Synthesis, morphological, electromechanical characterization of (CaMgFe\(_x\))Fe\(_{1-x}\)Ti\(_3\)O\(_{12-\delta}\)/PDMS nanocomposite thin films for energy storage application

Ashis Tripathy\(^1\), Priyaranjan Sharma\(^2\) and Narayan Sahoo\(^3\)
\(^1\)Department of Electronics and Communication Engineering, JK Lakshmipat University, Jaipur, India.
\(^2\)Department of Mechanical Engineering, JK Lakshmipat University, Jaipur, India.
\(^3\)Department of Electrical Engineering, JK Lakshmipat University, Jaipur, India.

*E-mail: ashisbidyarthi@gmail.com

Abstract. At the present time, flexible and stretchable electronics has intended to use the new cutting-edge technologies for advanced electronic application. Currently, Polymers are being employed for such applications but they are not effective due to their low dielectric constant. To enhance the dielectric properties of polymer for energy storage application, it is necessary to add ceramic material of high dielectric constant to synthesize a polymer-ceramic composite. Therefore, a novel attempt has been made to enhance the dielectric properties of the Polydimethylsiloxane (PDMS) polymer by adding (CaMgFe\(_x\))Fe\(_{1-x}\)Ti\(_3\)O\(_{12-\delta}\) (0<x<1, 0<\(\delta\)<6) (CMFTO) nanocomposite ceramic powder. The newly developed CMFTO2/PDMS composite based thin film shows a higher dielectric constant (\(\varepsilon'\)) value (~350), extremely low tangent loss (\(\tan \delta\)) (< 0.002) and excellent flexibility (static modulus ≈ 0.27 MPa and elongation > 90%), which can make it a potential material for advanced flexible electronic devices, energy storage and biomedical applications.

1. Introduction
Nowadays, polymer ceramic composites are gaining more and more interest of researchers due to versatility in the field of electronic materials, particularly in acoustic emission sensors, electronic packaging materials, energy-storage super capacitors and integrated decoupling capacitors[1,2]. Electroceramics are brittle in nature, exhibits medium dielectric strength and require high processing temperature; however, it exhibits high dielectric constant. Whereas polymers are flexible in nature followed by high dielectric breakdown voltage and low processing temperature, however they exhibit low dielectric constant. To obtain the collective benefits of polymer and electroceramic, it is necessary to develop polymer ceramic composite. Polymer ceramic composites can act as good dielectric materials. Therefore, it is necessary to develop suitable polymer ceramic composite in order to achieve better dielectric properties like dielectric constant, loss tangent and impedance at various frequency 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 a simple molding process. Moreover, a suitable polymer matrix can increase both rigidity and flexibility of ceramic composites for numerous advanced electronic applications [3]. Previous researchers [4,5] have attempted to develop various polymer ceramic composites to enhance the dielectric properties of
existing polymer. Still, there is a scope to enhance the dielectric constant of polymer by adding nanoceramic composite for several energy storage applications.

In this current study, synthesis of (CaMgFe)_{x-y}Fe_{y}Ti_{12-3y}O_{2}/PDMS based composite flexible films and modulation of their electrical and dielectric properties are reported. And, various performance attributes of polymer ceramic composite such as surface microstructure, electrical resistivity, mechanical flexibility and dielectric characteristics were analyzed.

