Influence of water ageing on variation in space charge and thermo-mechanical properties of epoxy micro-nano composites

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Abstract
Water ageing was carried out with epoxy micro–nano composite specimen. Silica micro particles and ion trapping nano particles were used as filler material in the composite specimens. Water ageing was carried out under room temperature and at 90 °C, to analyse the impact of water intake on space charge accumulation and charge decay characteristics. The threshold for space charge accumulation in epoxy specimens reduces, while the rate of space charge accumulation increases after water ageing. The initial surface potential had a marginal increment and the rate of surface potential decay has reduced significantly after water absorption. Trap distribution characteristics confirm the existence of deeper traps and charge mobility reduction in case of water aged specimens. The dynamic mechanical analysis have confirmed the viscoelastic behaviour of epoxy micro–nano composite specimens, is sensitive to the water absorption. Glass transition temperature of epoxy specimen after water absorption has shifted to lower temperatures due to plasticisation of polymer matrix and ascertained with the reduction in the activation energy. Digital image correlation method has been adopted to determine strain field distribution and displacement of the specimen under mechanical loading. Thermo gravimetric Analysis have confirmed the reduction in thermal stability resulting for water aged specimens.

1 INTRODUCTION

Epoxy resin is a highly crosslinked amorphous polymer, which is used as an insulating material for power system apparatus like rotating machines, cast resin dry type transformers. It is also used as spacer in GIS and in cable joints [1–2]. Epoxy base material is considered to be reinforced with small quantities of inorganic oxides as nano fillers, for reasonably tailoring the electrical properties such as lower space charge accumulation, better resistance to surface discharge and electrical treeing, along with improved thermal and mechanical properties [3–4].

Tsekmes et al. have stated that the epoxy micro–nano composites have the advantages of higher breakdown strength with improved thermal conductivity. In general, use of 60–70 wt% of micron-size silica in epoxy composite insulators, can be seen in industry [5]. Imai et al. have indicated that, the silica filler tends to exhibit low coefficient of thermal expansion [6]. Mishra et al., have studied about the corona discharges initiated due to water droplets, on IXEPLAS® filled epoxy nanocomposites. IXEPLAS is a hydrotalcite compound modified with zirconium phosphate. Inorganic ion exchangers like zirconium phosphate tend to exhibit good oxidation resistance along with high ion trapping ability. Hence, it can be applicable in the electrical insulation structures for improving their reliability [7]. One of the major concerns in epoxy composite specimens is their tendency of water intake in humid environmental conditions. Nogueira et al. have indicated that, water in epoxy composites, exist in two different forms: (i) water that is present in the free volume of the microcavities in the matrix and (ii) bound water which is in interaction with polar segments (hydrogen-bonding) of the composite [8]. In case of composite material, this phenomenon is severe compared to base epoxy, because the interface between matrix and the filler will act as a potential site for the water molecule to interact [9]. This phenomenon may possibly lead to...
significant irreversible material changes like swelling, plasticization and finally deterioration of insulating material [10]. Subjecting polymeric specimens to hot water (Hydrothermal aging) is one of the general methods to simulate the accelerated ageing or long-term consequences of water uptake phenomenon [11]. Mishra et al. in [7], have carried out water absorption studies with base epoxy resin and its nanocomposites. They have indicated that the percentage weight gain of base epoxy resin is around 0.5%. The epoxy micro–nano composite specimen used in the present study, has a percentage weight gain of around 0.2%. Base epoxy resin has more free volume available in the bulk of the specimen for the water to penetrate. Whereas, the filler particles will act as a barrier for water diffusion into the bulk volume of composite specimen reducing the water absorption compared to base epoxy [7]. Since, the water absorption of base epoxy resin is more than double that of water absorption in composite specimen, the present study is focussed more on epoxy micro–nano composite specimen, to understand the effect of water ageing on its space charge as well as its thermo-mechanical properties. Also, the study of water absorption phenomenon on epoxy micro–nano composites with ion trapping particle as nano filler is scanty. Hence, an attempt has been made to understand the influence of water ageing on electrical and thermo-mechanical behaviour of epoxy micro–nano composites.

Polymeric insulating materials, in case of high voltage DC applications tend to accumulate charge in the bulk of the specimen [12]. This accumulated space charge can alter the internal electric field, resulting in the early degradation of insulating material. Noah et al. have studied the space charge distribution on alumina filled epoxy resin for HVDC GIS insulating material. Mishra et al. have studied the space charge injection and accumulation in the epoxy resin [13]. In HVDC transmission systems, voltage polarity reversal phenomenon is required to achieve bi-directional flow of power. Presence of accumulated space charge during this reversal can possibly be a serious threat for the life of insulator [14]. Montanari et al., have indicated that the space charge accumulation in presence of humidity can affect trapping sites and distribution of trap depth [15]. Hence, it is necessary to study the impact of hydrothermal ageing on the space charge accumulation and charge decay characteristics of epoxy composite specimens.

Surface potential decay study is an effective method in understanding the different physical processes that occur in an insulating material such as surface conduction process and charge trapping phenomenon [16]. The interfacial bonding between matrix and the filler has a significant impact on strain distribution of a composite specimen. Water absorption can cause structural changes in polymer matrix, imparting adverse effects on mechanical properties of the material [17]. Digital image correlation (DIC) is an image-based non-contact optical method, applicable in mechanical analysis for strain field calculation and displacement measurement [18]. So, DIC method is adopted to tensile test, to understand the impact of water ageing on mechanical (Tensile) behaviour of epoxy micro–nano composites.

