

POLYMER-CERAMIC COMPOSITES WITH CONTROLLED DIELECTRIC PROPERTIES: INVESTIGATION ON ELECTRICAL & MECHANICAL PROPERTIES AND MODELING

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Abstract

The present study deals with the development of flexible polymer–ceramic composites with graded dielectric properties. Electro active ceramic material like titania (TiO_2), barium titanate (BaTiO_3), and doped BaTiO_3 were chosen as electro–active ceramic fillers to be added in polydimethylsiloxane (Silicone rubber) matrix. The relative proportion of ceramic filler with respect to polymer matrix controls dielectric properties of these composites. The effect of dopant in BaTiO_3 (at different temperature) on electrical properties of composites was also studied. Composites with variable dielectric properties could be obtained through change in composition of the composites. Different mechanical properties of these composites were also measured and presented as a function of filler concentration. The crystallographic state of pure polymer, TiO_2 , and TiO_2 filled composites were also studied through XRD analysis in order to find out the change in crystallinity with filler loading. Morphology and dispersion of these fillers in the composites were studied by FESEM and HRTEM. Finally, some theoretical dielectric models were applied for predicting dielectric constant of different composites and the best match between theoretical and experimental results was achieved for the Lichtenecker mode.

1. Introduction

Polymer ceramic composites have drawn great interest for its versatile applications in the field of electronic materials [1, 2] such as integrated decoupling capacitors, acoustic emission sensors, electronic packaging materials [2, 3–5] and angular acceleration accelerometers [6, 7]. Electro-ceramics possess very high dielectric constant but are brittle, and possess medium dielectric strength, and required very high temperature to process where as polymers are flexible in nature, can be processed at much low temperature and also have high dielectric breakdown voltage [8]. However, the combination of these two constituents in a single composite material will give the better performance compared to individual one. These types of materials with high dielectric

constant and high breakdown voltage can achieve high volume efficiency and energy storage density for applications as capacitors for electric energy storage devices. Polymer, ceramic composites can act as good dielectric materials [9, 10]. The selection of appropriate polymer matrix and oxide ceramic can lead to the development of graded dielectrics where dielectric properties like dielectric constant, loss tangent and impedance can be varied over a wide range by simply changing composite composition. These composites have good mechanical properties coupled with easy processing and can be formed into any typical shape through simple molding process. The proper selection of matrix polymer for such composites can give rise to both rigid and flexible composites which, can be used for various electrical and electronic applications. Recently, many studies have been done on TiO_2 due to their remarkable optical and electronic properties [11, 12].

In the present study, TiO_2 , BaTiO_3 as well as doped BaTiO_3 were used to develop polymer–ceramic composites based on silicone rubber (PDMS) as base matrix. Different electrical and mechanical properties of these composites at various filler contents were studied. The influences of these fillers on electrical and mechanical properties of these composites were also measured.

2. Experimental section

2.1. Materials used

Silicone rubber (Polydimethyl siloxane, PDMS) was purchased from D J Silicone in block form: its shore hardness was 40 and density 1.12 g/cc. Titanium dioxide (anatase) and Vanadium pentoxide (V_2O_5) were purchased from Merck chemicals (India) and used without further purification. Both neat and doped Barium titanate (BaTiO_3) (Alfa Aesar Chemicals) were used. The doping of Barium titanate was done with V_2O_5 . Dicumyl peroxide, MP = 80°C, purity = 98% (Sigma-Aldrich chemical company, USA) was used for curing purpose.

2.2. Preparation of composites and samples

Mixing of filler particles (TiO_2 , BaTiO_3 , and doped BaTiO_3) and other ingredients into rubber matrix (PDMS) were accomplished in an internal mixer (Brabender plasticorder) for 5 minutes. Monsanto rheometer R 100 was used to determine the optimum cure time at the moulding temperature of 150°C.

Characterization

Tensile tests and tear strength were carried out according to the ASTM D 412 and ASTM D 624 specifications. Shore–A hardness of all the nanocomposites were measured according to ASTM D 2240. The DC volume resistivity of neat elastomer and the composites were measured using high resistivity meter (Model. Agilent 4339B). The dielectric properties of the composites were measured using precision LCR meter (Model. Quad Tech 7600). The phase formation and crystallographic state of particulate fillers are determined by using a Philips X-ray diffractometer (Model. PW-1710). The morphology and dispersion of the filler in the polymer matrix were studied using both field emission scanning electron microscopes (model. SUPRA 40, Carl Zeiss SMT AG, Germany) and JEOL high resolution transmission electron microscope (model. JEM–2100).

