Dielectric spectroscopy of epoxy-based barium titanate nanocomposites: effect of temperature and humidity

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Abstract: The information contained in the dielectric response of materials is useful to study the charge transport behaviour of dielectric materials at the molecular level. Therefore, in this work, broadband dielectric spectroscopy is used to measure complex permittivity of epoxy resin and its nanocomposites over a wide frequency range of $10^{-3}$–$10^{6}$ Hz. Measurements are carried out at different temperatures (25–90°C) and relative humidities of 50% RH and 90% RH. Nanocomposites are prepared with as-received and surface-functionalised barium titanate (BaTiO$_3$) nanofillers incorporated into epoxy. Filler loading of 1–10% by volume are achieved and investigated. A detailed study of the effect of filler loading and surface functionalisation of particles before incorporation into the nanocomposite is included. It is seen that the addition of nanofillers increases both real and imaginary relative permittivity of the composite. Experiments are carried out to understand the effect of water content on epoxy and its nanocomposites. It reveals that low-frequency dispersion or quasi-DC conduction is exhibited at high humidity (90% RH) and high temperature (90°C).

1 Introduction

Nanodielectrics, with dielectric properties, have attracted the attention of researchers from the electrical power industry in the last two decades [1]. While many of the composite properties are significantly affected by the addition of a small quantity of nanofillers, high permittivity fillers at high filler loading is necessary for improvement of the composite permittivity [1, 2]. Uniform dispersion of the filler in the bulk matrix at high filler loadings is, however, a challenge.

In this research, barium titanate (BaTiO$_3$) nanofillers are incorporated into epoxy resin (prevalent as insulation in electric power apparatus) to prepare high permittivity nanocomposites. Epoxy resin is chosen as the base material for reasons of economy and ease of handling. Epoxy resins find wide applications in electrical power apparatus due to good insulating properties and low cost. They are used extensively in high voltage switchgear, generators and motors, spacers for gas insulated substations, bushings, bus-bars, cable terminations, and instrument transformers [3]. Filler materials are added to epoxy to increase structural strength and improve dielectric properties viz., corona resistance, and resistance to surface degradation [4].

In an effort to understand how the dielectric response of insulating materials sensitive to material changes (on the addition of nanofillers) at the molecular level, broadband dielectric spectroscopy is used to measure complex permittivity and several others dielectric properties of dielectric materials at the frequency domain at different temperatures and humidity conditions. The measured data is analysed to identify polarisation and relaxation mechanisms in the dielectric. Essentially frequency-domain spectroscopy gives information similar to that obtained through polarisation–depolarisation current measurements [5]. There is sufficient literature on the dielectric spectroscopy of polymeric dielectric materials. The dielectric behaviour of epoxy resin and epoxy filled with micro and nanofillers (TiO$_2$) was characterised by Nelson et al. [6, 7] in the frequency range $10^{-5}$–$10^{6}$ Hz. The effect of water uptake on the dielectric properties of neat epoxy and epoxy filled with micro and nano-sized silica particles were studied by Zou et al. [8]. Nanocomposites were seen to absorb significantly more water compared to neat epoxy and the extra water was thought to accumulate on the surface of nanofillers. Micro-composites absorbed less water compared to neat epoxy. A water shell model based on the Lewis [9] and Tanaka et al. [10] models was proposed by Zou et al. [8] to explain low-frequency dielectric relaxation behaviour under high temperature and humidity conditions. Dissado and Hill [11] presented a model to explain anomalous low-frequency dispersion (LFD) phenomena in terms of inter-cluster and intra-cluster charge transport. Maiti et al. [12] studied the dielectric behaviour of neat epoxy and epoxy filled with Al$_2$O$_3$ nanofillers. Dielectric spectroscopy measurements were reported in the frequency range of $10^{-3}$–$10^{3}$ Hz and at different temperatures (25, 50, 70, and 90°C). The study included the effect of both as-received and pre-processed nanofillers. Both real and imaginary relative permittivity of composites were lower than that of neat epoxy and this was attributed to the barrier effect of nanofillers on charge transport. The frequency-dependent dielectric behaviour of epoxy and nanocomposites were seen to exhibit LFD. Patel and Gupta [13] carried out dielectric spectroscopy of epoxy filled with various metal oxide nanofillers (Al$_2$O$_3$, TiO$_2$, and ZnO) in the frequency range of $10^{-4}$–$10^{3}$ Hz and in the temperature range of 25–90°C. The effect of LFD was observed only at high temperatures and high humidities. Losses increased with humidity. Singh et al. [14] studied complex permittivity of epoxy nanocomposites filled with Al$_2$O$_3$ and TiO$_2$ over a frequency range of $10^{2}$–400 Hz. The literature on the dielectric spectroscopy of epoxy filled with BaTiO$_3$ nanofillers [2, 15–18] shows that high permittivity BaTiO$_3$ fillers resulted in increased permittivity and loss values. The functionalisation of BaTiO$_3$ particles with silane improved the interfacial contact and enhanced the dielectric properties of these composites [15]. Huang et al. [16] prepared highly filled (50% volume fraction particle loading) epoxy composites with different kinds of surface-modified BaTiO$_3$ nanoparticles to study the effect of particle surface chemistry on the dielectric property of the nanocomposites over a wide temperature and frequency range. Their effect was seen to be pronounced at higher filler loadings. Ramajao et al. [18] reported the influence of silane functionalisation on dielectric properties and microstructure of highly loaded epoxy/ceramic composites. Even a low concentration of silane modified the interfaces and helped to retain the dielectric properties of composites. Higher concentrations of silane intensified the porosity and defects may lead to deteriorated electrical properties. A trade-off between the
concentration of silane, final microstructure, and dielectric properties was indicated. Polymer nanocomposites prepared with epoxy incorporated with high permittivity BaTiO$_3$ fillers were seen to exhibit remarkable changes in their dielectric properties (low/high electric field) and their relaxation dynamics, depending on the nanoparticle type and loading concentration, the particle size, and base matrix [2, 15].