Due to water ageing phenomena of the composite specimens, along with mechanical properties like tensile strength and Young’s modulus, another important mechanical property i.e. the mechanical loss tangent (\(\tan \delta\)) is affected significantly [18]. \(\tan \delta\), which is a measurement of damping, gives the relation between the elastic energy stored and the energy dissipated per one cycle of vibration. The properties of the composites in general, are governed by the interface between them. In case of vibration damping, the interface effects and adhesion degree are very important for determining the damping behaviour of composites. Dynamic mechanical analysis (DMA) is very useful in analysing the damping behaviour and interfacial properties of polymeric materials. DMA can be used to determine the modifications induced in the main mechanical relaxation of reinforced polymers due to ageing, which result from the changes in the molecular mobility of polymer matrix due to interactions at the polymer–filler interfaces. Also, addition of the silica micro filler improves storage modulus along with inhibiting thermal expansion coefficient of the composites [19]. Thus, in order to understand the effect of water ageing on storage modulus and loss tangent of silica and IXEPLAS® reinforced epoxy micro–nano composites, DMA is necessary.

Hence, to understand the influence of hydrothermal ageing on epoxy micro–nano composite samples, the subsequent studies were employed: (i) Water diffusion studies, (ii) space charge accumulation and charge decay characteristics, (iii) surface potential decay and trap distribution studies, (iv) study of visco-elastic properties through dynamic mechanical analysis (DMA) (V) mechanical (Tensile) analysis through digital image correlation (DIC) employed tensile test and (vi) thermal stability analysis of epoxy micro–nano composite insulating material by thermo gravimetric analysis (TGA).

2 | EXPERIMENTAL STUDIES

2.1 | Preparation of specimens

Epoxy micro–nano composite specimen used in the present study consists of base epoxy reinforced with crystalline SiO₂ micro filler of 66 wt% and IXE (ion trapping nano filler) of 0.7 wt%. The SiO₂ fillers have an average diameter of 14 \(\mu\)m and IXE nano fillers have diameter in the range 200–500 nm. Shear mixing, degassing, casting and curing techniques have been employed to prepare the samples (Figure 1) [20]. The uniform dispersion of nano fillers in epoxy base matrix was visualised through structured illumination microscopy (SIM)/transmission electron microscopy (TEM) analysis [20]. These epoxy composite specimens were immersed in deionized water for 240 h at room temperature (RT) and 90 °C respectively. The specimens were taken out from the water after 240 h and are kept for drying at room temperature, for a period of 24 h before subjecting to different characterizations. Thus, in the present study, three epoxy micro–nano composite specimens, unaged specimen, water aged specimens at room temperature (RT) and 90 °C were selected for further analysis.
2.2 Water diffusion studies

The amount of water diffused into the test specimens and their water diffusion coefficient can be determined with the help of water diffusion studies. Epoxy specimens with dimensions $20 \times 20 \times 2$ mm$^3$ were aged in deionised water at 90 $^\circ$C and room temperature for 240 h. The percentage weight gain of the immersed specimens was monitored with ageing time, until the weight gain of the specimens became almost zero. The weight of each test specimen was measured up to an accuracy of $10^{-4}$ g.

2.3 Space charge measurement

Figure 2 represents the typical experimental setup for measurement of space charge adopting pulsed electro acoustic (PEA) method. The experimental setup consists of Techimp PEA Flat cell and voltage pulse generator with a pulse width of 10 ns, frequency of 150 Hz and voltage magnitude of 0–500 V. It also consists of ± (0–30) kV high voltage DC source, an 18–24 V DC source for amplifier and a DPO (Tektronix DPO5034, 350 MHz, 5 GS/s). The dimensions of the test samples were selected as $40 \times 40 \times 1$ mm$^3$. The PEA system is verified for its performance at every time by adopting the procedure followed by assuming the whole PEA system including the detecting circuit can be treated as two LTI systems connected in cascade [21].

2.4 Surface potential decay measurement

In surface potential decay measurement (Figure 3) setup, needle-plane configuration of electrodes have been employed to spray charges on the epoxy specimen, by applying ±8 kV DC voltage. The DC voltage was applied with the help of a high voltage amplifier (Trek model 20/20 C). At position 1 (Figure 3), the charges are sprayed on the surface of sample and the potential developed on the surface of the sample is measured by using electrostatic voltmeter (Trek model 341B) at position 2.

2.5 Dynamic mechanical analysis

DMA was performed through three-point bending mode in order to obtain the viscoelastic properties like storage modulus and mechanical loss tangent ($\tan \delta$) of epoxy specimens. Experiment was conducted on Netzsch DMA-242C under controlled sinusoidal strain, for a temperature range of $−100$–$200$ $^\circ$C, at frequencies 1, 5 and 10 Hz. A heating rate of 3 $^\circ$C/min under controlled flow of liquid nitrogen is maintained. The dimensions of the test specimen were taken as $50 \times 11.5 \times 2$ mm$^3$.