3. Results and discussion

3.1. Electrical properties

Semi log plots of dielectric constant (ϵ') and dielectric loss (ϵ'') vs frequency for different composites are presented in **Fig. 1a&b**. The dielectric constant (ϵ') is found to increase with the increase in filler loading (**Fig. 1a**) but with the decrease is frequency. These composition and frequency dependencies of dielectric constant are more pronounced in lower frequency range ($f < 10^3$ Hz). The significant increase in dielectric constant especially at low frequency region is mainly due to the increase in interfacial polarization. Similarly, the dielectric loss is also increased with the increase in filler concentration (**Fig. 1b**). The peaks in dielectric loss vs frequency plots indicate occurrence of some relaxation process in the system. The DC volume resistivity of these composites decreased with increase in filler loading as shown in **Fig. 1c**. This is mainly because of the fact that DC resistivity of particulate filler is lesser than the matrix polymer.

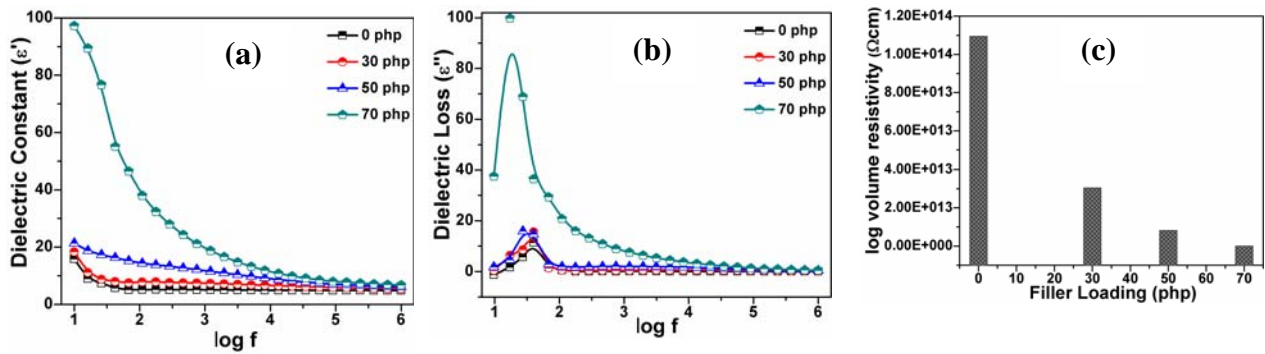


Fig. 1 Logf vs. ϵ' (a), logf vs. ϵ'' (b), and filler loading vs. log volume resistivity (c) plots for PDMS–TiO₂ composites

3.2. Effect of V₂O₅-doping in BaTiO₃ on dielectric properties of PDMS-BaTiO₃ composites

Fig. 2 presents semi-log plots of dielectric constant (ϵ') vs. frequency for PDMS–BaTiO₃ and PDMS– V₂O₅ doped BaTiO₃ composites. Different types of doped BaTiO₃ were prepared with varying doping level and doping conditions. Different PDMS– V₂O₅ doped BaTiO₃ composites were prepared. In all these cases, the filler loading is the same, i.e., 10 php but only difference exists in the filler type. It is observed that the composite containing 1 % V₂O₅ doped BaTiO₃ filler showed higher dielectric constant that of pure BaTiO₃ filled composite. But the temperature of doping has some significant effect on doped BaTiO₃ and also on the dielectric properties of composite made from it. It was found that the composite containing BaTiO₃ doped at 1000°C showed higher dielectric constant than that of the composite containing BaTiO₃ doped at 700°C. However, composite containing BaTiO₃ doped with 2 % V₂O₅ show decrease in dielectric constant value compared to one having BaTiO₃ doped with 1 % V₂O₅. So we can conclude that 1 % V₂O₅ is the optimum level of dopant concentration for BaTiO₃ for improvement of dielectric properties.

