phases of ZrO_2.

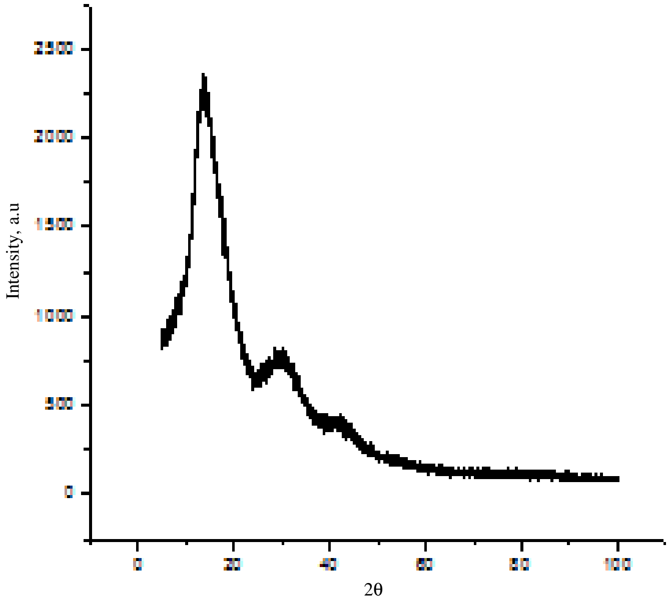

Figure 1. XRD of PMMA

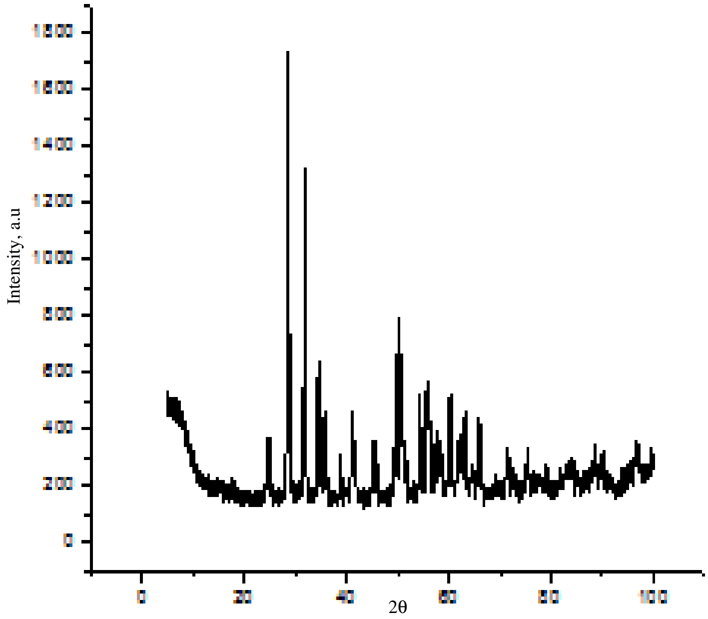

Figure 2. XRD of ZrO_2

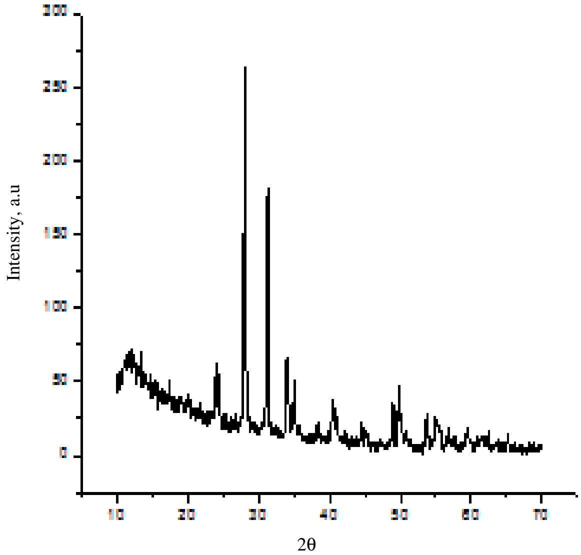

Figure 3. XRD of PMZr 6

The SEM images of PMMA, ZrO_2 and the composite, PMZr6 are shown in the Figures 4, 5 and 6 respectively. The composite possess smooth surface when compared to PMMA. The rough fractured surface of PMMA is changed due to the addition of zirconium oxide.