In this paper, the dielectric behaviour of neat epoxy is studied as a function of frequency, temperature, and humidity. Further, the effect of the addition of high permittivity BaTiO$_3$ nanofillers (with filler loading of 1–10% by volume) into epoxy is studied. Apart from the use of as-received fillers, the effect of using nanoparticles surface-functionalised with GPS (3-glycidoxypropyltrimethoxysilane) before use is also investigated. To study the principal polarisation/relaxation mechanisms into neat epoxy and its nanocomposites, dielectric spectroscopy measurements are carried out over a frequency range of $10^{-3}$–$10^6$ Hz and a temperature range of 25–90°C. Measurements are conducted to investigate the effect of water absorption in humid environments of 90% RH. An attempt is made to understand the dominant charge transport behaviour and the effect thereon of the addition of nanofillers.

### 2 Experimental

Flat specimens of neat epoxy with thickness of 200–300 μm are prepared using diglycidylether of bisphenol-A (LY556: density 1.17 g/cm$^3$ at 25°C) mixed with curing agent triethylenetetramine (HY951: density 0.98 g/cm$^3$ at 25°C) in 10:1 by weight. Epoxy resin and curing agent is supplied by Vantico Performance Polymers Pvt. Ltd., India. Nanocomposite samples are prepared with incorporating BaTiO$_3$ (average diameter: 90–100 nm, phase: cubic crystalline, density: 6.08 g/cm$^3$ at 25°C) into epoxy. The nanofillers are surface-functionalised with GPS (density 1.07 g/cm$^3$ at 25°C). Nanofillers and surface-modifying agents are supplied by Sigma-Aldrich USA. The following flat specimens are investigated:

(i) Neat epoxy (EP).
(ii) Nanocomposites with as-received BaTiO$_3$ fillers (AR).
(iii) Nanocomposites with surface-functionalised BaTiO$_3$ fillers (SF).

The preparation procedure of the above specimens is described in detail in [19].

Alpha-A frequency response analyser (Novocontrol Technologies, GmbH & Co., Germany) is used to measure permittivity (real and imaginary) of epoxy and its nanocomposites. Measurements are carried out over a wide frequency range of $10^{-2}$–$10^6$ Hz. All measurements are made with an applied voltage of 1 V$_{rms}$. Samples used are circular, 250–300 μm thick, and of 30 mm diameter. The effects of the following parameters are studied:

(i) Frequency: $10^3$–$10^6$ Hz.
(ii) Temperature: 25, 50, 70, and 90°C.
(iii) Humidity: 50% RH and 90% RH.
(iv) Filler concentrations: 1, 2, 5, and 10 vol.%.
(v) Pre-processing techniques: with or without surface-functionalisation of particles with GPS before use.

The schematic diagram of the experimental set-up used for dielectric spectroscopy is shown in Fig. 1. The test specimens are sandwiched between gold plated brass electrodes of 20 mm diameter mounted on a sample cell (shown in Fig. 1). A voltage of variable frequency is applied to the test specimen, and the magnitude and phase of the current flowing through the sample are measured. Test-cell with electrode assembly is placed in a temperature and humidity-controlled chamber. All samples are preconditioned for 48 h at 100°C in a vacuum oven before measurement. Measurements are repeated on several samples of each type.