2.6 Strain field analysis by digital image correlation

DIC technique, also known as photogrammetry is especially useful in determining the heterogeneity in strain field and calculating strain displacement. The principle of DIC is to recognize the geometrical change in surface pattern after straining, when compared to surface pattern before straining. It generally consists of speckle pattern formation, digital image acquisition, displacement and strain field calculation. To create
a speckle pattern as shown in Figure 4, the surface of the epoxy specimens are coated with a white spray paint, followed by placing random black dots of uniform size with permanent marker. The digital images of an object are acquired at different loading times using digital imaging devices. Then, image analysis is performed with the help of correlation-based tracking algorithms and numerical differentiation approaches to extract full-field displacement and strain responses of materials quantitatively. The static tensile test was performed with the help of universal testing machine (UTM). The images of the test object were recorded with the help of a Grasshopper CCD camera of 5.0MP with Sony-ICX 625 2/3″ sensor and a resolution of 2448×2048 pixels. While capturing the images, LED light have been used to illuminate the surface patterns on test specimen. For post-processing and strain analysis, the VIC-2D software developed by Correlated Solutions has been adopted. The initial image acquired is mapped by a grid of square subsets, defined by subset size and step size. The step size is set generally smaller than subset size, to optimize the spatial resolution. The subset size and step size of 29 and 5 are used respectively while performing the DIC.

2.7 Thermo gravimetric analysis

Thermogravimetric analysis is an efficient technique to study the thermal decomposition pattern of polymeric composite materials. It monitors the mass change of the material with respect to temperature, heated at a constant heating rate. The experiment was performed with Netzsch STA409C, at nitrogen ambience for temperature range of 30–800 °C and heating rate of 10 °C/min.

3 RESULTS AND DISCUSSION

3.1 Diffusion coefficient analysis

The percentage weight gain of test samples aged in deionized water, maintained at room temperature (RT) and 90 °C respectively, is calculated as

\[ P(t) = \frac{W(t) - W_O}{W_O} \times 100\% \]  

Where \( W(t) \) is the mass of test specimen at an ageing time \( t \) (g), \( W_O \) is the mass of unaged specimen (g) and \( P(t) \) is the percentage weight gain of the test specimen at an ageing time \( t \) (%). Figure 5 shows the percentage weight gain of epoxy nanocomposite specimen aged in deionised water, at room temperature and at 90 °C. It is observed that the weight gain reaches almost constant at 240 h. The weight of the immersed specimens increased rapidly during initial time (0–20 h) and later the increment was sluggish before the specimen gets saturated.

The accelerated ageing or long-term consequences of water uptake phenomenon can be simulated by subjecting test specimens to hydrothermal ageing [11]. It is well known that higher glass transition temperature, in general require longer immersion time and higher exposure time [22]. Also maintaining water above 90 °C can cause water to vapour fast. Thus, to acquire highest water intake into the bulk volume with minimal vaporisation, 90 °C is chosen. Huner et al. have studied the effect of water ageing at high temperatures on mechanical properties by immersing epoxy-flax fibre composite specimens in a de-ionized water bath at 25 and 90 °C and have indicated that the degradation of composite specimens induced due to water uptake was more significant at high temperatures [23]. It is observed that the initial rate of water diffusion and the final weight gain at steady state are found to be higher in the case of hydrothermal ageing (water ageing at 90 °C) compared to room temperature water ageing. The water diffusion coefficient can be calculated as [24].

\[ D = \frac{\pi t_{0.5}^2}{64\theta_{0.5}} \]  

Where \( D \) is the diffusion coefficient, \( L \) is the thickness of sample and \( t_{0.5} \) is time required for the specimen to reach half of the steady state value of percentage weight gain.

The diffusion coefficients of the epoxy specimen aged in deionized water at room temperature and 90 °C are \( 4.97 \times 10^{-12} \) m²/s and \( 7.74 \times 10^{-12} \) m²/s respectively. The water diffusion phenomenon mainly determined by the

![FIGURE 4 Digital image correlation setup](image)

![FIGURE 5 Percentage weight gain of epoxy samples subjected to water ageing at room temperature (RT) and 90 °C](image)
availability of free volume in the form of molecular size holes in the polymer matrix and the water affinity of polymer. This availability of free volume depends on crosslink density, morphology and structure of polymer. The water affinity of polymer requires hydrogen bonding sites to be present along polymer chains, and structure of polymer. The water affinity of polymer requires the ability of free volume depends on crosslink density, morphology and structure of polymer. This allows water molecules to diffuse more into the polymer matrix and the water affinity of polymer. This availability of free volume depends on crosslink density, morphology and structure of polymer. This allows water molecules to diffuse more into the specimen aged at 90 °C rather than specimen aged at room temperature.

3.2 Impact of water ageing on space charge dynamics

The mean value of absolute space charge density can be determined as shown in Equation (3) [25].

$$q(E,t) = \frac{1}{x_1 - x_0} \int_{x_0}^{x_1} q_p(x; t; E) \, dx$$ (3)

Where, $q_p(x; t; E)$ is space charge density at an applied electric field $E$, time $t$ and position $x$; $x_0$ and $x_1$ indicate the position of the electrodes.