2. Experimental section

2.1. Synthesis of (CaMgFe)_{x-y}Fe_{y}Ti_{12-3y} nanocomposite and flexible film

The empirical formulas of the nanocomposite used for the current study were CaMgFe_{0.33}Ti_{12} (CMFTO1) and CaMgFe_{0.67}Ti_{12} (CMFTO2). The initial raw materials used for the study were Calcium Oxide (CaO), Magnesium Carbonate (MgCO_{3}), Hematite (Fe_{2}O_{3}), and Titania (TiO_{2}). Initially, these oxide powders were mixed with 70% ethyl alcohol in a ball milling machine using Zirconia balls. Then, mixed slurry was placed in an oven at 150 °C to remove the moisture and alcohol. The dry powder was sintered at 1050 °C for 16 h to form desired nanocomposite. Then, the sintered powder of CMFTO1 and CMFTO2 were ball milled into fine powder form and mixed with PDMS. To enhance crosslinking in PDMS chain, a curing agent was added to the mixture of CMFTO and PDMS. At 3000 rpm, CMFTO/PDMS mixture was spin coated on a glass container for 20 s under vacuum environment to form a thin film. To remove the micro-bubbles from the prepared thin films, they were kept in a self-drying vacuum pump under the pressure of 500 mbar for a period of 10 min. At last, flexible film of CMFTO/PDMS composite were obtained by curing at a temperature of 60 °C for 5 h. The synthesis process of the CMFTO nanocomposite and its PDMS based flexible composite film has been shown in figure 1.

![Figure 1. Synthesis process of CMFTO nanocomposites and CMFTO/PDMS thin films.](image)

2.2. Characterizations

The impedance and dielectric characteristics of composite films were measured with the help of an LCR meter (3532-50 LCR Hi tester, Hioki, Ueda, Japan). The dispersion of filler in the polymer matrix and surface morphology of polymer ceramic composite were studied by using field emission scanning electron microscope (FESEM). A universal testing machine (5848, InstronMicro Tester) was used to measure the flexibility of the PDMS and CMFTO/PDMS composite films.

3. Results and discussion

3.1. Microstructural studies

FESEM images of the CMFTO2/PDMS and CMFTO1/PDMS composite films were shown in figure 2(a) and 2(b). The flexible CMFTO1/PDMS and CMFTO2/PDMS composite films show good particle matrix bonding at the polymer-ceramic interface. Inset of figures 2(a) and 2(b) shows the digital image of CMFTO2/PDMS and CMFTO1/PDMS composite film respectively. Uniform dispersion of ceramic composite particles in PDMS has been observed in the both the FESEM images. Due to the reunion mechanism, CMFTO nanocomposite agglomerate in certain areas which has been highlighted by the yellow circle in micrograph as shown in figure 2(a-b).
Figure 2. Field emission scanning electron microscope (FESEM) images of (a) CMFTO2/PDMS and (b) CMFTO1/PDMS composite films.

3.2. Impedance and dielectric spectroscopy
The frequency dependent real (Z') and imaginary (Z'') parts of the impedance at room temperature for both the CMFTO/PDMS samples are depicted in figure 3(a) and 3(b), respectively. From the figure 3(a), it has been observed that at the low frequency range, Z' shows a larger value and it decreases significantly with increased frequency. It may be due to polarization effect in the samples. This decreasing trend in Z'-value shows a prospective of enhancement in the alternating current (AC) conductivity (σ_ac) with an increase in frequency. It has been also found that the impedance value decreases due to increase of Fe concentration. In higher frequency range, the Z' merges together, which gives a hint of probable discharge of space charge and a subsequent dropping of the barrier characteristics in the polymer ceramic composite [6].

Figure 3. Variations of (a) real (Z') impedance (b) imaginary (Z'') impedance, of the CMFTO1/PDMS and CMFTO2/PDMS composite films as a function of frequency in logarithmic scale at 25°C.

The appearance of peak in the Z'' with frequency (see figure 3b) recommends the presence of relaxation phenomena of the material. Due to increasing of Fe concentration, more broadening of peak is observed. The unequal expansion of the peak recommends the existence of electrical processes in the composite film with distribution of relaxation time [6]. This broadening of peak after addition of Fe may be due to some relaxation phenomena caused by hopping of electrons/oxygen ion vacancy/defects among the available localized sites [6]. Gathering of space charge of the ceramic-polymer nanocomposite may be the possible reason for the monotonous decrease of Z''-value with increasing frequency after maxima.

