Development of Poly(dimethylsiloxane)–Titania Nanocomposites with Controlled Dielectric Properties: Effect of Heat Treatment of Titania on Electrical Properties

Suryakanta Nayak,1 Mostafizur Rahaman,1 A. K. Pandey,2 Dipak Kumar Setua,2 Tapan Kumar Chaki,1 Dipak Khastgir1
1Rubber Technology Centre, Indian Institute of Technology, Kharagpur, W.B. 721302, India
2Defence Materials and Stores Research and Development Establishment, Kanpur, India 208013

Correspondence to: D. Khastgir (E-mail: khasdi@rtc.iitkgp.ernet.in)

ABSTRACT: Polymer–ceramic composites were prepared using poly(dimethylsiloxane) as base matrix and normal as well as heat-treated titania as fillers. Dielectric and mechanical properties of the composites were measured and found that dielectric constant of the composites was increased dramatically with the addition of filler, whereas resistivity was decreased. Hardness and modulus were found to increase but tensile strength, % elongation at break, and tear strength were decreased with the filler loading. Neat titania contains some moisture (physiosorbed and chemisorbed) as revealed from thermogravimetric analysis. Both electrical and mechanical properties of the composites were affected by filler heat treatment. Further, untreated titania contains Ti3+ and Ti4+, which on heat treatment, increases the concentration of Ti4+, as a result electrical properties were affected. Filler dispersion in the composites was studied by field emission scanning electron microscopy and high resolution transmission electron microscopy. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 127: 784–796, 2013

KEYWORDS: silicone; nanocomposites; titania; electrical properties; mechanical properties; heat treatment

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INTRODUCTION
Polymer-based nanocomposites have attracted attention of many researchers for their novel properties.1,2 Most of these composites have either nanoclay or carbon nanotube dispersed in appropriate polymer matrix.3,4 In fact, nanocomposites can also be derived from dispersion of metal oxide ceramic fillers in suitable polymer matrix. Polymer–ceramic composites have fascinated great attention due to their novel electronic and electrical properties.5,6 These composites have some potential applications as integrated decoupling capacitors, acoustic emission sensors, electronic packaging materials,7–10 and angular acceleration accelerometers.11,12 General properties of ceramic–polymer composites depend on intrinsic properties of the ceramic and polymer such as relative proportion, connectivity of phases, and polarizability of the dispersed phase and matrix polymer. In fact, ferroelectric composites derived from ceramic particles dispersed in polymer matrices have been currently developed for use in the electrical devices. Various advantages of these materials are high dielectric constant, lightweight, good mechanical strength coupled with good flexibility.13 Polymer–ceramic composites can act as good dielectric materials.14 Polymeric materials with high dielectric constants are highly desirable for use in actuators, artificial muscles, and charge–storage devices.15–17 The dielectric properties of polymer composites with metallic fillers are attributed to the formation of infinite number of tiny capacitors with many conducting particles separated by thin insulating layers. Thus, a heterogeneous system of polymer–ceramic composite can act as a capacitor with excellent dielectric characteristics suitable for high charge storage.8 Apart from metallic fillers, different types of carbon filler when added to polymer matrix can also change electrical characteristics of these systems. Polymer–carbon composite can lead to formation of composites with high dielectric constant as well as conducting composites.18–20 Even conducting polymers such as polyaniline, polythiophene, polypyrrole, when mixed with insulating matrix can give rise to composites with high dielectric constant. But all these composites with conductive additives like carbon fillers or conducting polymers suffer from one serious disadvantage as
they have high dielectric loss. However, polymer containing appropriate amount of high dielectric constant ceramic powder can produce composite with increased dielectric constant but without significant increase in dielectric loss. In fact, the selection of appropriate polymer matrix and ceramic oxide can lead to the formation of graded dielectric materials, whereas dielectric properties such as dielectric constant, loss tangent, and impedance can be varied over a wide range through simple variation in the composition. There is also an advantage (processing point of view), polymer–ceramic composites can be designed into any intricate shape easily at much lower temperature because processing temperature of polymers are much lower than that of ceramic materials. The proper selection of polymer matrix for such composites can give rise to both rigid and flexible ceramic–polymer composites, which can be used for various electrical and electronic applications.

