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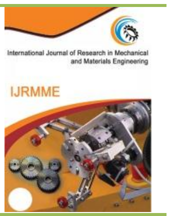

THE EFFECT OF ZIRCONIUM DIOXIDE ON DIELECTRIC PROPERTIES AND THERMAL CONDUCTIVITY OF POLYMERS

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ABSTRACT

The aim of this study is to investigate the effect of zirconium dioxide (ZrO_2) on dielectric properties of polymers. In this study epoxy is used as the base polymer insulator. The relative permittivity (ε), dissipation factor (tanδ), and electrical conductivity (σ) of polymers are measured as a function of ZrO_2 concentration in epoxy samples. Experimental measurements show that adding of ZrO2 to Epoxy has an influence for good in samples which is going to be used in electrical applications. Thermal conductivity of zirconium dioxide filled epoxy composite as a function to volume fraction of filler content, were studied. Thermal conductivity of the composite were found to increase with increases in volume fraction of filler content.

INTRODUCTION

Epoxy resins are widely used for many applications from microelectronics to space vessels in modern technology (encapsulating, thin film coating, packing of electronic circuits, protective coatings etc.) because of mechanical and electrical properties, easily processed, and low cost. In the case of using many different areas in technology, the epoxy resins are an important polymer group. However the pure epoxy resins have been poor electrical, thermal and mechanical stability, therefore the various methods have been used to improve these properties. Because of good adhesive properties, many modifiers can be easily doped to the resins [1]. The dielectric properties of the polymer composites are significantly dependent on the shape, size, and the conductivity of the fillers. The interface properties also strongly affect the dielectric behavior because interfaces act as the charge carrier trapping sites, which determine the charge carrier transport and storage. So the modifiers can significantly change thermal and dielectric characteristic of polymers. It has been shown by previous researches that ceramic fillers could be used to increase the electrical, thermal conductivity of the epoxy resin. Recently, property enhancement of epoxy resin with the incorporation of inorganic particles has attracted great attentions because the inorganic particle filled epoxy can exhibit enhanced thermal, electrical and mechanical [3,4] properties at relatively low loadings. Jean et al [5] were studied the electrical properties of zirconia–alumina composites. They found that both grain conductivity and dielectric constant show the highest value when the concentration increased. Aravindan et al [6] were prepared a novel lithium bis (oxalato) borate (LiBOB)-based zirconium dioxide dispersed Poly (vinylidenefluoride) (PVdF)/poly vinyl chloride (PVC) blend composite polymer electrolytes (CPE) using conventional solution casting technique by varying the filler concentrations. The conductivity results show that the enhanced conductivity 1.53×10^{-3} S/cm at 343K is obtained only for 2.5wt% filler containing membrane.In this study initially the relative dielectric permittivity, electrical conductivity, and dissipation factor (tanδ) of ZrO_2 added to epoxy is measured. Subsequently, thermal conductivity measurements of the same samples were carried out with Lee's disc apparatus.

EXPERIMENTAL

Materials

The polymer used in this work is epoxy which is commercial adhesive grade at room temperature curable araldite Euxit 50 resin K (Epoxy) supplied by the Egyptian swiss chemical industrials Co., with formulated amine hardener in ratio 3:1 for curing. The epoxy resin is a liquid with low viscosity and transparent in color, the specific gravity of it at 20°C is 1.05 g/cm^3. The filler component was zirconium dioxide (ZrO_2) with apparent density 0.586 g/cm^{3}Which was purchased from Aldrich Co.

Processing of composite

To prepare the composite samples, a mould of size 150×150×1 mm^3 was made from glass. Glass silicon was used for joining frames, and then plastic sheet was placed in the bottom of the mould. The composites were prepared with hand lay-up technique. The epoxy/ZrO_2 composites were prepared with 5, 10and 15 wt. % filler content. Initially epoxy resin and hardener were mixed together based on the weight ratio (3:1) to form a matrix. Then some of the weighted filler were added to epoxy resin with continuous mixing. This process was continued until weighted materials were finished. The mixture was poured into the mould. Then it was covered by plastic sheet. The curing time was around 24 hr at room temperature 23°C. The composite was taken out of the mould in the form of a plate and was cut and machined to produce samples conforming to the a.c measurement, each sample was in-shape like disc with diameter of 30 mm and thickness of 1 mm. A thin aluminum deposited on both sides of each sample by evaporation technique under pressure of 10^{-9} bar, using coating unite type Edward (E306A), to minimize the contact resistance and space charge effects. The thermal conductivity test samples were cut with 85mm of diameter and 1-2 mm of thickness.