It is well known that the magnitude of accumulated space charge strongly depends on electric field applied across the specimen. The plot representing the relation between average value of absolute space charge density and electric field applied, is depicted in Figure 6. Parameters like threshold for space charge accumulation ($E_T$) and rate of space charge accumulation ($b$) can be determined from the characteristic plot shown in Figure 6. The parameters $E_T$ and $b$ were determined by considering the mean value of absolute space charge density just after poling time of 3600 s (after reaching quasi-steady state [26]), at each value of applied electric field. Montanari et al. have evaluated DC insulation performance based on space-charge measurements and accelerated life tests and have observed that the rate of space charge accumulation ($b$) is in between 1 and 2 [26]. Similar phenomenon is observed in the present study. The parameter $E_T$ can be defined as electric field above which, the accumulated space charge can be noticed significantly. The parameter $b$ can be obtained from the slope of fitted line corresponding to fields greater than the threshold ($E_T$) [26]. The threshold ($E_T$) of epoxy specimen is observed to reduce significantly after ageing in water (Table 1). Whereas, the parameter $b$ is noticed to increase after water absorption process. According to Schottky phenomenon of charge injection, whenever the insulating material is stressed under a sufficient amount of electric field, the potential barrier that is required by the charge carriers to overcome near the electrode-specimen interface reduces, resulting in the charge carriers to enter into the bulk of the specimen [27]. Decrease in the threshold electric field ($E_T$) with ageing, is a well-supported observation to confirm the reduction in the potential barrier making the charge injection phenomenon easier. Therefore, the decrement in the value of $E_T$ and increment in parameter $b$ after water ageing, is an indication for the early deterioration of the insulating material leading to premature breakdown.

The parameter $E_T$ of the test samples is noticed to be lesser than 8 kV mm$^{-1}$. Therefore, 10 kV mm$^{-1}$ is taken as applied electric field. Spatial distribution curves of accumulated charge across the thickness of the test samples at various poling times, are represented in Figure 7. Accumulation of homo-charge is noticed in test samples, which is an indication that the charge injection rate is higher than that of the charge transportation rate [27]. A slight increment in the homo-charge accumulation with respect to poling time, is observed in case of unaged specimen. Where as in case of water aged specimens this increment is more significant and can clearly depicted from Figure 8. Figure 9 represents the spatial distribution of charge accumulated in epoxy composites at various instants of depoling time. The interfacial charge induced at the interface of electrode and sample has reduced as soon as applied voltage is reduced to zero. Then, only the accumulated space charge is left behind. In general, the decay rate of this accumulated charge very less compared to the decay rate of interfacial charge induced at the electrode-specimen interface.

The mean value of absolute space charge density in the epoxy micro–nano composites during both the poling time and depoling time are depicted in Figure 10. This mean value of absolute charge density during poling time is higher in case of water aged specimens compared to unaged specimen. (Figure 10(a)).
Fabiani et al. have studied the effect of water contamination on the electric properties of nanostructured insulating materials and have indicated that the increase in the amount of water absorption into the bulk of the specimen leads to increment in space charge accumulation [28]. It is because the potential barrier of charge injection at the electrode-sample interface will be reduced in the presence of water molecules, thus allows more charge to inject into the bulk of the insulating material [28]. Thus, the average value of absolute charge density will be directly proportional to the amount of water absorption into the insulating material. The trapping and de-trapping phenomena are mostly related to the charge trap distribution in terms of energy depths. In terms of energy levels, it is possible that traps may have several discrete energy depths or even continuous energy distribution. To simplify the mathematics involved, it is assumed that the traps are uniformly distributed across the specimen and have only two trap energy levels, i.e. one representing shallow trap and another representing deep trap [29]. In general, a trapping model depends on phenomena like charge injection, trapping/de-trapping and kinetics of trapping and de-trapping process. For further simplification of the model, charge injection process is assumed to follow Schottky injection, and the current increases exponentially with the applied electric field and decays exponentially with the depoling time. In addition, recombination process is also neglected. Hence, the decay characteristics of charge density during depoling have been modelled as a double exponential function as shown in Equation (4).

$$ n(t) = n_1 e^{-at} + n_2 e^{-bt} $$  (4)
Where summation of $n_1$ and $n_2$ gives the mean magnitude of charge density just before depoling, $a$ and $b$ are the exponential factors which represent the charge decay rates.

The parameters obtained by modelling the mean value of absolute charge density during depoling time are represented in Table 2. Zhou et al. have stated that these parameters $a$, $b$, $n_1$, and $n_2$ are potentially related to microstructure of the material and any change in parameters will reflect ageing phenomenon taken place in the material [29]. Figure 11 depicts the mean magnitude of initial charge density just before depoling and the mean life time of the charge decay characteristics that are calculated from the parameters shown in Table 2. The charge decay rate “$b$” is order of $10^{-5}$, which indicates that the charge decay corresponding to the part $n_2$ almost negligible when compared to charge decay of the part $n_1$. Hence, to compare the charge decay parameters of unaged and water aged specimens during depoling time, only charge decay rate “$a$” is considered for calculating mean life time of charge decay. It is observed that the mean life time of the charge decay characteristics during depoling is more in case of epoxy specimen aged at 90 °C in water, followed by water aged specimen at RT and unaged specimen respectively. The charge carriers that enter into the material, through charge injection are being trapped by the localized states present in the bulk of the material. These localized trapping sites can originate because of matrix-filler interface, crystal defects and catalyst residues [25]. The microstructural deformation occurring in the bulk of the specimen during hydrothermal ageing can increase the number of localized trapping sites eventually leading to the decrement in the decay rate of accumulated space charge.