Both barium titanate (BaTiO3) and titania (TiO2) as dielectric fillers have attracted many researchers for making electroactive composites. In this study, both untreated and heat-treated titania (TiO2) are used to develop polymer–ceramic composites using silicone elastomer (PDMS) as a matrix. Silicone elastomer is often considered as an inorganic polymer with relatively wide temperature range for application. Different electrical and mechanical properties of these composites were measured and found that dielectric constant of the composites was increased dramatically with the addition of filler, whereas resistivity was decreased. Mechanical properties of the composites were also affected by filler heat treatment. Further, untreated titania contains both Ti3+ and Ti4+, which on heat treatment, increases the concentration of Ti4+ as a result electrical properties were affected. An effort was made to correlate these properties with morphology of the composites. To our knowledge, there is no study regarding the heat treatment effect of titania on the electrical and mechanical properties of PDMS–titania composites.

**EXPERIMENTAL**

**Raw Materials**
The materials used in this study are all commercially available. The base matrix silicone elastomer (PDMS) was purchased from D. J. Silicone in block form: its density was 1.12 g/cc. Anatase titanium dioxide (Merck India, Ltd.) was subjected to ball milling for 10 min using ethanol as the solvent to get nano-sized particles before use. Dicumyl peroxide (melting point = 80°C, purity of 98%, Sigma–Aldrich chemical company, USA) was used as curing agent.

**Preparation of Nanocomposites**
Efficient dispersion of the titanium dioxide particles was achieved by mixing these with silicone elastomer (PDMS) using an internal mixer (Brabender–plasti corder, Model PLE 330) for 4 min at room temperature with 40 rpm shear rate. The titania particulate filler and the crosslinking agent were mixed with the neat silicone elastomer in a sequential manner as per formulations given in Table I. Finally, the resultant composites were sheeted out by passing through two roll mill. Cure characteristics of compounded elastomer were evaluated by Monsanto Rheometer 100 operating at 150°C. From the rheograph obtained from this equipment, one can find optimum cure time, scorch time, and cure rate. The compounded elastomers were cast into moulds and cured at 150°C for 10 min (obtained from Monsanto Rheometer) at a pressure of 7 MPa.

Different composites were designated by using alpha numerical number, for example, P100T30 means composition of silicone elastomer (PDMS) and TiO2 containing 30 parts of titanium dioxide by weight per hundred parts of polymer (php) and so on, where P stands for PDMS and T stands for titanium dioxide. In all the composites, the curing amount was kept constant.

**Characterization**

**Dynamic Light Scattering.** The hydrodynamic sizes of the titania particles were measured by dynamic light scattering (DLS) technique, using a particle size analyzer (Brookhaven 90 Plus). The laser light of wavelength (λ = 660 nm) was scattered with an angle θ = 90° at 27°C placing the dispersion in a polystyrene cuvette.

**Volume Resistivity.** The DC volume resistivity of neat PDMS and the composites were measured using high resistivity meter (Model Agilent 4339B) attached with a resistivity cell (Model Agilent 16088B).

**Dielectric Properties.** The dielectric properties of the composites were measured using precision LCR meter (Model. Quad Tech 7600) coupled with a homemade cell that has parallel plate circular electrodes. The test was carried out over frequency range 10–106 Hz.

**Mechanical Properties.** Tensile and tear properties were measured using universal testing machine (model H10KS, Hounsfield) in accordance with ASTM-D-412 and ASTM-D-624, respectively. Hardness (Shore–A) was measured according to ASTM-D-2240 using Durometer Type A (Shore instrument & MFG. Co. Inc., New York, USA).