Electrical measurements

Capacitance (C) and tan δ values were measured by using LCR Meter model (HP-4275) in the room temperature. Dielectric constant ($\acute{\varepsilon}$) of composite has been calculated by using the following relation

$$\varepsilon' = C/C_o \qquad (1)$$

where C and C_0 are the capacitance with and without dielectric, respectively; C_0 in pF is given by

where ε_o is the permittivity of free space, A (cm^2) is the area of the electrodes and d (cm) the thickness of the sample.

$$C_o = \varepsilon_o A/d$$

a.c. conductivity (σa.c.) was calculated from the relation where, tan δ the dielectric dissipation factor and ω the angular frequency.

$$\sigma_{a.c.} = \varepsilon_o \, \omega \, \varepsilon' \tan\delta \qquad (2)$$

Dielectric dissipation factor (tan δ) is defined as follows

$$\tan\delta = \varepsilon'' / \varepsilon' \qquad (3)$$

where ε'' is the dielectric loss[7].

Thermal conductivity measurement

The thermal conductivity measured in this work using Lee's disc apparatus. This apparatus is working under the principle that when heat is transferred by conduction through unit cross-sectional area of material then a temperature gradient is generated perpendicular to the area which will results in a steady state after some time. At steady state heat conducted through the sample epoxy/ZrO_2composite is equal to the heat radiated from the Lee's disc. By definition thermal conductivity means ‘‘the material property that describes the rate at which heat flows with in a body for a given temperature change.” For one-dimensional heat conduction the formula can be given as

$$Q = k\,A\,\frac{T_2 - T_1}{x} \qquad (4)$$

where Q is the heat flux (W), k is the thermal conductivity of the sample(W/m.°K), A is the cross sectional area (m$^{2)}$ and $T_2 - T_1$ is the temperature difference across the sample of thickness x(m). The thin sample is sandwiched between the metal (brass) disc and brass base of the steam chest. The rate of heat conduction through the brass disc must be equal to the rate of heat loss due to cooling by air convection from the bottom of the brass disc. If the disc cools down at a rate dT/dt then the rate of heat loss is given by:

$$Q = mc\,\frac{dT}{dt} \qquad (5)$$

where m is the mass of the brass disc(kg), c is the specific heat capacity of brass(c=380J/kg.°K). k can be calculated following the Equs. (4) and (5) as follows [8]:

$$k = \frac{Q\,x}{A\,(T_2 - T_1)} \qquad (6)$$

Many theoretical models have been proposed to predict the effective thermal conductivity of two-phase mixtures. For a two-component composite the simplest alternatives would be with the materials arranged in either parallel or series with respect to heat flow, which gives the upper or lower bounds of effective thermal conductivity. For the parallel conduction model

$$k_c = (1\text{-}\phi)\,k_m + \phi\,k_f \qquad (7)$$

where k_c, k_m, k_f are the thermal conductivities of the composite, the matrix and the filler respectively and Ø is the volume fraction of filler. For series conduction model:

$$\frac{1}{k_c} = \frac{1-\phi}{k_m} + \frac{\phi}{k_f} \qquad (8)$$

The correlations presented by equations 7 and 8 are derived on the basis of the rules-of-mixture. For an infinitely dilute composite of spherical particles, the exact expression for the effective thermal conductivity is given as:

$$\frac{k}{k_c} = 1+3\left(\frac{k_d - k_c}{kd + 2k_c}\right)\phi \qquad (9)$$

where k, k_c and k_d are thermal conductivities of composite, continuous-phase (matrix), and dispersed-phase (filler), respectively, and Ø is the volume fraction of the dispersed-phase. Equation 9 is the well-known Maxwell equation [9] for dilute composites.