To investigate the impact of voltage polarity reversal, the epoxy specimens were stressed under positive DC field of 10 kV mm$^{-1}$ for 1800 s before polarity reversal and were stressed under a negative DC field of 10 kV mm$^{-1}$ for 1800 s after voltage polarity reversal, In between, the polarity reversal period is fixed at 40 s i.e. from 1800 to 1840 s. Figures 12 and 13...
FIGURE 9  Space charge characteristics during depoling in (a) unaged specimen, (b) water aged specimen at RT and (c) water aged specimen at 90 °C.

depict the accumulated charge density and electric field profile of epoxy micro–nano composite specimens at various instants of time. It is noticed that some part of homo charge accumulated in the bulk of the test samples up to the instant of polarity reversal i.e. at 1800 s, is retained after the change in the voltage polarity. It is because the period of polarity reversal is lesser compared to the time required for the accumulated space charge to decay. This retained charge after voltage polarity reversal acts as hetero charge and can affect the local electric field distribution. But, the charge that is being accumulated in the bulk of the specimen after the charge in the voltage polarity i.e. at 1840 s, reduces the retained charge and nullifies it. Later, space charge with polarity opposite to that of initial space charge, is being accumulated in the epoxy specimen at the instant of 1800 s after polarity reversal i.e. at 3640 s. Wang et al. have noticed the same pattern in CB/LDPE composite specimens and have stated that, homo charge accumulated before voltage polarity reversal will remain as hetero charge after the change in the polarity of the applied voltage [30]. Presence of space charge can distort the internal electric field of the specimen, which can either increase or decrease the electric field, depending on the type of accumulated space charge. Homo charges near the electrode-sample interface, tend to reduce the local electric field, while hetero-charges enhance the local electric field. The retained homo-charge in the epoxy specimens, just after polarity reversal (1840 s), tends to act as hetero-charge, enhancing the local electric field near the electrode-specimen interface. The magnitude of this field distortion can be quantified with the help of the field enhancement factor [31]. It is represented as shown in Equation (5)
\[ F = \frac{E - E_a}{E_a} \times 100\% \]  

(5)

Where \( E \) is maximum electric field (kV mm\(^{-1}\)), \( E_a \) is applied electric field (kV mm\(^{-1}\)) and \( F \) is field enhancement factor (%).

The field enhancement factor of epoxy composite samples at the instant of 1800 and 3640 s is depicted in the Figure 14. The field enhancement factor of test samples is more in case of epoxy micro–nano composite specimen aged at 90 °C in water, followed by water aged specimen at RT and unaged specimen respectively. It confirms that the aged specimens are subjected to higher field distortion. This higher field distortions in hydrothermally aged specimens, minimizes the insulator reliability and life span.

3.3 | Surface potential decay measurement and trap distribution characteristics

The surface potential decay curves of epoxy composite specimens under \( \pm 8 \) kV DC voltages (Figure 15), are modelled as exponential function shown in Equation (6).

\[ V(t) = V_0 e^{-\lambda t} \]  

(6)

Where \( V_0 \) is the initial surface potential accumulated, \( \lambda \) is decay rate of surface potential, \( \tau \) is mean life time of surface potential decay and its value can be obtained from the inverse of surface potential decay rate (\( \lambda \)).

The initial surface potential and the mean life time (\( \tau \)) of potential decay of test samples were represented in Tables 3 and 4. The initial surface potential has increased slightly, whereas the decay rate of water aged specimens reduced significantly, compared to unaged epoxy composite specimen. The surface potential decay rate of the epoxy specimens has followed similar pattern as that of space charge decay characteristics (Figure 10(b)). Lesser decay rate in case of water aged specimens indicate the possibility of higher surface charge accumulation. The charge trap density function \( (N(E)) \) of holes or electrons can be expressed as shown in Equation (7) [32].

\[ N(E) = \frac{2 \varepsilon_0 \varepsilon_r}{qL^2 kT \int_0^E \frac{dV}{dt}} \]  

(7)
FIGURE 12  Space charge characteristics under voltage polarity reversal in (a) unaged specimen, (b) water aged specimen at RT and (c) water aged specimen at 90 °C

Where $q$ is the electron charge, $L$ is thickness of sample, $k$ is Boltzmann constant ($1.38 \times 10^{-23} \text{ m}^2\text{kg} \text{s}^{-2}\text{K}^{-1}$), $T$ is absolute temperature, $t$ is time, and $f_0(E)$ is the initial electron occupancy rate.

The trap depth ($\Delta E$) of the epoxy specimens can be obtained from the equation shown in Equation (8)

$$\Delta E = E_C - E_M = kT \ln (\#)$$  \hspace{1cm} (8)

Where $\Delta E$ is trap depth, $E_M$ is demarcation energy, $E_C$ is conduction band energy and $r$ is the attempt to escape frequency ($10^{12} \text{ Hz}$).