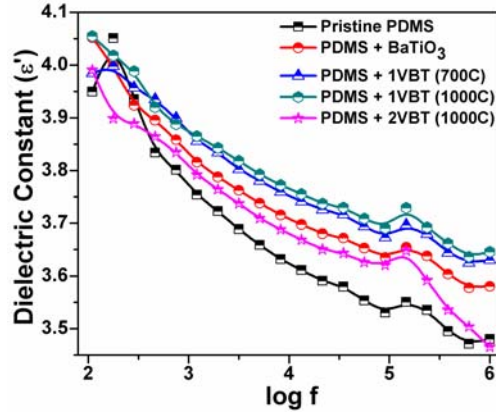


Fig. 2 Effect of V–doping in BaTiO₃ on dielectric properties of PDMS–BaTiO₃ or PDMS-V doped BaTiO₃ composites

3.3. Mechanical properties

Mechanical properties of titania filled PDMS are given in **Table 1**. The addition of titania in PDMS matrix decreased tensile strength, tear strength and elongation at break (% E.B.). The decrease in mechanical properties of composites due to the addition of filler indicates that titania acts as a non-reinforcing filler for PDMS matrix. Poor polymer-filler interaction was found from Kraus plot (figure not shown) for PDMS-titania system. However both modulus@100% strain and hardness were found to increase with the increase in titania concentration. Density of composites increased with the increase in titania loading as titania has higher density (4.2) than PDMS matrix (1.12).

Table 1 Mechanical property of PDMS-TiO₂ composites

Titania Content (php)	Tensile Strength (Mpa)	% E. B.	Tensile Modulus @100 % (Mpa)	Hardness (Shore-A)	Density (g/cm³)	Tear (N/mm)
0	5.55	460	1.032	40	1.12	19.8
30	4.89	395	1.36	48	1.22	16.36
50	4.56	352.5	1.464	51	---	14.5
70	3.875	342.4	1.713	57	1.47	15.78

3.4. X-ray diffraction analysis

XRD plot of neat titania and its nanocomposites is presented in **Fig. 3**. The figure showed distinct crystalline peaks for titania in each composites and peak intensity increases with increase in titania concentration in the composite.

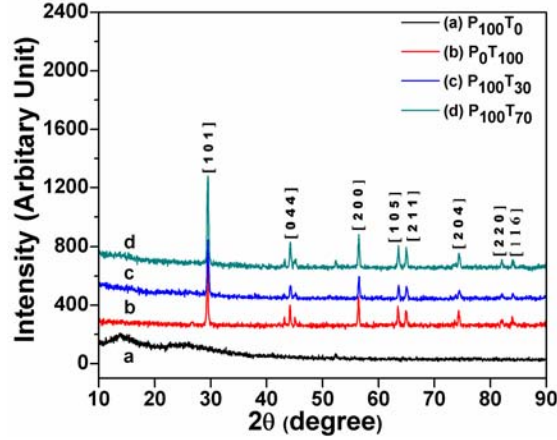


Fig. 3 XRD pattern of normal titania and their nanocomposites

3.5. Applicability of different theoretical models to predict permittivity of mixture for PDMS-Titania composites.

The two insulating components of the composites cannot exchange electric charges at their separation surfaces; this gives rise to Maxwell-Wagner interfacial polarization. For the present systems, the resulting dispersive behaviour appeared to be located at low frequencies, so that at frequency range > 1000 Hz it seemed to be reasonable to assume the dielectric permittivity to be almost completely unrelaxed with respect to this process. Several dielectric mixing models have been proposed to account for the effective permittivity (ϵ_c) of the two immiscible components of the composite materials, made of polymer matrix having dielectric permittivity (ϵ_1) and volume fraction (v_1), filled with ceramic fillers of permittivity (ϵ_2) and volume fraction ($v_2=1-v_1$). Among those models, models having spherical particles are of special interest:

(i) Maxwell-Wagner [13] or Maxwell-Garnett [14] equation:

$$\epsilon_c = \epsilon_1 \left[1 + \frac{3v_2(\epsilon_2 - \epsilon_1)}{2\epsilon_1 + \epsilon_2 - v_2(\epsilon_2 - \epsilon_1)} \right] \quad (1a)$$

The above equation can also be written as:

$$\frac{\epsilon_c - \epsilon_1}{\epsilon_c + 2\epsilon_1} = v_2 \frac{(\epsilon_2 - \epsilon_1)}{\epsilon_2 + 2\epsilon_1} \quad (1b)$$