### 3 Results and discussions

#### 3.1 Water uptake

Epoxy and its nanocomposite samples (prepared with as-received and surface-functionalised BaTiO$_3$ fillers) are immersed in de-ionised water in a sealed glass container at room temperature for two weeks. The sample is weighed before and after water absorption with a microbalance (AB-135S, Mettler Toledo Switzerland) to an accuracy of 0.1 mg. The water absorption, $P_p$, is expressed in mass percent (wt.%) with reference to dried samples, and is calculated as [8]

$$H\% = \frac{M_w - M_d}{M_d} \times 100\%$$

where $M_w$ is the weight of the water-suffused specimen, and $M_d$ is the weight of the dry specimen.

In Fig. 2, it is seen that water uptake is lowest for a specimen with 0% filler loading, i.e. neat epoxy (EP). It is seen that in nanocomposites water uptake increases with filler concentration. The increase is especially marked in specimens with 5 and 10 vol.% loading. It is observed that composites with surface-functionalised particles take up less water than nanocomposites with as-received particles for the same filler concentrations.

In the presence of water, the bonding between filler and matrix is thermodynamically unstable. As we increase the filler concentration, there are more dangling –OH molecules on the particle surface, allowing more water to be absorbed. Composites prepared with surface-modified fillers reduce water uptake due to modification at the interface. Dangling –OH groups are replaced by strong covalent bonds between the silane group and nanoparticles.
by Si–O–Ti bonds [19], preventing water uptake on the particle surface.

### 3.2 Dielectric properties of neat epoxy

#### 3.2.1 Effect of temperature:

In order to study the principal polarisation mechanisms in a neat epoxy resin, measurements are carried out at four discrete temperatures (25, 50, 70, and 90°C) and at 50% relative humidity (RH). The complex permittivity (real and imaginary components) of epoxy resin at different temperatures are shown in Figs. 3a and b. The real relative permittivity of epoxy is almost constant over the frequency range of 1 MHz–0.1 Hz and imaginary relative permittivity is inversely proportional to a fractional power (<1) of the frequency. The permittivity of neat epoxy resin is expectedly seen to increase manifold at low frequencies. The increase is more pronounced at high temperatures.

Polarisation mechanisms that are likely to achieve prominence at lower frequencies (below 1 Hz), causing the permittivity to increase might be related to reversible storage of charge in the bulk of material [20]. The slope (\(\tau=1\)) of imaginary permittivity versus frequency characteristics, i.e. \(\varepsilon''(f)\) gives a not-quite-de response (i.e. a small additive contribution from DC conduction acting in parallel with another mechanism, which may be a diffusion process). Similar dielectric behaviour in a wide range of material is widely reported [20, 21]. The physical significance lies in the fact that the strong increase of real permittivity versus frequency characteristics, i.e. \(\varepsilon'(f)\) (shown in Fig. 3a) in the low-frequency region \((10^{-1}–10^{-3}\) Hz) implies a finite and reversible storage of charge in the bulk of material, which discerns it from pure-de-conduction response in which no charge storage takes place, and therefore, \(\varepsilon'(f)\) is frequency independent [21]. An increase in the slope of real relative permittivity versus frequency plot is observed in the low-frequency region \((10^{-1}–10^{-3}\) Hz) with temperature, indicating certain slow polarisation mechanisms likely to be active, but the increase is not pronounced. The imaginary permittivity is seen to vary inversely with frequency. The higher value of \(\varepsilon''(f)\) at low-frequency and high temperature is due to motion of charge carrier within the bulk of specimen. The slope of the \(\varepsilon''\) versus \(f\) curve (Fig. 3b) is seen to vary from −0.5049 at 25°C to −0.6536 at 90°C. Thus, the slope increases with temperature. Similar kind of dielectric behaviour was observed by Neagu et al. [22] in polyethylene terephthalate (PET) and Kochetov et al. [23] in epoxy and its nanocomposites (with different loading of nanofillers viz., boron nitride and aluminium nitride). Neagu et al. [22] suggested that DC conductivity dominates at low frequency \((10^{-1}–10^{-3}\) Hz) and high temperature \((90°C)\). Kochetov et al. [23] attributed the increase of slope with temperature at low-frequency and high temperature to DC conductivity.

Jonscher [20, 21] also suggest that, this kind of variation is indicative of DC conduction acting in parallel with other mechanisms.