Figure 16 represents the trap density variation with respect to trap depth, in virgin and water aged epoxy composites. The charge migration phenomenon of surface charge mainly follows three routes such as, along the surface through hopping transfer, towards the surrounding ambience and into the sample. Surface traps are considered to be formed on the surface of the specimen, due to chemical and physical defects such as, un-saturated bonds (dangling bonds), molecular adsorption, chain ends or impurities. These surface traps tend to capture the charges that are present on the surface of the material. These charges therefore migrate from trap to trap (hopping transfer) with very less charge mobility [33]. The mobility of the charge carriers depends on the trap density and the depth of traps present on the surface of the sample. More the trap density and trap depth, lesser will be the charge mobility and there will be more chance for charge accumulation on the surface of the specimen.
The maximum value of trap density and its corresponding trap depth of epoxy composite specimens is represented in Tables 3 and 4. It is noticed that there is slight reduction in the density of surface traps. This can slightly increase the mobility of charge carriers. A right shift in the trap distribution characteristics of the water aged specimens is noticed compared to unaged epoxy specimen. This right shift in the trap distribution characteristics indicates the increment in the trap depth at maximum charge density, confirming the charges being trapped in deeper traps in case of water aged samples compared to unaged samples. This reduces the charge carrier mobility. Since the reduction in maximum value of trap density is negligible compared to increment in its corresponding trap depth, the water aged specimens will possess a risk of higher surface charge accumulation compared to virgin specimen.

**Figure 13** Electric field characteristics under voltage polarity reversal in (a) unaged specimen, (b) water aged specimen at RT and (c) water aged specimen at 90 °C

A: Initial Potential  B: Mean Life time  C: Maximum value of trap density  D: Trap depth at maximum value of trap density

### 3.4 Dynamic mechanical analysis

Typical plots representing storage modulus and mechanical loss tangent (tan δ) at frequencies 1, 5 and 10 Hz are shown in Figure 17. A significant reduction in storage modulus of water aged epoxy specimens compared to unaged specimen is noticed. It is because of the plasticisation of polymer matrix and deterioration of the epoxy-filler interfaces due to the penetration of water molecules [10]. The magnitude of α-relaxation peak of tan δ plot is noticed to increase after water ageing. The glass transition temperatures ($T_g$) obtained from tan δ plot were depicted in
Table 5. The glass transition temperature values are lower in case of epoxy specimen aged at 90 °C in water, followed by water aged specimen at RT and unaged specimen respectively. Wang et al. have indicated that, exposing the specimen to hydrothermal conditions can greatly influence the relaxation behaviour of the material. It results in the shift of α-relaxation peak of tan δ curve, towards lower temperatures [10]. Similar characteristics have been observed here, with a left shift in α-relaxation peak of epoxy composite specimens after ageing in water, indicating the reduction in glass transition temperature after water absorption. The activation energy \( (E_a) \) of the test samples can be obtained through Arrhenius equation as shown in Equation (9) [34].

\[
f = f_0 \exp \left[ \frac{-E_a}{RT} \right]
\]  

(9)

Where \( E_a \) is activation energy for the relaxation process, \( T \) is absolute temperature, \( R \) is universal gas constant, \( f \) is test frequency and \( f_0 \) is pre-exponential constant.

Mishra et al., have carried out DMA studies with base epoxy resin and its nanocomposites and have indicated that the activation energy of epoxy nanocomposites has a considerable increment with respect to base epoxy resin [7]. In comparison of the epoxy micro–nano composite material in the present study, with base epoxy resin, it is noticed that the glass transition temperature has not changed after addition of filler material. It is also observed that, a considerable increase in the activation energy of epoxy micro–nano composite specimen compared to base epoxy resin, indicating that the epoxy composite specimen is more stable mechanically compared to base epoxy resin. The activation energy of the test samples, calculated from the Arrhenius plot depicted in Figure 18, is lower in case of epoxy specimen aged at 90 °C in water, followed by water aged specimen at RT and unaged specimen respectively. (Table 5). It indicates the decrement in activation energy of test specimens with water ageing. Thus, plasticisation effect and weakening of matrix-filler interfacial bonding in test samples S3 and S2 can be confirmed by the reduction in activation energy. Under hydrothermal ageing (water ageing specimen at 90 °C), the diffusion of water
into the specimen will be more compared to water ageing at room temperature, resulting in more weakening of interfacial bonds leading to relatively lesser activation energy in water aged specimen at 90 °C. Thus, the decrement in the activation energy can be correlated with the higher diffusion coefficient of water under hydrothermal ageing.

**FIGURE 17** Storage modulus and tan δ of epoxy micro-nano composites at (a) 1 Hz, (b) 5 Hz and (c) 10 Hz

**TABLE 5** $T_g$ and $E_a$ of epoxy micro–nano composites

| Specimens       | $T_g$ (°C) |       |       | $E_a$ (kJ mol$^{-1}$) |
|-----------------|------------|-------|-------|----------------------|
| Unaged          | 156.6      | 160.9 | 163.5 | 526.84               |
| Aged at RT      | 156.0      | 160.4 | 163.1 | 510.94               |
| Aged at 90 °C   | 155.1      | 159.8 | 162.3 | 500.08               |

**FIGURE 18** Arrhenius plot of epoxy micro–nano composites
Thermal stability analysis by \( s \)ile strain values of epoxy micro–nano composite specimens

Relation between tensile strain values and loading time. Ten-
vues of tensile strain at break point. Figure 19(b) depicts the
tion effect and weaker interfacial bonds, leading to higher val-
the specimen will be more, which results in more plasticiza-
With hydrothermal ageing, the diffusion of water molecules into
Water molecules act as a plasticizer in composite materials
fusing along the epoxy-filler interface rather than diffusing into
filler interface. The water molecules are more likely to dif-
crease in the UTS of epoxy specimens with water ageing. It
Presented in Table 6. It is observed that there is a significant
break point) and tensile modulus of test specimens are rep-
the sample can withstand without breaking.

