

## EFFECT OF TEMPERATURE ON DIELECTRIC RESPONSE AND CHARGE TRANSFER BEHAVIOUR OF SILANE CAPPED (Fe-O) SINGLE CRYSTAL REINFORCED EPOXY THIN FILM

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A high dielectric stable epoxy composite was prepared and characterized for their dielectric response and charge transfer properties at elevated temperatures. The principal aim of this work is to develop high stable (insulative) particle dispersed epoxy composites for high temperature and structural applications. The Fe-O single crystal was prepared via co-precipitation and surface capped by capping agent to restrict the abrupt mobility of electrons. The dielectric results show that addition of Fe-O into epoxy resin increase the charge transfer up to 7.4 (dielectric constant). Whereas addition of silane capped FeO particles not altered the dielectric constant and conductance. The increase of temperature on dielectric fetched more dissipation but in surface capped FeO dispersed composite its lower. The addition of surface capped Fe-O particle dispersed epoxy resin composite gives improved mechanical strength than as-received one. The SEM and TEM morphological behaviour confirms the uniform dispersion and adhesion of Fe-O particles on matrix. These mechanically toughened high stable dielectric epoxy composites could be used in VLSI and embedded board fabrication industries because of their better insulation properties even in high temperature.

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### 1. Introduction

Particle dispersed polymer matrix composites are having attractive applications in structural and high thermal stability required zones [1]. Particle addition is an easy and effective process where process parameters are lower. Adding nano or micro particles may fetch incredible effects on mechanical and thermal behaviour [2]. Reinforcing conductive or ceramic fine particles into epoxy resin increase the load sharing ability by compromising the promising insulation behaviour of thermosets like epoxy, vinyl ester and unsaturated polyester. Modify the surface of reinforcements may avoid the changes in dielectric properties of base matrix. Now the base matrix is mechanically tougher without affecting the core properties of base matrix [3]. Epoxy is an aromatic high strength thermoset plastic having very high insulation (dielectric strength up to 9.6 KV/mm) and mechanical properties. Generally epoxy is a thermoset with brittle nature; hence mechanical property enhancement could be a prime issue. Iron oxide (Fe-O) single crystal fine particles of varying volume percentage may fetch improved mechanical properties in the sense of tensile, flexural, impact and hardness. But addition of particle affects the superior insulation of base epoxy by enforcing the electron flow. The Fe-O single crystal particles could be prepared using co-precipitation method with simple processing steps [4]. The surface of fine Fe-O particle could be modified by APTES to ensure better adhesion with matrix and also providing more tightness between primary and secondary molecular chain. The surface modification process could be done by acid hydrolysis, since the capping process required a wet method. The composites could be prepared using hand layup process where low process parameters are employed. The casted FeO-epoxy composites could be tested based on ASTM standards [5]. When the particle

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filled epoxy composites are tougher in mechanical and also maintain very high insulation stability, they could be used in electronic industries where epoxy encapsulation is required.

## 2. Experimental procedures

### 2.1. Materials

Epoxy resin used for the current investigation was a DGEBA type of resin (Huntsman India Ltd. Mumbai, Araldite LY556) having an equivalent epoxide group of 195 g/mol with kinematic viscosity of 12000 cps and density of 1.2g/cm<sup>3</sup> at room temperature. The hardener used for curing the sample was Triethylenetetramine (TETA, Huntsman India Ltd. Mumbai. HY951), low viscosity aliphatic amine having density of 0.98g/cm<sup>3</sup>. The capping agent 3-Aminopropyltriethoxysilane was purchased from Sigma Aldrich USA. Ferric chloride of molecular weight 169.8 g/mol and NaOH of molecular weight 40 g/mol were collected from MERCK India Ltd. All the chemicals and materials were used in as received condition without any post process treatments.

### 2.2. Co-Precipitation process

The nano-scale single crystal Fe-O particles are prepared via co-precipitation method. In this ferric chloride of 2 mol is dissolved in 1N of NaOH solution at controlled temperature of 80 °C. The reacted precipitate is settle down at the bottom of beaker due to rapid cooling of solution. By this process the nucleation is controlled and very fine crystalline Fe-O was formed. The precipitated Fe(OH)<sub>2</sub> substance was separated using whatman filter paper. The brown colour precipitation was then dehydrated by heating the precipitate above 110 °C until the aqua molecules are get evaporated. Thus ultra fine Fe-O particles were formed. Fig. 1 shows XRD plot of Fe-O crystal from co-precipitation process. A strong peak at 22, 24 and 34 ° 2θ confirms the presence of simple cubic crystal structured Fe-O. The crystallite size, which was calculated using Debye sheerer equation, was 23 nm. Fig. 2 shows the TEM image of Fe-O fine particle, which confirms the single crystalline nature. There was no poly-phase structures were found [6].