It has been reported that, with increase in temperature, polymeric materials are liable to show increase in movement of ions, intrinsic to their lattice structure or extrinsic impurities. This may lead to expected DC conduction or in many cases LFD/QDC [20]. A broad \(\beta\) relaxation characteristic peak is observed in the imaginary relative permittivity \(\varepsilon''(f)\) at \(2.77 \times 10^5\) Hz at 25°C with a magnitude of 0.0899. The peak magnitude increases with temperature and occurs at higher frequencies at high temperatures. This is an indication of a thermally activated relaxation process. A similar behaviour was observed in epoxy resin and its nanocomposites by Patel and Gupta [13], and Kochetov et al. [23], and in PET by Neagu et al. [22]. While some other relaxation processes cannot be ruled out at low frequencies, the dominant mechanism is a small contribution of DC conduction acting in parallel with other mechanisms may be a diffusion process.

Fig. 4 shows the effect of temperature on the position of the \(\beta\)-characteristic peak in the frequency spectrum. The \(\beta\)-characteristic is associated with the relaxation of side groups viz., −CH₂Cl and −COOC₂H₅ about the C–C chain or localised motion of the dipolar group across the main chain [2, 20, 21]. The slope of a straight line fitted to the frequency versus temperature data in Fig. 4 yields a single activation energy. Thus, the \(\beta\)-characteristics follow the classical Arrhenius relation with the activation energy given by [20]

\[
\frac{1}{\tau} = \omega_s = b \exp \left( - \frac{E_a}{kT} \right)
\]
where $E_a$ is the activation energy, $r$ is the relaxation time, $o_r$ is the horizontal shift of loss frequency, $b$ is the pre-exponential factor, and $k$ is Boltzmann constant. The minimum amount of energy required to initiate a molecular relaxation process is called activation energy. The physical significance of activation energy in dielectric relaxation is to identify subtle molecular transitions (viz., $\alpha$, $\beta$, and $\gamma$ relaxation) which are not easily distinguishable by other thermal analysis techniques. In case of $\beta$ and $\gamma$ relaxation (faster relaxation processes that occur below glass transition temperature), the activation energy usually describes the process of change of conformation (structure shape) of molecule. $\alpha$ relaxation (slow relaxation process usually occurs above glass transition temperature of material) is related to the cooperative motion of molecules, thus activation energy would be related to the translation of molecules through the medium.

In this case, the activation energy describes $\beta$ relaxation process in epoxy and its nanocomposites. For neat epoxy activation energy is calculated to be 0.627 eV.

### 3.2.2 Effect of humidity: In this section, the dielectric behaviour of neat epoxy is studied under high humidity. The measurements in Section 3.2.1 are repeated at 90% RH. The temperature dependence is similar to that at low humidity as shown in Fig. 5. The activation energy of epoxy is calculated under high humidity and is found to be 0.532 eV. Thus, the activation energy of epoxy is reduced at high humidity. The temperature dependence of $\beta$ relaxation peak is similar to that at low humidity as shown in Fig. 5. The low-frequency process has different temperature dependence. Additionally, at 90°C, the dielectric behaviour of epoxy resin shows a change. In Fig. 6, in the low-frequency region (below 0.1 Hz) the slopes of real and imaginary permittivity are seen to become parallel. That is

$$\epsilon'(\omega) \propto \epsilon''(\omega) \propto \omega^{-n}, \quad \omega > o_r, \quad \epsilon'(\omega) \propto \epsilon''(\omega) \propto \omega^{b}, \quad \omega < o_r.$$  

where $o_r$ represents the point of overlap of real and imaginary characteristics represented by (3)-(4), $0.7 < p < 1$ and $n=0.3$ [11]. The imaginary part of relative permittivity is seen to increase with temperature. The ratio of the imaginary and real part of relative permittivity at high frequency is independent of frequency and is given by [20]  

$$\frac{\epsilon''(\omega)}{\epsilon'(\omega)} \approx \cot \left( \frac{(1 - p)\omega}{2} \right), \quad 0 < p < 1.$$  

These dependencies are characteristic of quasi-DC (QDC) conduction. Possibly, water accumulates in the low-density region, submicron voids, defects, or cracks in a sample placed in a highly humid environment, and this facilitates QDC [8].