The changes in dielectric constant (ε ') and dielectric loss (ε '') for CMFTO1/PDMS and CMFTO2/PDMS composite films are shown in figure 4(a) and 4(b) as a function of frequency in logarithm scale at 25 °C. The value of ε' was increased with the increased concentration of Fe but decreased with increase in frequency as shown in figure 4(a). The concentration variation and frequency dependency of dielectric constant are more pronounced in the lower frequency range (f<10^3 Hz). Enhancement of interfacial polarization is the main cause for the significant improvement of ε' at the lower frequency range. In the same fashion, the ε'' was also increased with the increased concentration of Fe (figure 2b). The peaks in dielectric loss vs. frequency plot indicate the occurrence
of some relaxation process in the system. Due to the extremely high $\varepsilon'$ value of CMFTO2/PDMS composite, it could be used for various capacitive and electric energy storage applications.

\[\text{Figure 4. The variations of (a) Dielectric constant ($\varepsilon'$), (b) Dielectric loss ($\varepsilon''$) versus frequency plots of the CMFTO1/PDMS and CMFTO2/PDMS composite films.}\]

Frequency dependent dielectric constant ($\varepsilon'$) and tanδ response for CMFTO2/PDMS and CMFTO1/PDMS composite films are shown in figure 5(a-b) respectively. CMFTO2/PDMS film shows a higher dielectric value (~350) and extremely low tanδ (< 0.002). Extremely high $\varepsilon'$ and low tanδ value of CMFTO2/PDMS composite film can make it a highly prospective candidate for high energy storage capacitor applications. In the figure it is also observed that the CMFTO1/PDMS composite film shows lower $\varepsilon'$ (i.e., ~160) than the CMFTO2/PDMS composite film, but effectively greater than the pure PDMS ($\varepsilon'$ ~10)) and PDMS based nanocomposites [7].

\[\text{Figure 5. A typical comparison in $\varepsilon'$ and tanδ of (a) CMFTO2/PDMS and (b) CMFTO1/PDMS composite film at different frequency.}\]

AC conductivity ($\sigma_{ac}$) vs. frequency response of CMFTO1/PDMS and CMFTO2/PDMS composite film has been shown in the figure 6. From the response, it was observed that $\sigma_{ac}$ of both the ceramic-polymer composite slowly increased up to $\log(f) = 4.4$ Hz and increased faster after this frequency.

\[\text{Figure 6. Frequency dependent AC conductivity ($\sigma_{ac}$) of CMFTO1/PDMS and CMFTO2/PDMS composite film.}\]
The observed characteristics are a clear evidence of the transition of composite from an insulator to semiconductor zone. These effects in the crystalline oxide based materials are mainly developed due to the hopping of ions, which has greater possibility in both the flexible composite films [8].

The complex impedance spectra ($Z'$ vs. $Z''$) for both the CMFTO/PDMS composite films in the frequency range of $10^2$-$10^6$ Hz are depicted in figure 7. The complex impedance plot of both the CMFTO/PDMS composite films show identical behavior. In the plot of figure 7, it could be observed that, the response curve diverges significantly from that of one impedance semi-circular arc. It could be noticed that the complex impedance spectra of both the composite film initiated to form a semicircle at $1.1 \times 10^3$ Hz before it diverged. These characteristics may be due to the conduction phenomenon, which happens due to the mobility of free electrons in the CMFTO/PDMS composite films.

![Figure 7. Nyquist plots of CMFTO1/PDMS and CMFTO2/PDMS composite films.](image)

3.3. Mechanical properties

Static tensile characteristics of both the CMFTO/PDMS composite films and PDMS are presented in figure 8. Flexibility of CMFTO/PDMS composite films was evaluated by comparing with PDMS film. The Young’s modulus of the composite films was evaluated in the strain range of 15-45%. The flexibility of both the composite films was tested by elongating the thin film up to 90%. The Young’s modulus of CMFTO1/PDMS and CMFTO2/PDMS composite films was $0.53 \pm 0.49$ and $0.80 \pm 0.21$ MPa, respectively. Both the film shows extensively larger modulus value than the PDMS film, which is $0.27 \pm 0.08$ MPa. The 90% elongation of both the composite film, suggest identical flexibility characteristic with PDMS film. Significantly lower Young’s modulus of the CMFTO2/PDMS composite film than the PDMS film, confirms its excellent flexibility characteristics [9].