(ii) Coherent potential equation [13]

$$\frac{\epsilon_c - \epsilon_1}{4\epsilon_c - \epsilon_1} = v_2 \frac{(\epsilon_2 - \epsilon_1)}{3\epsilon_c + \epsilon_2 - \epsilon_1} \quad (2)$$

(iii) Lichtenecker equation [14]

$$\ln(\epsilon_c) = v_1 \ln(\epsilon_1) + v_2 \ln(\epsilon_2) \quad (3)$$

Where, v_i , m_i , and ρ_i (for $i = 1, 2$) respectively represent volume, mass, and density of the phase i (Polymer/filler) of the composite. The density of neat silicone elastomer is $\rho_1 = 1.12 \text{ g/cm}^3$ and

the density of titanium dioxide is $\rho_2 \approx 4.2 \text{ g/cm}^3$. The filler volume fractions corresponding to different composites were $v_2=0.074, 0.118, \text{ and } 0.157\text{vol } \%$.

Table 2: Dielectric constant of silicone/titanium dioxide composites at different frequency

TiO ₂ volume Fraction	ϵ' (100 Hz)	ϵ' (1 kHz)	ϵ' (10 kHz)
0.000	5.16	5.03	4.94
0.074	7.80	7.28	6.66
0.118	14.33	11.47	9.16
0.157	37.99	18.72	11.88
1.000	32801.88	5073.69	1226.21

Data for filler contents up to 22.7 % and that of pure titanium dioxide are measured.

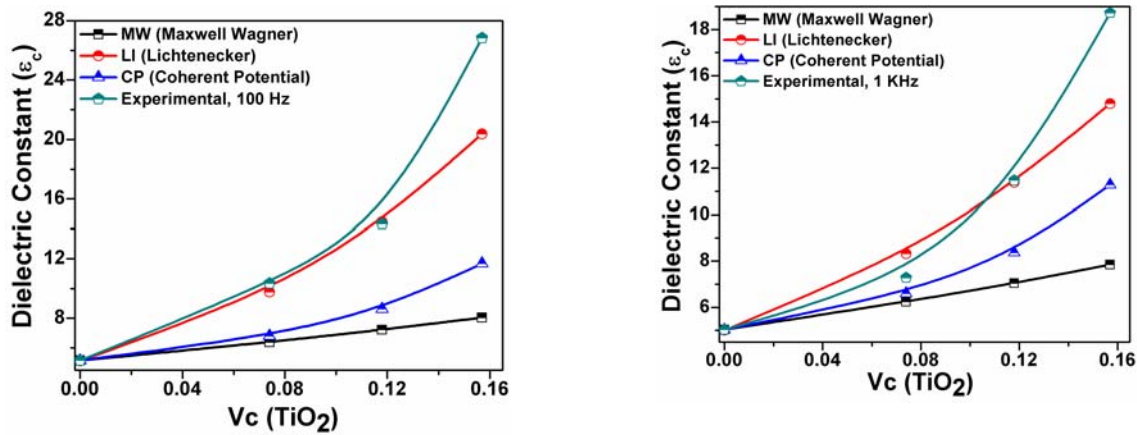


Fig. 4 (a) Experimental ϵ_c data of PDMS-TiO₂ composites at 100 Hz at various filler contents (V_2), compared with specified models, (b) Experimental ϵ_c data of PDMS-TiO₂ composites at 1 KHz at various filler contents (V_2), compared with specified models

Experimental and theoretical values of dielectric constant derived from different above mentioned equations are presented in Table 2 and in Figures. 1a and 1b for comparison. Notably, the Lichtenecker model showed the best agreement with the experimental results over wide composition range.

4. Conclusions

The composition dependent graded dielectric could be made through the addition of titanium dioxide to silicone elastomer (PDMS) where both dielectric constant and loss factor increased with the increase in titania content in the composites. However titania acted as a non-reinforcing filler for PDMS matrix. The tensile strength, tear strength, and % elongation at break (% EB) decreased with the increase in TiO₂, but the modulus and hardness were found to increase. Some composites were made with doped barium titanate filled in PDMS. The doping of vanadium pentoxide in BaTiO₃ enhanced the dielectric constant of PDMS-BaTiO₃ composite and the optimum dopant concentration was found to be 1%.

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