**Thermogravimetric Analysis.** Thermogravimetric analysis was carried out in TA Instruments (model Q 50), at a heating rate of 20°C/min under nitrogen atmosphere up to 600°C. The data were analyzed by TA universal software on TA computer attached to the machine.

| Table I. Formulations of Silicone Elastomer (PDMS)–TiO2 Nanocomposites |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ingredients                      | P100T0 | P100T30 | P100T50 | P100T70 | P100T90 | P100T110 |
| PDMS                            | 100    | 100    | 100    | 100    | 100    | 100    |
| TiO2                             | 0      | 30     | 50     | 70     | 90     | 110    |
| Dicumyl peroxide                 | 1.5    | 1.5    | 1.5    | 1.5    | 1.5    | 1.5    |

**RAW TEXT END**
Fourier Transform Infrared Analysis. The presence of surface functional groups were investigated by Fourier transform infrared (FTIR) spectroscopy. The powder sample was prepared in KBr medium, whereas pure polymer and composites were made into thin transparent films. FTIR spectra were recorded on a spectrophotometer (model spectrum RX–I, PerkinElmer, Inc., MA, USA) in the range 400–4400 cm$^{-1}$.

X-Ray Diffraction Study. The phase formation and crystallographic state of untreated and heat-treated titanium dioxide were determined using a Philips X–ray diffractometer (Model. PW–1710) with Ni–filtered Co-K$_\alpha$ radiation ($\lambda = 0.179$ nm). The diffractograms were scanned in the 2$\theta$ range from 10$^\circ$ to 80$^\circ$ at a rate of 3$^\circ$/min.

SEM-EDX Analysis. The morphology and dispersion of the filer was studied with a scanning electron microscope (Model SUPRA 40 Field Emission Scanning Electron Microscope) from Carl Zeiss SMT AG (Germany). Energy dispersive X–ray (EDX) analysis was done to quantify the Ti, Si, C, and O contents in the composite.

High-Resolution Transmission Electron Microscope. The size, morphology, and dispersion of particulate titania filler in the elastomer matrix were observed using a JEOL high resolution transmission electron microscope (Model JEM–2100 HRTEM). Samples having thickness 300 nm were prepared using ultra microtome technique with the help of an instrument (Model TEM LEICA EMFCS) and these samples were placed on the copper grid.

RESULTS AND DISCUSSION

Properties of Normal and Heat-Treated Titania
Anatase grade of titanium dioxide is used for this investigation. The supplied titania has contained both the physiosorbed and chemisorbed moisture as revealed from thermogravimetric analysis given in Figure 1. A continuous decrease in weight was observed during heating up to 500°C with a small slope change (in loss in weight vs. temperature plot) at ~ 220°C. The decrease in weight before 220°C was due to the loss of physiosorbed moisture present in titania system whereas loss in weight after 220°C was expected to be due to chemisorbed moisture attached more firmly with titania particles. Figure 2 shows the X-ray diffraction pattern for the untreated as well as heat treated (at 600°C) titania. In both the cases, the characteristic peaks were observed at same values, which indicate moisture has no effect on the phase and crystallinity of the particulate titania filler.

However, electrical properties of titania as well as polymer–titania composites were affected by the presence of moisture. Apart from moisture, heat treatment of titania filler also affected the oxidation states of titania, hence electrical properties is affected. Common titania contains Ti$^{3+}$ as well as Ti$^{4+}$ ions. It has been reported that heat treatment of titania in presence of hydrogen converts Ti$^{4+}$ to Ti$^{3+}$ (eq. 1) leading to increase in conductivity of the system. In presence of oxygen, heat treatment may cause conversion of Ti$^{2+}$ to Ti$^{4+}$ where conductivity is expected to fall.$^{31}$

$$2\text{TiO}_2 + \text{H}_2 \rightarrow \text{Ti}_2\text{O}_3 + \text{H}_2\text{O} \quad (1)$$