Dissado and Hill [11] explained QDC conduction in terms of inter-cluster and intra-cluster motion of charge carriers. Displacement of charge over macroscopic distances evolves into identical displacement of charges within the clusters (intra-cluster); hence effective displacement of charge is related to the cluster size. At longer times and with increased energy, ion exchange between clusters transports an effective charge over long distances. As a result, the internal structure of the intervening clusters is altered. This constitutes inter-cluster charge transfer. The characteristic time is defined as the time at which cross-over occurs, i.e., $t = 1/\omega_c$. The power-law exponent $p$ is associated with the fractal structure along which the carriers move between clusters [24]. For a higher value of $p$, clusters are wider. The cross-over from short-range to long-range mobility of charge carrier becomes possible at high temperature in high humidities.

Thus in neat epoxy, the principal low-frequency charge transport mechanism at high temperatures and high humidities is QDC. In a composite, interfacial polarisation might be expected. Interfacial polarisation builds up due to a difference in the conductivities and permittivities at the microscopic interfaces. Interfacial polarisation would be indicated if, $\epsilon'' \propto \omega$ and $\epsilon' \propto \omega^{-1}$ and $\epsilon'' \propto \omega^{-2}$ and the ratio of the real and imaginary components of complex permittivity is proportional to frequency. This kind of correlation is not seen and therefore, the possibility of interfacial polarisation is ruled out. Thus, it might be concluded that a small contribution of DC conduction along with the diffusion process is the dominant mechanisms in neat epoxy under ambient condition. QDC sets in at high temperature and high humidity. The findings are in keeping with those of Patel and Gupta [13].

### 3.3 Effect of incorporation of nanofillers

In this section, dielectric spectroscopy of epoxy and its nanocomposites prepared with as-received BaTiO$_3$ nanofillers is discussed. Fig. 7 shows the real and imaginary components of the complex permittivity of nanocomposites prepared with as-received particles (1 vol.%) and epoxy (for comparison) at temperatures between 25 and 90°C at 50% RH. It is seen that addition of BaTiO$_3$ nanofillers causes an increase in the permittivity. The increase in both real and imaginary components of permittivity is significant in the low-frequency region (1 mHz–1 Hz) at all temperatures. The real permittivity characteristics of nanocomposites are similar to that of neat epoxy at all temperatures (25–90°C). In the low-frequency region, imaginary permittivity of nanocomposites varies inversely with frequency at all temperatures, as shown in Figs. 7a and b. The low-frequency response of the imaginary permittivity has a frequency dependence, with a power varying between $-0.4$ and $-0.55$ in Figs. 7a and 7b.

An analysis of the data similar to that detailed in the previous section for epoxy, indicates that the principal mechanism in the
nanocomposite is the same as in the neat epoxy viz., DC conduction acting in parallel with some another mechanism, which may be a diffusion process.

The complex permittivity of epoxy and its nanocomposites (prepared with 1 vol.% as-received BaTiO$_3$ fillers) at different temperatures (25–70°C) at 90% RH are studied (not presented here). It is seen that both real and imaginary components of permittivity of nanocomposite increases with humidity at all temperatures (25–70°C). At high temperature (90°C) and high humidity (90% RH), the effect of LFD is observed in the nanocomposite (prepared with 1 vol.% as-received BaTiO$_3$) just as in neat epoxy as shown in Fig. 8. The parameters describing the dielectric characteristics of epoxy and its nanocomposites are shown in Table 1. The characteristic frequency $\omega_c$ (the crossover from short-range mobility to long-range mobility) and the slope $p$ increases with the addition of nanofillers. Thus, the presence of nanofillers affect the charge carrier mobility and hence polarisability of the material. For nanocomposites, the increasing value of slope ($p = df/dw$, where $df$ is the fractal dimensions of the structure that the carriers move on between clusters as proposed by Hill et al. [24] and $dw$ is the walk dimension defined by the number of steps $R^{dw}$ required to travel distance $R$) indicates a walk dimension approaching more closely to that of the fractal structure (i.e. a more efficient exploration of the paths available for the carrier to move) usually indicating a less branched structure.

When a composite is prepared with as-received nanofillers, a large number of hydroxyl groups (–OH molecules) are present on the surfaces of the nanofillers. These absorb water from the ambience, resulting in a significant amount of absorbed moisture on the nanoparticle surface [8, 13]. According to the water shell model of Zou et al. [8], a water shell is formed around the nanoparticle surface constraining of three layers as shown in Fig. 9. The first and second layers provide a channel for charge carriers and the third layer is conductive. The presence of water in nano-filled composites frees up the ionic carriers from the nanoparticle surface by shielding the charge from counter ions. This might explain to increase in complex permittivity due to addition of nanofillers in epoxy. This effect is more pronounced at high humidity [13].