RESULT AND DISCUSSION

The variation of relative permittivity as a function of composition at three different frequencies is shown in Figure 1. It is seen from this figure that the relative permittivity increased as the content of ZrO_2 in the polymer matrix is increased.

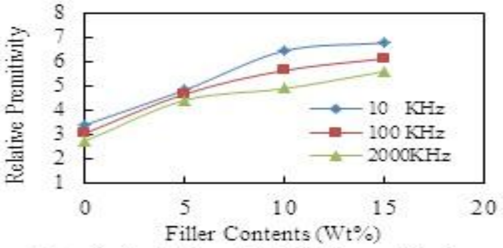

Fig. 1: Variation of relative premitivity with ZrO_2 content.

This permittivity enhancement is attributed to interfacial polarization, also referred to as the Maxwell–Wagner–Sillars (MWS) effect or polarization, phenomenon that appears in heterogeneous media consisting of phases with different dielectric permittivity and conductivity, attributed to the accumulation of charges at the interfaces [10]. In the present case, the system under investigation is heterogeneous one, that is, epoxy/ZrO_2 composites with different concentrations of zirconium dioxide particles dispersed in the epoxy risen . Epoxy has a lacunars structure with micro spherical voids and consequently consists of two phases: air and polymeric matter. It becomes more heterogeneous as filler is added to it because of the formation of interfaces between the dispersed phase and the epoxy matrix. When the ZrO_2 content is low, theZrO_2 particles are isolated, that is, placed so far apart that there is no interaction between them. As the ZrO_2 content is raised, clusters of ZrO_2particles are formed. A cluster may be considered as a region in the polymer matrix where ZrO_2 particles are in physical contact or very close to each other. The average polarization associated with a cluster is larger than that of an individual particle because of an increase in the dimensions of the inclusion and, hence greater interfacial area [10].

As can be seen from this figure the dielectric constant decreases as the frequency is increased. The decrease in the dielectric constant with increase in frequency is explained by the fact that as the frequency is raised, the interfacial dipoles have less time to orient themselves in the direction of the alternating field.

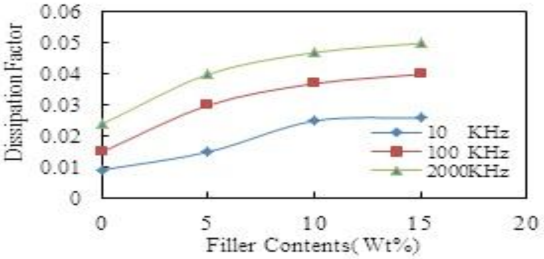

Fig. 2: Variation of dissipation factor with ZrO_2 content.

Dissipation factor measurement for epoxy samples according to filler weight is given in Figure 2. There is a sharp increase in dissipation factor continued through ZrO_2 added sample, with increasing ZrO_2 loading, there is an enhancement of charge carriers contributing the dielectric loss and in consequence the introduction of ZrO_2 starts to cause an increase of dielectric loss in the composites. It can be seen from Figure 2 that the dissipation factor of the neat epoxy and the epoxy/ZrO_2 composites increased with frequency , it can be explained that the charges overcome the barrier with tunneling, the charges reduce at the interfaces in the other words the permittivity decreases and the dissipation factor increases.

The change in conductivity according to ZrO_2 concentration at 100 KHz is given in Figure 3. Increasing the filler content in epoxy samples also increase electrical conductivity.

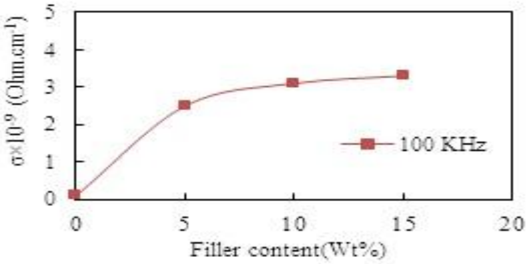

Fig 3: Variation of electrical conductivity with ZrO_2 content at 10KHz

In this study, the filler content was varied from 0.918, 1.918 and 3.013 vol%.Thermal conductivity of the epoxy resin was found to be 0.2W/m.K which is in good agreement with the value 0.19 W/m.K quoted in the literature [11]. At this level of thermal conductivity the epoxy resin is basically a thermal insulator. However, by incorporating ZrO_2 particle into the epoxy matrix, the resulting composite exhibited a marked improvement in thermal conductivity as shown in figure 4. The thermal conductivity was found to increase with increased in volume fraction of filler content, That is because the porosity of the pure sample is greater than the other samples which are doped with ZrO_2, and also because the thermal conductivity of ZrO_2 is larger than epoxy resin[12].