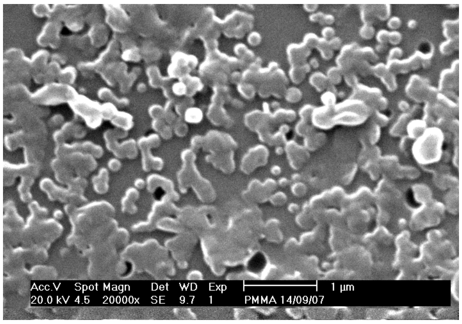

Figure 4. SEM image of PMMA

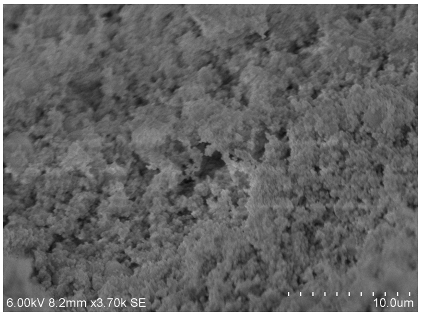

Figure 5. SEM image of ZrO_2

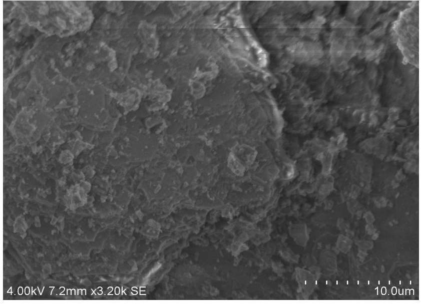

Figure 6. SEM image of PMZr6

The micrograph of pure PMMA shows a homogenous phase. SEM showed how the PMMA microspheres are inserted in the fine-grained solid-organic matrix. However, the

PMMA contraction was found favorable, since this non-rigid behavior avoided the formation of cracks due to the absence of tensile stresses in the matrix. No density gradients of templates were observed in the cross sections analyzed by SEM, showing in all cases a homogenous microstructure. The inorganic moieties are well dispersed in the PMMA matrices. From the above observations it can be concluded that in our composite systems there is a good compatibility between the organic and inorganic components and the micro metred sized inorganic particles are well dispersed in the PMMA matrix**.**

AC conductivity of PMMA/ZrO$_2$ composites

The measured conductance G, from 50 Hz to 5000000Hz used to calculate ac conductivity, σ(ac) using the following expression:

$$\sigma(ac) = G\, d/A$$

Where, d is the thickness of the sample and A is the cross sectional area of the electrode. The AC conductivity of PMZr composites at different temperatures are shown in Table 1.

Table 1. AC conductivity of PMZr composites at different temperatures

	Conductivity (S/cm)		
System studied	313K	323K	333K
PMZr1	1.66×10^{-7}	1.72×10^{-6}	1.89×10^{-5}
PMZr2	2.37×10^{-7}	2.56×10^{-6}	2.98×10^{-5}
PMZr3	3.10×10^{-7}	3.85×10^{-6}	3.90×10^{-5}
PMZr4	4.41×10^{-7}	4.52×10^{-6}	4.84×10^{-5}
PMZr5	5.82×10^{-7}	5.84×10^{-6}	5.95×10^{-5}
PMZr 6	6.09×10^{-7}	6.40×10^{-6}	6.71×10^{-5}

Polymer materials in pure state are electrical insulators. However they are filled with specific additives, as metallic powders metallic fibers, ionic conductive polymers, *etc*. The conductivity of pure PMMA was found[11] to be 5×10^{-18} S/cm. The electrical conductivity of thecomposite increases with the ZrO$_2$content. The conductivity of polymer, PMMA is about 10^{-18}S/cm this is consistent with the magnitude of an insulator. The electrical conductivity of the composites exhibited a pronounced transition with the increase of ZrO$_2$ content, from an insulator to nearly a semiconductor. This transition can be satisfactorily explained and described by the formation of the conductive network in the composite[12]. Table 1 shows the variation of conductivity with ZrO$_2$ concentration for different temperatures. As the temperature increases the charge carries are thermally activated and the free volume increases and more vacant sites are created for the motion of ions, which in turn enhances the conductivity.