The activation energy of the nanocomposite specimens prepared with as-received BaTiO$_3$ filler is calculated using (2) and found to be 0.807 eV, i.e. higher than that of neat epoxy. A similar increase in activation energy was reported with the addition of as-received alumina nanofillers (1 vol.%) into neat epoxy by Maity et al. [12]. The characteristic frequency is also seen to increase. The movement of charge in the nanocomposites needs greater energy and time and this is reflected in the increase in activation energy and characteristic time.

![Fig. 7](image1.png)

**Fig. 7** Complex permittivity versus frequency characteristics of neat epoxy (EP) and its nanocomposites with as-received BaTiO$_3$ fillers (AR) of 1 vol.% loading at 50% RH and temperatures of (a) 25°C, (b) 90°C.

![Fig. 8](image2.png)

**Fig. 8** Real and imaginary components of complex permittivity of neat epoxy (EP) and nanocomposites with as-received BaTiO$_3$ filler (AR) of 1 vol.% loading at 90°C and 90% RH.

![Fig. 9](image3.png)

**Fig. 9** Water shell model of nanocomposites [8].

(a) Schematic diagram, (b) Charge carrier movement NP = nanoparticle.

Table 1 Dielectric characteristics of epoxy and its nanocomposites with 1 vol.% as-received BaTiO$_3$ filler (AR) at a temperature of 90°C and 90% RH

| Specimen          | Slope $p$ | $\omega_c$ Hz |
|-------------------|-----------|---------------|
| epoxy (EP)        | -0.7468   | 0.366         |
| nanocomposites (AR) | -0.8295  | 4.444         |
3.4 Effect of filler loading

Dielectric spectroscopy measurements are repeated at different filler concentrations (1–10 vol.%) of as-received BaTiO$_3$ at various temperatures (25, 50, 70, and 90°C). It is seen that the real and imaginary components of complex permittivity increase with increasing filler concentration. The increase in effective permittivity is significant at higher filler loadings of 5 and 10 vol.%. A small additive contribution of DC conduction along with a diffusion process is the principal mechanism. At higher loadings, the inter-particle distance is smaller, hence the interfacial regions might overlap significantly providing a continuous path for charge carriers. From the imaginary permittivity characteristics, it is seen that the $\beta$ relaxation peaks of imaginary permittivity (shown in Fig. 10) shift towards higher frequency with filler loading. Figs. 10 and 11 show the effective permittivity of composites with filler loading at a temperature of 25 and 90°C at 50% RH and 90% RH. The slope of the permittivity versus frequency characteristics and the characteristic frequency for varying temperature and filler loading are given in Table 2. It is seen that the characteristic frequency shifts to a higher frequency with increasing filler concentration.

As we increase the filler loading from 1 vol.% the slope increases up to 5 vol.% at all temperature, as shown in Table 2. But beyond 5 vol.% there is a slight decrease in slope. This could be attributed to a lower rate of increase in interfacial region with increase in filler loading from 5 to 10 vol.%, either due to lower uniformity in the particle dispersion at 10 vol.%, or due to increased overlap between adjacent interfacial regions.

3.5 Effect of surface functionalisation

In this section, the dielectric behaviour of nanocomposites prepared with surface-functionalised fillers is studied. It is observed that both real and imaginary components of relative permittivity of nanocomposites (with 1 vol.% loading) are higher in SF at all temperatures (25, 50, 70, and 90°C). There is no evidence of LFD or QDC is observed in neat epoxy and its nanocomposites at 50% RH. Further, the experiment is repeated for high humidity (90% RH) with all temperature. It is seen that there is a marginal increase in effective permittivity of the surface-modified composite. The effect of LFD or QDC can be observed in epoxy and its nanocomposites prepared with both as-received and surface-functionalised composites at 90°C and 90% RH (shown in Fig. 12).

In nanocomposites, the slope of the permittivity versus frequency plot and the characteristic frequency increases after surface-functionalisation as depicted in Table 3. This may be attributed to the modification of molecular chain mobility at low frequencies due to the incorporation of nanofillers. Chain mobilities appear to be fully restrained with surface functionalised fillers.

The activation energy of nanocomposites computed (as discussed in Section 3.2) is shown in Table 4. Incorporation of BaTiO$_3$ nanofillers (both as-received and surface-functionalised) increases activation energy. This result is in agreement with Maity.
et al. [12]. In the case of nanocomposites with surface-functionalised BaTiO$_3$ (SF), the activation energy is marginally higher than that of as-received nanocomposites (AR) for all filler loading. This might be attributed to the strong covalent bonding and absence of dangling –OH bonds at the particle surface. In nanocomposites, the activation energy increases with increasing filler loading. This is contrary to expectations since high humidity is expected to aid charge carrier movement [8]. But it might be remembered that the activation energy shown in Table 4 corresponds to the $\beta$ relaxation process only and not to QDC, and therefore might be hindered by the presence of water.