Figure 3(a) shows the log–log plot of frequency vs. dielectric constant ($\varepsilon'$) for untreated and heat-treated TiO$_2$ whereas semi-log plot of tan $\delta$ and frequency for both types of titania (untreated and heat treated) and pure polymer (PDMS) is presented in Figure 3(b). It is observed from Figure 3(a) that there was drastic decrease in dielectric constant ($\varepsilon'$) with respect to increasing frequency for both untreated and heat-treated titania. However, at any particular frequency the difference in dielectric constant of untreated titania compared with heat treated one was relatively small (in logarithmic scale). In case of log $f$ vs. tan $\delta$ plot [Figure 3(b)], two relaxation peaks were observed at higher frequency for both untreated and heat-treated titania. It is also observed that there was a decrease in tan $\delta$ value for
heat-treated titania compared with untreated one at higher frequency range. There was no relaxation for pure polymer at higher frequency region but very small relaxation was observed at lower frequency region [Figure 3(b)]. The decrease in dielectric constant (\(\varepsilon\)) and tan \(\delta\) values for heat-treated titania at higher frequency may be due to the removal of both physisorbed and chemisorbed moisture from titania surface. The strong dielectric relaxation observed at higher frequency region for normal titania was due to chemisorbed H\(_2\)O molecule on titania surface. The ambient temperature dielectric relaxation at lower frequency region was mainly due to interfacial polarization (physically adsorbed water–titania interface).\(^{32}\) In fact, presence of two types of water molecules on titania surface was mentioned in earlier literature. Water is associated with titania through both physical and chemical adsorption which significantly affects its surface property.\(^{33}\) The schematic representation of H\(_2\)O adsorbed on TiO\(_2\) surface is depicted in Scheme 1.

The electrical conductivity of particulate titania filler was also influenced by heat treatment process as seen from Figure 4. It is interesting to note that heat-treated titania have less electrical conductivity than the untreated titania. On heat treatment, there was loss of moisture as well as conversion of Ti\(^{3+}\) to Ti\(^{4+}\), as a result there was reduction in conductivity of the titania particles. HRTEM image and DLS particle size distribution of particulate titania filler are given in Figure 5. From the figure, it is observed that the average particle size found through DLS was 272.5 nm, which was twofold more than that found from

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**Figure 3.** (a) Log–log plot of dielectric constant against frequency for normal (untreated) and heat-treated TiO\(_2\), (b) Semi-log plot of loss tangent (tan \(\delta\)) against frequency for normal (untreated) and heat-treated TiO\(_2\), and pure polymer (PDMS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Figure 4.** AC resistivity/conductivity (in inset) at different frequencies for normal and heat-treated titania particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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**Scheme 1.** Schematic representation of adsorbed H\(_2\)O on TiO\(_2\) surface. (a) Surface hydroxyl layer and (b) the first physisorption layer of H\(_2\)O on surface hydroxyls. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
TEM study, where average particle size was found to be ~ 100 nm. Bigger particle size as found from DLS may be due to association of water molecules with titania particles.

**Processability of PDMS-Titania Composites**

Processability of PDMS-TiO$_2$ composites can be understood from Mooney viscosity. With the increase in TiO$_2$ content from 0 to 110 php, Mooney viscosity ML$_{1+4}$ was increased from 15.7 to 54.0. This means viscosity of polymer composite increased with increase in filler content and it was quite expected. Density of the system also increased with the increase in TiO$_2$ content as density of TiO$_2$ (3.8–4.2) is higher than that of PDMS (1.12). The increased viscosity with increase in TiO$_2$ content leads to increase in shear force during mixing process consequently results in better dispersion of filler into polymer matrix. Mooney viscosity ML$_{1+4}$ at 100°C and density of the neat PDMS and composites are shown in Table II.

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>TiO$_2$ (php)</th>
<th>ML$_{1+4}$ at 100°C</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>0</td>
<td>15.7</td>
<td>1.12</td>
</tr>
<tr>
<td>PDMS</td>
<td>30</td>
<td>20.9</td>
<td>1.22</td>
</tr>
<tr>
<td>PDMS</td>
<td>70</td>
<td>31.2</td>
<td>1.47</td>
</tr>
<tr>
<td>PDMS</td>
<td>110</td>
<td>54.0</td>
<td>1.55</td>
</tr>
</tbody>
</table>