The UTS, maximum load, tensile strain at UTS (strain at
break point) and tensile modulus of test specimens are rep-
resented in Table 6. It is observed that there is a significant
decrease in the UTS of epoxy specimens with water ageing. It
is because of the interaction of water molecules with matrix-
filler interface. The water molecules are more likely to dif-
fuse along the epoxy-filler interface rather than diffusing into
the epoxy matrix. This will deteriorate the interfacial bond-
ing between epoxy and the filler, reducing its tensile strength.
Water molecules act as a plasticizer in composite materials
which may result in the increase of the maximum strain [17].
With hydrothermal ageing, the diffusion of water molecules into
the specimen will be more, which results in more plasticiza-
tion effect and weaker interfacial bonds, leading to higher val-
ses of tensile strain at break point. Figure 19(b) depicts the
relation between tensile strain values and loading time. Ten-
sile strain values of epoxy micro–nano composite specimens
are higher in case of epoxy specimen aged at 90 °C in water,
followed by water aged specimen at RT and unaged specimen
respectively. Also, there is a reduction in time taken for reach-
ing break point in water aged epoxy specimens, indicating that
the water aged specimens are experiencing more strain even for
lesser loading conditions, compared to virgin specimens. The
trap depth measurement and the strain measured shows direct
 correlation. Also, correlating space charge decay characteristics
and the strain, it shows inverse correlation.

Figure 20 represents the strain field distribution on the sur-
face of the test samples, at different loading times. Both the con-
ventional tensile testing and DIC analysis were simultaneously
performed. For each specimen, the image at \( t = 1 \) s is taken as
reference image and the speckle pattern in the images starting
from \( t = 2 \) to until the time of breakage are compared to calcu-
late the displacement and thereby strain contours are developed.
In Figure 20, it is noticed that the strain deformation is present
more in the breakpoint region and is clearly represented in red
colour. Thus, the strain field distribution can be used in identi-
fying the high-stress concentrated areas, before breaking. In this
case, the DIC technique employed tensile testing has an advan-
tage over the conventional tensile test providing the strain field
at different levels of deformation. [35].

The strain along the tensile direction i.e. elongation \( (e_{yy}) \)
is represented as a function of loading time, by choosing the loca-
tion near to the break point (maximum strain region) of the
specimen. Figure 21 represents the linear fit of the elongation
\( (e_{yy}) \) with respect to loading time. It is observed that the water
aged specimens are experiencing more elongation \( (e_{yy}) \) along
tensile direction, even for lesser loading times compared to vir-
gin specimen. The higher values of tensile strain could be due to
plasticization of polymer matrix and weaker matrix-filler inter-
facial bonding, leading to improper transfer of load between
filler and matrix. It finally deteriorates the tensile strength and
tensile modulus of the specimen resulting in the early break-
age under mechanical loading conditions. The strain distribu-
tion along the tensile direction with respect to time, obtained
through DIC technique in Figure 21 has a similar trend to that of
the strain plot obtained through conventional tensile testing as
represented in Figure 19(b). It confirms that the DIC technique
employed tensile setup can detect both the strain field deforma-
tion and strain displacement of the specimen under mechanical
stress.

### 3.5 | Strain field analysis by digital image correlation

The impact of water ageing on tensile behaviour of test epoxy
composite specimens can be studied with the help of DIC tech-
nique employed tensile test setup. The specimens required for
tensile test were prepared according to ASTM D638 standard.
The tensile stress versus strain characteristics of virgin and water
aged epoxy composite specimens were depicted in Figure 19(a).
It is observed that the tensile stress versus strain characteristics
were found to increase monotonically up to a certain extent
and after that it suddenly falls. The stress at which the specimen
becomes brittle and breaks is termed as ultimate tensile strength
(UTS). The load corresponding to it is the maximum load that
the sample can withstand without breaking.

The UTS, maximum load, tensile strain at UTS (strain at
break point) and tensile modulus of test specimens are rep-
resented in Table 6. It is observed that there is a significant
decrease in the UTS of epoxy specimens with water ageing. It
is because of the interaction of water molecules with matrix-
filler interface. The water molecules are more likely to dif-
fuse along the epoxy-filler interface rather than diffusing into
the epoxy matrix. This will deteriorate the interfacial bond-
ing between epoxy and the filler, reducing its tensile strength.
Water molecules act as a plasticizer in composite materials
which may result in the increase of the maximum strain [17].
With hydrothermal ageing, the diffusion of water molecules into
the specimen will be more, which results in more plasticiza-
tion effect and weaker interfacial bonds, leading to higher val-
ses of tensile strain at break point. Figure 19(b) depicts the
relation between tensile strain values and loading time. Ten-
sile strain values of epoxy micro–nano composite specimens
are higher in case of epoxy specimen aged at 90 °C in water,
followed by water aged specimen at RT and unaged specimen
respectively. Also, there is a reduction in time taken for reach-
ing break point in water aged epoxy specimens, indicating that
the water aged specimens are experiencing more strain even for
lesser loading conditions, compared to virgin specimens. The
trap depth measurement and the strain measured shows direct
 correlation. Also, correlating space charge decay characteristics
and the strain, it shows inverse correlation.