### 4 Conclusions

The frequency dependence of the dielectric characteristics of unfilled epoxy and epoxy filled with high permittivity BaTiO$_3$ nanofillers (both as-received and surface-functionalised) are studied from dielectric spectroscopy data. The important findings are as follows:

1. The real and imaginary permittivity of epoxy increases with the addition of BaTiO$_3$ nanofillers. It is observed that permittivity of nanocomposites increases with filler loading.
2. The $\beta$ relaxation peak follows the classical Arrhenius relation to temperature and exhibits a well-defined single activation energy.
3. Activation energy increases with the incorporation of nanoparticles. However, high humidity increases activation energy, facilitating charge carrier movement.
4. It is seen that the principal dielectric relaxation process shifts from typical DC conduction to QDC mechanism in the low-frequency region under high temperature (90°C) and high humidity (90% RH), for both epoxy and its nanocomposites.

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**Table 2** Characteristic frequency ($\omega_c$) and slope of the permittivity versus frequency plot of epoxy and its nanocomposites with as-received fillers (AR) at various filler loadings at different temperatures (90% RH)

| Specimen | $\omega_c$, Hz | Slope | $\omega_c$, Hz |
|----------|----------------|-------|----------------|
| epoxy    | <0.001         | -0.5314 | 0.366          |
| 1 vol.%  | <0.001         | -0.5395 | 4.444          |
| 2 vol.%  | <0.001         | -0.5210 | 284.4          |
| 5 vol.%  | <0.001         | -0.5935 | 306.8          |
| 10 vol.% | <0.001         | -0.5385 | 343.5          |

**Table 3** Dielectric characteristics of epoxy (EP) and its nanocomposites with as-received (AR) and surface functionalised (SF) fillers at 90% RH and 90°C

| Specimen | $\omega_c$, Hz |
|----------|----------------|
| EP       | 0.387          |
| AR       | 34.67          |
| SF       | 124.20         |

**Table 4** Activation energy of nanocomposites with as-received (AR) and surface-functionalised (SF) BaTiO$_3$ fillers

| Specimens | Activation energy (50% RH), eV | Activation energy (90% RH), eV |
|-----------|-------------------------------|-------------------------------|
| Nano-composites | AR | SF | AR | SF |
| 1 vol.%  | 0.807 | 0.839 | 1.099 | 1.284 |
| 2 vol.%  | 0.835 | 0.849 | 1.098 | 1.068 |
| 5 vol.%  | 0.851 | 0.909 | 0.973 | 1.082 |
| 10 vol.% | 0.898 | 0.915 | 1.202 | 1.210 |

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Fig. 12 Complex permittivity versus frequency characteristics of epoxy (EP) and its nanocomposites with as-received (AR), and surface-functionalised (SF), BaTiO$_3$ filler of 1 vol. % loading at 90% RH and 90°C

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6 References

[1] Nelson, J.K.: 'Dielectric polymer nanocomposites' (Springer, New York, USA, 2010, 1st edn.)

[2] Prateek, , Thakur, V.K., Gupta, R.K.: ‘Recent progress on ferroelectric polymer-based nanocomposites for high energy density capacitors: synthesis, dielectric properties, and future aspects’, Chem. Rev., 2016, 116, (7), pp. 4260–4317

[3] Dakin, T.W.: ‘Application of epoxy resin in electrical apparatus’, IEEE Trans. Dielectr. Electr. Insul., 1974, 9, (4), pp. 121–128

[4] Maiy, P., Kasisomayajula, S.V., Venkitanarayanan, P., et al.: ‘Improvement in surface degradation properties of polymer composites due to pre-processed nanometric alumina fillers’, IEEE Trans. Dielectr. Electr. Insul., 2008, 15, (1), pp. 63–72

[5] Zaengl, W.S.: ‘Dielectric spectroscopy in time and frequency domain for HV power equipment, part I: theoretical considerations’, IEEE Electr. Insul. Mag., 2003, 19, (5), pp. 5–19

[6] Nelson, J.K., Hu, Y., Thiticharwnpong, J.: ‘Electrical properties of TiO2 nanocomposites’. IEEE Annual Report Conf. Electrical Insulation and Dielectric Phenomena, Albuquerque, NM, USA, October 2003, pp. 719–722