**Electrical Properties**

**DC Volume Resistivity.** The resistivity of the composites mainly depends on the resistivity of polymer matrix as well as contribution of filler. The DC resistivity of the composite systems containing untreated and heat-treated TiO$_2$ were found to decrease with the increase in filler loading as shown in Figure 6. This was mainly because of the fact that the DC resistivity of particulate filler is lower than the matrix polymer. Further, particulate inorganic filler is always associated with some moisture as mentioned earlier, as a result with the increased filler loading, DC resistivity of the composites decreased. Generally, resistivity of insulating polymer matrix reduces with the incorporation of particulate inorganic filler as these fillers are associated with moisture. Presence of moisture aids in ionization of any ionic species in the system which decreases electrical resistivity of the composites. This can be further established when composites of PDMS with heat-treated titania instead of untreated (normal) one showed increase in resistivity compared with composites with normal filler at same filler concentration. Out of all the composites, composites containing heat-treated TiO$_2$ showed higher resistivity compared with that of untreated titania. The effect of filler heat treatment was also reflected in other electrical properties such as dielectric constant and loss factor/loss tangent.

**Dielectric Properties**

Log–log plots of dielectric constant and loss factor vs. frequency for different PDMS–TiO$_2$ composites have been presented in Figure 5.
Figure 7(a,b), respectively. There was a large change in both
dielectric constant and loss factor with the change in frequency
and filler loadings. Moreover, at any particular frequency, the
dielectric constant increased with the increase in titania content.
This was mainly because dielectric constant of PDMS varies
between 2.5 and 4.8 and that of titania between 85 and 120 as
reported in literature. Dielectric constant of any composition
increased significantly with the decrease in frequency. This was
mainly because of strong contributions of interfacial and dipolar
polarization occurring at lower frequency range. Over the fre-
quency range $3 \times 10^2$–$10^6$ Hz, the dielectric constant shows
some step of rise as the frequency was lowered, which indicates
the existence of some kind of relaxation process over this fre-
quency region.

Dielectric loss also increased with the increase in titania loading
at any particular frequency. The log $f$ vs. loss tangent (tan $\delta$)
plot for composites containing filler loadings 30–70 php and
110 php (in inset) are presented in Figure 8. It can be seen
from the figure that two relaxation peaks were observed for
composites containing 30 and 50 php of filler loading. One
broad peak is spread over frequency region $3 \times 10^2$–$10^6$ Hz,
and a very sharp peak at lower frequency region $10^2$–$10^5$ Hz,
which is also observed for neat PDMS [Figure 3(b)]. However,
composites containing loading of 70 and 110 php two peaks are
not observed. In fact, there was also one strong relaxation peak
observed at somewhat lower frequency range within $10^2$–$10^1$ Hz
for composite containing 30, 50, 70, and 110 php TiO$_2$. The
high frequency broad peak may be due to dielectric relaxation
of titania system. This is apparent from tan $\delta$ vs. log $f$ plot for
compressed titania powder as shown in Figure 3(b). The exist-
tence of two distinctly different relaxation regions for compos-
ites containing 30 and 50 php filler loading is also apparent
from cole–cole plots (Figure 9). The existence of two semi cir-
cular arcs are indicative of existence of two relaxation processes
in the 30 and 50 php composite systems. High frequency relaxa-
tion process may be attributed to induced polarization process
occurring in titania, as titania shows strong induced polarization
under the applied electric field. This induced polarization is
somewhat modified due to presence of matrix polymer (poly-
dimethylsiloxane). When the filler was heat treated, the high
frequency broad peak was observed for composites having 30, 50,
and 70 php TiO$_2$ but not for composite with 110 php filler. It
is also noteworthy that the low frequency peak was very weak
or absent for composites containing heat-treated filler as
depicted in Figure 10. Hence, low frequency peak may be due
to the presence of moisture in the neat titania powder, which
cannot be detected for composites containing heat-treated filler.
The broad high frequency peak observed for filler loading 30,
50, and 70 php at high frequency and cannot be detected for
110 php may be due to effect of ionic conductivity as well as
strong effect of interfacial polarization. Heat treatment of TiO$_2$
converts Ti$^{3+}$ ion to Ti$^{4+}$, as a result there was reduction in
conduction of heat-treated TiO$_2$ as discussed earlier. This reduc-
tion in conductivity weakens the interfacial polarization which
depends on difference in dielectric constant and conductivity of
two phases present in the system. However, the relatively sharp
peak at low frequency which was observed for all composites
containing untreated filler having moisture may be attributed to
the interaction between moist titania with matrix polymer
PDMS (Scheme 2). In fact, the low frequency relaxation for
composites containing heat-treated titania was very weak and it
is not detected for all the compositions. Thus, it can be con-
cluded that the presence of moisture associated with neat titania