![Figure 8. Static tensile properties of PDMS, CMFTO1/PDMS and CMFTO2/PDMS composite films.](image)
4. Conclusions
In the current study, a new polymer ceramic composite was developed which shows higher dielectric constant (CMFTO2 ~350 & CMFTO1 ~150) than the previous results reported in the literature. The overall $\sigma_{dc}$ of both the composite films was in increasing trend with increasing in applied alternating frequency, which indicates that dielectric characteristics of composite could be changed by the dynamic behavior of the polymer matrix. The dielectric constant of the newly developed CMFTO2/PDMS composite flexible film is significantly higher than results reported in the literature [10,11]. Therefore, the novel nanocomposite of CMFTO and PDMS composite film with trace amount of ferrous ferrite structures developed by solid-state step-sintering technique would be a potential dielectric material for several electronic miniaturization devices for capacitive memory, energy storage devices, actuators, sensor, switching and high frequency applications.

Acknowledgments
The authors are grateful to Prof. Noor Azuan Abu Osman and Dr. Sumit Pramanik for their motivation and support.

References
[1] Ramajo, L. A., Reboredo, M. M., & Castro, M. S. (2007). Characterisation of epoxy/BaTiO3 composites processed by dipping for integral capacitor films (ICF). Journal of Materials Science, 42(10), 3685-3691.
[2] Dias, C. J., Igreja, R., Marat-Mendes, R., Inacio, P., Marat-Mendes, J. N., & Das-Gupta, D. K. (2004). Recent advances in ceramic-polymer composite electrets. IEEE transactions on dielectrics and electrical insulation, 11(1), 35-40.
[3] Tripathy, A., Pramanik, S., Manna, A., Azrin Shah, N. F., Shasmin, H. N., Radzi, Z., & Abu Osman, N. A. (2016). Synthesis and characterizations of novel Ca-Mg-Ti-Fe-oxides based ceramic nanocrystals and flexible film of polydimethylsiloxane composite with improved mechanical and dielectric properties for sensors. Sensors, 16(3), 292.
[4] Zhang, L., Shan, X., Bass, P., Tong, Y., Rolin, T.D., Hill, C.W., Brewer, J.C., Tucker, D.S. and Cheng, Z.Y. (2016). Process and microstructure to achieve ultra-high dielectric constant in ceramic-polymer composites. Scientific reports, 6, 35763.
[5] Popielarz, R., Chiang, C. K., Nozaki, R., & Obrzut, J. (2001). Dielectric properties of polymer/ferroelectric ceramic composites from 100 Hz to 10 GHz. Macromolecules, 34(17), 5910-5915.
[6] Kumar, A., Singh, B. P., Choudhary, R. N. P., & Thakur, A. K. (2006). Characterization of electrical properties of Pb-modified BaSnO 3 using impedance spectroscopy. Materials chemistry and physics, 99(1), 150-159.
[7] Du, P., Lin, X., & Zhang, X. (2011, June). Dielectric constants of PDMS nanocomposites using conducting polymer nanowires. In Solid-State Sensors, Actuators and Microsystems Conference (TRANSDUCERS), 2011 16th IEEE International (pp. 645-648).
[8] George, M., Nair, S. S., John, A. M., Joy, P. A., & Anantharaman, M. R. (2006). Structural, magnetic and electrical properties of the sol-gel prepared Li0. 5Fe2. 5O4 fine particles. Journal of Physics D: Applied Physics, 39(5), 900.
[9] Aatoolahi, F., Pramanik, S., Moradi, A., Daliliotojari, A., Pingguan-Murphy, B., Abas, W., Bakar, W.A., Osman, A. and Azuan, N. (2015). Endothelial cell responses in terms of adhesion, proliferation, and morphology to stiffness of polydimethylsiloxane elastomer substrates. Journal of biomedical materials research Part A, 103(7), 2203-2213.
[10] Nayak, S., Sahoo, B., Chaki, T. K., & Khastgir, D. (2013). Development of polyurethane–titania nanocomposites as dielectric and piezoelectric material. RSC Advances, 3(8), 2620-2631.
[11] Gan, W. C., & Majid, W. A. (2014). Effect of TiO2 on enhanced pyroelectric activity of PVDF composite. Smart Materials and Structures, 23(4), 045026.