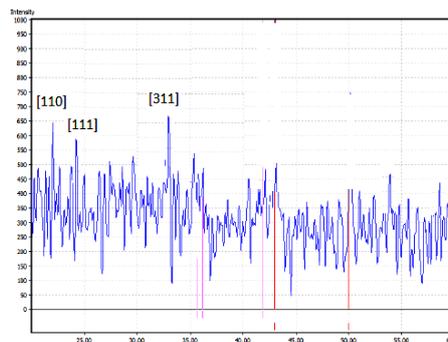


Fig. 1. XRD plot of Fe-O particle.

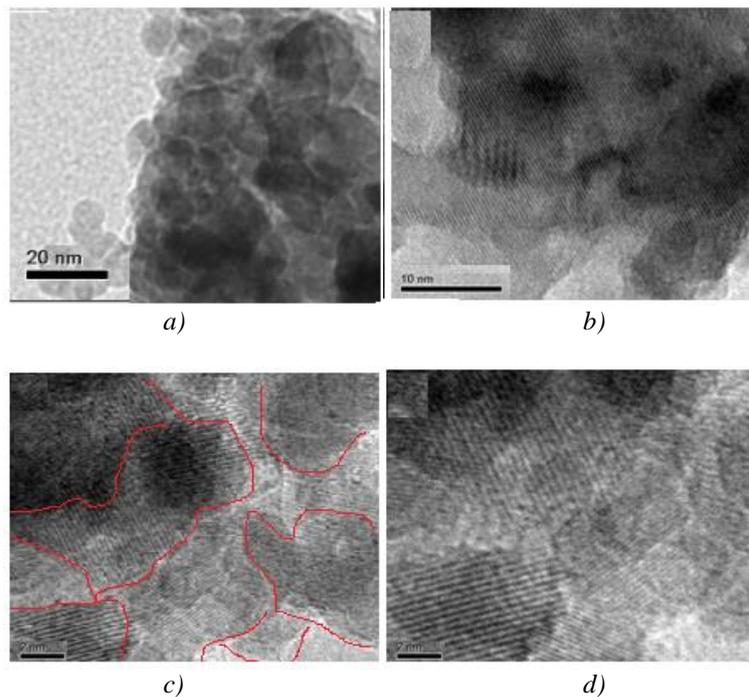


Fig. 2. TEM images of Fe-O single crystal.

### 2.3. Surface capping process

The capping of co-precipitated particle's surface is done by silane capping agent via aqueous solution method. In this process the APTES silane solution was mixed with ethanol of 95%. Water and acetic acid was added with solution to adjust the pH of silane-ethanol solution to enforce the acid hydrolysis process. The fine Fe-O nano particles then immersed into silane-ethanol solution and allowed to float for 10 min. In this process the silane element was attached on the surface of nano Fe-O particles as outer ring. The attached silane, which consists of NH<sub>2</sub> functional group, is free from reaction and present on the surface of particle. Figure 3 shows the TEM and graphical representation of surface capped Fe-O nano particle under high resolution. The attached NMR spectral PPM at 4.5 confirmed the presence of APTES on the particle surface. Thus the process of surface capping enhanced the silane attachment on particle surface, which may increase the adhesion of particles with polymer and hinder the mobility of molecular chain [7].

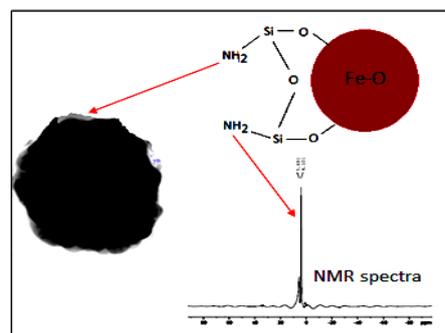


Fig. 3. TEM and graphical representation of surface capped Fe-O nano particle.

### 2.4. Composite thin film preparation

The surface capped Fe-O nano particles were dispersed in epoxy resin in various volume fractions. The particle dispersed epoxy resin mixture is stirred continuously until the degassing completed. The resulted colloidal suspension was then mixed with curing hardener and poured into

a thin silica rubber mould (0.3 mm). The poured suspension was cured at room temperature for 24 h and post cured at 48 h [8].

Table 1. Designation and add-on elements of composites.

S.No	Designation	Epoxy vol.%	Fe-O particle vol.%
1.	E	100.00	0.00
2.	EI <sub>1</sub>	99.75	0.25
3.	EI <sub>2</sub>	99.50	0.50
4.	EI <sub>3</sub>	99.00	1.00
5.	EI <sub>4</sub>	98.00	2.00
6.	EI <sub>5</sub>	96.00	4.00

E-Epoxy; I-Iron Oxide

### 3. General characterization

The fabricated FeO-epoxy composites were tested for revealing the mechanical and dielectrical behaviour following ASTM standards. The mechanical results were analyzed using ASTM D-638 with an Instron 368 model. The dielectric behaviour of composites was unveiled using a LCR meter following ASTM D 150 with a LCR hi-tester HIOKI, 3532-50 JAPAN. The operating range used for the present study was 50 Hz to 500Hz. The Scanning electron microscopy used for investigating the morphology was a Thermic SEM, HITACHI, S1500, JAPAN.