Figure 8. Log $f$ vs. tan $\delta$ for PDMS/untreated TiO$_2$ composites at various
filler loading. [Color figure can be viewed in the online issue, which is available at
wileyonlinelibrary.com.]
has significant effect on low frequency relaxation process. The composites having untreated titania contain both physisorbed and chemisorbed moisture which may help interaction of filler –OH groups with the polymer matrix through H–bonding. Traces amount of moisture can be present in the polymer matrix which may take part in formation of hydrogen bonding even with dried titania as evidenced from a broad peak at 3391.37 cm\(^{-1}\) in IR spectra given in Figure 11(a). In fact, a broad peak is also observed at 3394.11 cm\(^{-1}\) for neat titania [Figure 11(b)], whereas PDMS–TiO\(_2\) composite [Figure 11(c)] also showed a broad peak at lower frequency (3384.36 cm\(^{-1}\)) compared with both PDMS and titania. This shifting of IR peak in case of composite indicates existence of some kind of interaction between polymer matrix and additive. Following types of complexes are most likely to be formed in PDMS-titania nanocomposites as presented in Scheme 2:

The variation of dielectric constant with filler loading at three particular frequencies (10 Hz, 1 KHz, and 1 MHz) is presented in Figure 12. With the increase in filler concentration, dielectric constant was found to increase at different frequencies both for
untreated and heat-treated titania filler. The change in dielectric constant with filler loading was more pronounced as the measurement frequency is decreased. This is because as the frequency was lowered, contribution from interfacial polarization to dielectric constant is increasing. That is why the rate of change of dielectric constant with filler loading increased sharply as the frequency is lowered from $10^6$ to $10^3$ to 10 Hz.

**Mechanical Properties**

The adsorbed moisture on titania particles found to have some effect on different mechanical properties of composites. Variations of tensile strength and percentage elongation at break (% EB) for different PDMS–titania composites containing both untreated and heat-treated titania against filler loading are presented in Figure 13. With the increase in concentration of both types of titania in the composites, continuous decrease in tensile strength as well as % EB are observed. This reflects that both untreated and heat-treated titania act as non-reinforcing fillers for PDMS matrix. The decrease in mechanical properties was mainly due to poor polymer–filler interactions that exist between matrix polymer (PDMS) and particulate TiO$_2$. However, more reduction in properties with increased filler loading is encountered for heat-treated filler. Polymer–filler interaction can be estimated from the Kraus plot in accordance with the eq. (2).$^{36}$

$$\frac{V_\infty}{V_{ef}} = 1 - \frac{m\phi}{1 - \phi}$$

**Figure 11.** FTIR spectra of (a) pure PDMS, (b) TiO$_2$, (c) PDMS/(30 wt %) of TiO$_2$ composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Figure 12.** Dielectric constant vs. filler loading at three different frequencies for composites containing normal and heat-treated titania. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Figure 13.** Plots of tensile strength and % elongation against the filler concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
where $V_0$ is the volume fraction of elastomer phase in the swollen gel of unfilled gum elastomer vulcanizate, and $V_f$ is the volume fraction of elastomer phase in the swollen gel of filled elastomer vulcanizate, $\phi_f$ is the volume fraction of filler, and $m$ is the polymer–filler interaction parameter obtained from the slope of the plot of $V_0/V_f$ against $\phi/(1 – \phi)$. According to the Kraus equation, the plot of $V_0/V_f$ vs. $\phi/(1 – \phi)$ should be a straight line. Positive slope of this plot represents strong polymer–filler interaction (reinforcing) whereas negative slope represents weak polymer–filler interaction (non-reinforcing). For the present system (Figure 14), the negative slope for Kraus plot is observed as the value of $V_0/V_f$ is continuously increasing with the filler loading. This indicates that both normal and heat-treated titania act as non–reinforcing fillers. However, the presence of moisture in filler also has some effect on tensile strength and % EB. The composites containing heat-treated filler have less tensile strength and % EB compared with composites containing untreated one. The volume fraction of elastomer ($V_r$) was calculated by using eq. (3).

$$V_r = \frac{(D – FT)\rho_r^{-1}}{(D – FT)\rho_r^{-1} + A_0 \rho_s^{-1}}$$

where $T$, weight of the test specimen; $D$, de–swollen weight of the test specimen; $F$, weight fraction of the insoluble component in the sample; $A_0$, weight of absorbed solvent; $\rho_r$, density of elastomer; and $\rho_s$, density of solvent.