[7] Nelson, J.K., Fothergill, J.C.: ‘Internal charge behavior of nanocomposites’, Nanotechnology, 2004, 15, (5), pp. 586–595

[8] Zou, C., Fothergill, J.C., Rowe, S.W.: ‘The effect of water absorption on the dielectric properties of epoxy nanocomposites’, IEEE Trans. Dielectr. Electr. Insul., 2008, 15, (1), pp. 106–117

[9] Lewis, T.J.: ‘Interfaces are the dominant feature of dielectrics at the nanometric level’, IEEE Trans. Dielectr. Electr. Insul., 2004, 11, (5), pp. 739–753

[10] Tanaka, T., Kozako, M., Fuee, N., et al.: ‘Proposal of a multi-core model for polymer nanocomposite dielectrics’, IEEE Trans. Dielectr. Electr. Insul., 2003, 12, (4), pp. 669–681

[11] Dissado, L.A., Hill, R.M.: ‘Anomalous low-frequency dispersion near direct current conductivity in disordered low-dimensional materials’, J. Chem. Soc., Faraday Trans. II, 1984, 80, (3), pp. 291–319

[12] Maiy, P., Poovannam, P.K., Basu, S., et al.: ‘Dielectric spectroscopy of epoxy resin with and without nanometric alumina fillers’, IEEE Trans. Dielectr. Electr. Insul., 2009, 16, (5), 1481–1488

[13] Patei, R.R., Gupta, N.: ‘Effect of humidity on the complex permittivity of epoxy-based nanodielectrics with metal oxide fillers’, Int. Trans. Electr. Energ. Syst., 2012, 23, (6), pp. 846–852

[14] Singha, S., Thomas, M.J., Kulkarni, A.: ‘Complex permittivity characteristics of epoxy nanocomposites at low frequencies’, IEEE Trans. Dielectr. Electr. Insul., 2010, 17, (4), pp. 1249–1258

[15] Tomar, V., Polizoz, G., Mannias, E., et al.: ‘Epoxy-based nanocomposites for electrical energy storage. I: effects of montmorillonite and barium titanate nanofillers’, J. Appl. Phys., 2010, 108, (074116), pp. 1–14

[16] Huang, X., Nie, L., Yang, K., et al.: ‘Role of interface in highly filled epoxy/ BaTiO3 nanocomposites. Part II: effect of nanoparticle surface chemistry on processing, thermal expansion, energy storage and breakdown strength of the nanocomposites’, IEEE Trans. Dielectr. Electr. Insul., 2014, 21, (2), pp. 480–487

[17] Liang, S., Chong, S.R., Giannelis, E.P.: ‘Barium titanate/epoxy composites dielectric materials for integrated thin film capacitors’. IEEE Electronic Components and Technology Conf., Seattle, WA, USA, May 1998, pp. 171–175

[18] Ramajo, L., Castro, M.S., Reboredo, M.M.: ‘Effect of silane as coupling agent on the dielectric properties of BaTiO3–epoxy composites’, Sci. Direct Comp. 4, 2007, 38, (8), pp. 1852–1859

[19] Zafar, R., Gupta, N.: ‘Pre-processing of BaTiO3 nanofillers in improving dielectric response of epoxy nanocomposites at higher filler concentrations’. IEEE Annual Report Conf. Electrical Insulation and Dielectric Phenomena, Fort Worth, TX, USA, October 2017, vol. 1, pp. 477–480

[20] Jonscher, A.K.: ‘Dielectric relaxation in solids’ (Chelsea Dielectrics Press Limited, London, 1983, 1st edn.)

[21] Jonscher, A.K.: ‘Dielectric relaxation in solids’, J. Phys. D, Appl. Phys., 1999, 32, (14), pp. R57–R70

[22] Neagu, E., Pissis, P., Apekis, L.: ‘Electrical conductivity effects in polyethylene terephthalate films’, J. Appl. Phys., 2000, 87, (6), pp. 2914–2922

[23] Kochetov, R., Andritsch, T., Lafont, U., et al.: ‘Preparation and dielectric properties of epoxy–BN and epoxy–Aln nanocomposites’. IEEE Int. Conf. Electrical Insulation, Montreal, QC, Canada, June 2009, vol. 1, pp. 397–400

[24] Hill, R.M., Dissado, L.A., Nigmatullin, R.R.: ‘Invariant behaviour classes for the response of simple fractal circuits’, J. Phys.: Condens. Matter, 1991, 3, (48), pp. 9773–9790