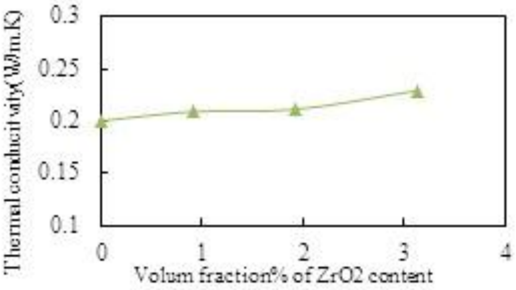

Figure 4:Variation of thermal conductivity with volume fraction of ZrO2 content.

Table 1. Compares the experimental results with those found from calculated of two models for the thermal conductivity of a two phase system , the rules-of-mixture and the Maxwell equation for dilute composite by using equations 8 and 9.

Table 1. Thermal conductivity values for composites obtained from different methods.

$K_{maxwell}$	$K_{rule\ mix}$	K_{exp}	**Vol.%**	**W%**
0.19	0.19	0.2	0	0
0.2040	0.2018	0.209	0.918	5
0.2098	0.2036	0.211	1.918	10
0.2147	0.2057	0.229	3.13	15

The values of thermal conductivity calculated using the rules-of–mixture and Maxwell equation are accurate with respect to the experimental values.

CONCLUSIONS

Both dielectric constant and dissipation factor of epoxy/ZrO_2 composites increased with an increasing content of ZrO_2, which has been attributed to interfacial polarization. The dielectric constant of epoxy/ZrO_2 composites decreased with an increase in frequency, and the dissipation factor of the epoxy/ZrO_2 composites increased with an incensing frequency. Increasing the volume content of ZrO_2 in epoxy improves the thermal conductivity of composite.

REFERENCES

1. Psarras GC, E Manolakaki, GM Tsangaris. (2002). Electrical relaxations in polymeric particulate composites of epoxy resin and metal particles. *Composites: Part A*, 33 375–384.
2. Zhou D Yu. (2010). Thermal and dielectric properties of the aluminum particle/epoxy resin composites. *J Appl Polym Sci*, 118 3156-3166.
3. Wong CP, Bollampally RS. (1999). Thermal conductivity, elastic modulus, and coefficient of thermal expansion of polymer composites filled with ceramic particles for electronic packaging. *J Appl Polym Sci*, 74(14), 3396–403.
4. Sanada K, Tada Y, Shindo Y. (2009). Thermal conductivity of polymer composites with close-packed structure of nano and micro fillers. *Composites: Part A*, 40(6–7), 724–730.
5. M'Peko JC et al. (2003). Electrical properties of zirconia–alumina composites) / *Solid State Ionics*, 156, 59–69.
6. Aravindan V, Vickraman P, T. Prem Kumar. (2007). ZrO2 nanofiller incorporated PVC/PVdF blend-based composite polymer electrolytes (CPE) complexed with LiBOB. *Journal of Membrane Science*, 305, 146–151.
7. Tarev B. Physics of dielectric materials. Mir Publisher Co, (1979).
8. Roy SK. (2001). Thermal Physics and Statistical Mechanics. New Age International Ltd. New Delhi, 157-159.
9. Nayaka RT, Dora P, A Satapathy. (2010). A computational and experimental investigation on thermal conductivity of particle reinforced epoxy composites. *Computational Materials Science*, 48 576–581.
10. Singh V, Kulkarni AR, Rama Mohan T R. (2003). Dielectric Properties of aluminums–Epoxy Composites. *Journal of Applied Polymer Science*, 90, 3602–3608
11. Callister WD. Materials Science and Engineering. John Willy and sons, Inc., London, 2003.
12. Sombatsompop N, A K Wood. (1997). Measurement of thermal conductivity of polymers using an improved Lee's Disc apparatus, *Polymer Testing*, 16, 203-223.