The effect of titania loading on high strain tensile modulus is presented in Figure 15. High strain modulus at 100% and 200% elongation was found to increase marginally with the increase in both types of titania loading. Generally, it has been observed that both reinforcing and non-forcing fillers have some positive effect on modulus unlike tensile strength up to a certain level of filler concentration. Here, we found that modulus at 200% elongation showed an increment up to 70 php titania loading thereafter the modulus decreased with further loading of fillers. The hardness may be considered as very low strain modulus, which progressively increased with increase in filler loading.
However, the rate of increase is found to be sharp up to 70 phr thereafter the increase is relatively marginal. For polymer composites, the tear strength is considered as one of the important functional properties. The tear strength is found to decrease with the increase in filler loading as depicted in Figure 16(a). However, compared with untreated (neat) filler containing composites, the composites with heat-treated filler showed better properties with slower rate of decrease in tear strength against concentration. This comparatively better tear strength for composites containing heat-treated titania may be attributed to the higher clustering of heat-treated titania particles in matrix polymer compared with untreated one. In fact, these particle clusters acts as a hindrance to crack propagation process, through diverting the crack path. Longer crack path indicates better tear resistance [Figure 16(b)].

Table III. SEM-EDX Values of the PDMS/TiO2 Composite

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Ti</th>
<th>Total</th>
</tr>
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<tbody>
<tr>
<td>Spectrum 1</td>
<td>7.84</td>
<td>35.02</td>
<td>21.98</td>
<td>35.16</td>
<td>100.00</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>10.88</td>
<td>45.95</td>
<td>17.19</td>
<td>25.98</td>
<td>100.00</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>11.88</td>
<td>36.53</td>
<td>22.13</td>
<td>29.46</td>
<td>100.00</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>11.40</td>
<td>38.70</td>
<td>21.11</td>
<td>28.79</td>
<td>100.00</td>
</tr>
<tr>
<td>Max.</td>
<td>11.88</td>
<td>45.95</td>
<td>22.13</td>
<td>35.16</td>
<td></td>
</tr>
<tr>
<td>Min.</td>
<td>7.84</td>
<td>35.02</td>
<td>17.19</td>
<td>25.98</td>
<td></td>
</tr>
</tbody>
</table>

Processing option: All elements analyzed (normalized), all results in weight %

Figure 17. FESEM micrographs of cryo-fractures samples: (a) PDMS + 30 wt % untreated TiO2, (b) PDMS + 70 wt % untreated TiO2, (c) PDMS + 110 wt % untreated TiO2, (d) PDMS + 110 wt % heat-treated TiO2, and (e) SEM-EDX photograph of PDMS + 110 wt % untreated TiO2 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
It is very clear from these figures that at lower loading, filler particles are well coated by polymer matrix. It means filler particles are properly wetted by polymer chains. However, as the filler loading is increased, wettability of filler particles by polymer chains is reduced because of dilution effect. Further, it is interesting to see that when the titania loading increased from 30 to 110 php gradually; coating of polymer over titania particles is continuously reduced. It is observed that with the increase in filler concentration in the polymer matrix, the tendency of clustering of fillers increases which revealed that in a big cluster all the filler particles are not properly wetted to the polymer matrix. In fact, detached filler particles act as stress raiser (failure initiation sight) when applied force is continuously increasing during mechanical testing. Consequently, it is expected that the strength of the matrix will be reduced with the increase in filler loading and that is observed in case of change in mechanical properties like tensile strength and % elongation at break. At higher titania loading, big aggregates of titania particles are found to be distributed in the matrix polymer and many such filler particles/clusters are seen to be projected out from the matrix polymer and it can be clearly seen that top surface of filler does not have any polymer coating over them as apparent from Figure 17(c) containing 110 php TiO$_2$.