Figure 20 represents the strain field distribution on the sur-
face of the test samples, at different loading times. Both the con-
ventional tensile testing and DIC analysis were simultaneously
performed. For each specimen, the image at \( t = 1 \) s is taken as
reference image and the speckle pattern in the images starting
from \( t = 2 \) to until the time of breakage are compared to calcu-
late the displacement and thereby strain contours are developed.
In Figure 20, it is noticed that the strain deformation is present
more in the breakpoint region and is clearly represented in red
colour. Thus, the strain field distribution can be used in identi-
fying the high-stress concentrated areas, before breaking. In this
case, the DIC technique employed tensile testing has an advan-
tage over the conventional tensile test providing the strain field
at different levels of deformation. [35].

The strain along the tensile direction i.e. elongation \( (e_{yy}) \) is
represented as a function of loading time, by choosing the loca-
tion near to the break point (maximum strain region) of the
specimen. Figure 21 represents the linear fit of the elongation
\( (e_{yy}) \) with respect to loading time. It is observed that the water
aged specimens are experiencing more elongation \( (e_{yy}) \) along
tensile direction, even for lesser loading times compared to vir-
gin specimen. The higher values of tensile strain could be due to
plasticization of polymer matrix and weaker matrix-filler inter-
facial bonding, leading to improper transfer of load between
filler and matrix. It finally deteriorates the tensile strength and
tensile modulus of the specimen resulting in the early break-
age under mechanical loading conditions. The strain distribu-
tion along the tensile direction with respect to time, obtained
through DIC technique in Figure 21 has a similar trend to that of
the strain plot obtained through conventional tensile testing as
represented in Figure 19(b). It confirms that the DIC technique
employed tensile setup can detect both the strain field deforma-
tion and strain displacement of the specimen under mechanical
stress.

### 3.6 | Thermal stability analysis by thermo-gravimetric studies

Figure 22 represent the thermogravimetric (TG) and Diff-
ential thermogravimetric (DTG) characteristics of epoxy
composite specimens. The temperature at which 5% weight loss
occurred [termed as IDT (initial decomposition temperature)]
and the maximum degradation temperature \( (T_{\text{max}}) \) can be cal-
culated from TG and DTG curves respectively. It is observed
that the IDT and \( T_{\text{max}} \) values are lower in case of epoxy speci-
men aged at 90 °C in water, followed by water aged specimen at
RT and unaged specimen respectively (Table 7). Also, the mass
loss profiles of water aged specimens are shifted towards the left side compared to that of unaged epoxy specimen, indicating that the thermal degradation is occurring in relatively lesser temperatures. The early thermal degradation in case of water aged specimens, could be due to degraded interphase region between the epoxy matrix and filler due to water ageing [36].

| Specimens         | IDT [°C] | $T_{\text{max}}$ [°C] | Reduced weight at 800 °C [%] |
|-------------------|----------|-----------------------|------------------------------|
| Unaged            | 361.8    | 387.1                 | 29.85                        |
| Aged at RT        | 352.9    | 382.9                 | 30.91                        |
| Aged at 90 °C     | 347.3    | 370.3                 | 31.84                        |
4 | CONCLUSION

The variation in space charge and thermo-mechanical properties of virgin and water aged epoxy composite samples were investigated in the current study and the conclusions are as follows:

- The water diffusion coefficient of the epoxy specimen aged under 90 °C is greater than that of specimen aged at room temperature indicating the higher amount of water absorption in case of hydrothermal ageing.
- Space charge accumulation especially homo charge, is observed to be more significant in case of hydrothermally aged specimens compared to other specimens.
- The mean value of absolute space charge density during poling time and mean life time of charge decay during depoling time had a significant increment after water absorption, on application of 10 kV mm\(^{-1}\) positive DC field.
- The initial surface potential of the test specimens has a marginal increment after water ageing, whereas the decay rate of surface potential has resulted in significant reduction.
- The trap depth of the test epoxy specimen has increased after water ageing, indicating the presence of relatively deeper traps after water intake.
- The tan δ value obtained from DMA has a slight increment after water absorption and the storage modulus had resulted in significant reduction.
- The activation energy and the glass transition temperature of epoxy micro–nano composites are lower in case of epoxy specimen aged at 90 °C in water, than water aged specimen at RT, confirming that hydrothermal ageing is causing more mechanical degradation compared to water ageing at room temperature.
- The reduction in tensile strength, tensile modulus and increment in tensile strain at tensile mechanical loadings indicated the degradation in mechanical properties of epoxy specimens after water absorption.
- The trap depth measurement and the strain measured shows direct correlation. Also, correlating space charge decay characteristics and the strain, it shows inverse relationship.
- It is observed that the values of IDT and \( T_{\text{max}} \) are in the order are lower in case of water aged specimen at 90 °C, followed by water aged specimen at RT and unaged specimen respectively. It indicates the occurrence of early thermal degradation in case of hydrothermally aged specimens.

Thus, based on results of the present study, it can be concluded that the water ageing results in weakening of interfacial bonding between epoxy matrix and filler, leading to a significant degradation in space charge and thermo-mechanical properties. This deterioration of space charge and thermo-mechanical properties are noticed to be more severe in case of hydrothermal ageing compared to water ageing at room temperature, reducing the reliability and life expectancy of insulating material.

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