Dielectric properties

The higher value of dielectric constant is due to higher grain size. The dielectric constant strongly depends on the grain size. The dielectric constant of materials is due to the electronic, ionic, dipolar and surface charge polarizations which depend on the frequencies. The large value of dielectric constant at lower frequency may be due space charge polarization arising at the grain boundary interfaces. Figures 7 and 8 shows the variation of dielectric loss and dielectric constant as functions of frequency. In both the plots the dielectric loss and dielectric constant decreases with the increase of frequency, which was in good agreement with the reported value[13].

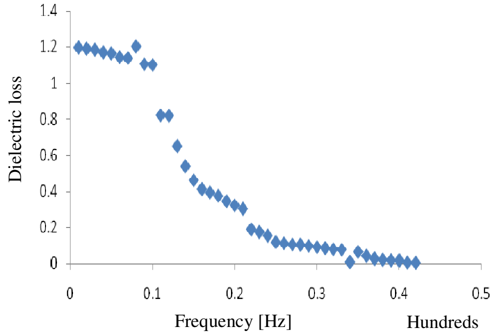

Figure 7. Variation of dielectric loss with frequency at 333K for PMZr6

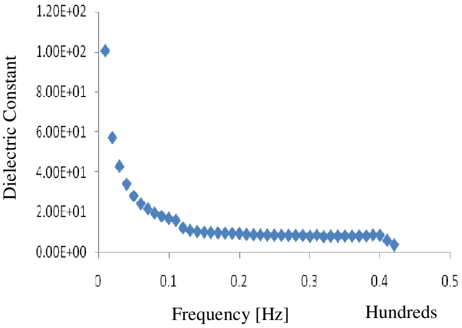

Figure 8. Variation of dielectric constant with frequency at 333K for PMZr6

Conclusion

PMMA / ZrO_2 composites were prepared by sol gel method. The polymer composites were characterized using PXRD and SEM. The electrical conductivity and dielectric properties of the polymer composites were measured. The A.C electrical conductivity of the composites increases by increasing the ZrO_2 concentrations and with increased temperature. As the temperature increases the charge carries are thermally activated and the free volume increases and more vacant sites are created for the motion of ions, which in turn enhances the conductivity. The dielectric loss and dielectric constant decreases with the increase of frequency. This is due to the electronic, ionic, dipolar and surface charge polarizations which depend on the frequencies. The large value of dielectric constant at lower frequency may be due space charge polarization arising at the grain boundary interfaces.

References

1. Itoh K, Kanda M and Nishi Y, *J Japan Inst Metals,* 2006, **70,** 940-944.
2. Kanda M, Itoh K and Nishi Y, *J Japan Inst Metals,* 2006, **70,** 945-949.
3. Kanda M and Nishi Y, *Mater Trans.,* 2009, **50,** 177-181.
4. Wenderlinch B, Macromolecular Physics, Academic press, New York, 1973.
5. Kryezewski M, *Polym Sci Polym Symp* (*USA*), 1975, **50** 359.
6. Mead C A, *J Appl Phys USA,* 1961, **33,** 646.
7. Chakraborty S C, Patil N B, Das S K and Basu S, *Indian J Pure Appl Phys.,* 1991, **29,** 478.
8. Belsare N G and Deogaonkar V S, *Indian J Pure Appl Phys.,* 1998, **36,** 280.
9. Deshmukh S H, Burghate D K, Deogaonkar V S and Deshmukh P T, *Indian J Phys*., 2005, **79(11),** 1263-1267.
10. Devikala S and Kamaraj P, *J Chem*., 2011, **8(S1)**, S165-S170.
11. El-Bashir S M and Hendi A, *Polym Plast Technol Eng*., 2010, **49**, 78-82.
12. Pan Y X, Yu Z Z, Ou Y C and Hu G H, *J Polym Sci Part B: Polym Phys*., 2000, 38, 1626-33.
13. Fang X S, Ye C H, Xie T, Wong Z Y, Zhao J W and Zhang L D, *Appl Phys Lett*., 2006, **88**, 013101-013103.