There is also some difference in the degree of coating of filler by polymer in case of normal and heat-treated filler. Compared with normal filler, the wettability of heat-treated filler by polymer is found to be somewhat less as seen from the Figure 17(c,d). This is because the extent of polymer–filler interaction occurring through the formation of H-bonding is expected to be less pronounced in case of heat-treated filler where there is loss of moisture due to heating. The presence of water plays an important role in formation of H–bonding between polymer and filler as discussed earlier. This is also reflected in case of mechanical properties like tensile strength and % EB which decreased in case of heat-treated filler composites. To understand the filler distribution in the polymer matrix, EDX picture of 110 php composite is displayed in Figure 17(c). Various regions were targeted for analysis of elemental composition and found that the different regions contain more or less some amount of “Si” from PDMS matrix and “Ti” from titanium

![Figure 18. Distribution of “Ti” in the polymer matrix (a) PDMS + 30 wt % TiO$_2$, (b) PDMS + 70 wt % TiO$_2$, (c) PDMS + 110 wt % TiO$_2$.](image)

![Figure 19. TEM images of PDMS/TiO$_2$ composites: (a) PDMS + 30 wt % TiO$_2$, (b) PDMS + 70 wt % TiO$_2$, (c) PDMS + 110 wt % TiO$_2$.](image)
dioxide as given in Table III. The particle dispersion at different filler loading can also be seen from area mapping of composites with respect to titanium “Ti” concentration as presented in Figure 18(a–c). As seen from FESEM images, the distributions of particles are more or less uniform throughout the matrix when concentration of particles increased.

**HRTEM**

The typical HRTEM images of composites containing 30, 70, and 110 php of TiO$_2$ filler are presented in Figure 19(a–c), respectively. The dispersion of titania particles can be understood from these figures. It is found that filler particles are more or less well dispersed in matrix polymer. However, there is clear evidence of particle agglomeration in polymer matrix. From these pictures, it is revealed that the particles are not only distributed in cluster form but also as individual particles. It is also apparent from these figures that more or less the shape of particles are spherical in nature and particle size varies from <100 to 200 nm which is smaller as determined by DLS method. Bigger particle size as found from DLS study may be due to association of water molecules with titania particles as discussed earlier. There are some particles whose size exceeds 250 nm. Particle distribution also depends on concentration of titania in the matrix. At low filler loading, there are more free regions in the matrix. However, clustering tendency can also be visualized even at low filler loading. With the increase in filler content more or less uniform distributions of filler is observed where regions without filler is less. At very high filler loading a close network of filler particles is formed in the matrix polymer where average gap between filler particle is much less. Moreover, tendency of distribution of particles in the form of particle cluster is more pronounced.

**CONCLUSIONS**

Graded dielectric material with varying dielectric properties can be made from PDMS–TiO$_2$ composite with varying amount of filler. The addition of titanium dioxide to silicone elastomer (PDMS) increased both dielectric constant and loss factor of the resultant composite. Titania is non–reinforcing filler for PDMS matrix as apparent from Kraus plot showing degree of polymer–filler interaction. However, titania unlike silica does not act like reinforcing filler because of somewhat higher particle size and less polymer–filler interaction. In fact, often silane coupling agent is also used to further enhance polymer–filler interaction in the case of PDMS–silica system to improve mechanical properties. There are different types of change in properties for example, tensile strength, tear strength, and % elongation at break (% EB) decreased with increase in TiO$_2$, but modulus and hardness increased. Heat treatment of titania particles has affected both electrical and mechanical properties of the composites. Heat treatment decreased the moisture content and also affected concentration of T$^+$ in TiO$_2$ a system which in turn affects electrical properties of the system. From heat treatment observation it is confirmed that presence of surface hydroxyl groups enhances the dielectric constant of composites. There is some kind of physico–chemical interaction between the matrix polymer (PDMS) and titania (TiO$_2$) filler.

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**REFERENCES**