## 4. Results and discussion

### 4.1. Dielectric analysis

#### 4.1.1 As-received Fe-O single crystal composites

Fig. 4 shows the dielectric constant graphs of various composites in room temperature and elevated temperature used in the present study. The addition of Fe-O single crystal into epoxy resin marginally increased the permittivity of dielectric composite. This is because of adding polar Fe-O particles into epoxy resin, which improves the charge transfer under external frequency. It is observed that the additions more volume of particles greatly increased the dielectric constant. This is because of presence of more active polarity sites, which are presented in matrix. It is further noted that when temperature of composite is increases the dielectric constant also increases. Fig. 4(a) shows the dielectric constant of epoxy composites in room temperature. The maximum dielectric constant of 7.4 was observed for composite designation EI<sub>5</sub> at 100 Hz. This improvement is the result of dielectric polarization and charge transfer by incorporation of single crystal Fe-O particles. The Fe<sup>+</sup> and O<sup>-</sup> will acts as dipole, which induce the charge transfer. It is observed that when frequency increases the dielectric constant getting decreases. This phenomenon is the result of poor dielectric polarization due to very high frequency and poor relaxation time [9 & 10]. It is noted that most of the composites are polarized at the frequency 100 Hz because most of the polymer dielectrics polarized at radio frequency. Figure 4(b) shows the dielectric constant at 100 °C. A maximum dielectric constant of 5.4 was observed for composite designation EI<sub>5</sub> at 100 Hz. The lowering dielectric constant of 27% was observed for similar composite designation EI<sub>5</sub> in 100 °C. This reduction in dielectric constant was the result of improved kinetic energy of epoxy molecules under elevated temperature. Because epoxy having glass transition temperature of around 70 °C. When temperature increased to 100 °C the epoxy molecules had enough energy and start rotate around the primary C-C axis. This led poor polarization thereby affecting charge mobility [12].

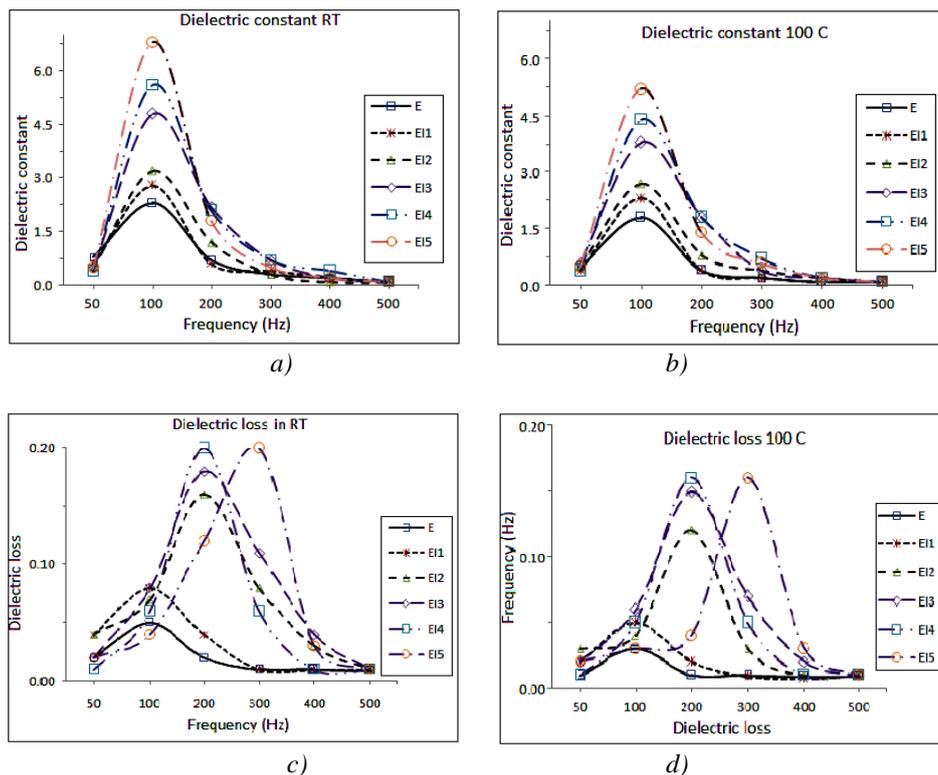


Fig. 4. Dielectric constant and loss of as-received Fe-O epoxy composites.

Fig. 4(c) shows the dielectric loss of various composites in room temperature. The maximum dielectric loss of 0.2 is observed for composite designation EI<sub>4</sub> and EI<sub>5</sub>. This is near 98% of improvement. This huge improvement is the results of adding single crystal Fe-O particles and larger frequencies. When frequency increases the relaxation time for dielectric getting polarized also less. This phenomenon is because of at high frequencies the epoxy and Fe-O molecules cannot orient and forms polarization. This poor polarization led more dissipation of heat. Similar effects were observed for composites in 100 °C also. Maximum dielectric loss of 0.15 was observed for composite designation EI<sub>4</sub> and EI<sub>5</sub>. This reduction in dielectric loss is the results of improved kinetic energy of epoxy molecules does not polarized for external frequency, which led lower dielectric loss at increased temperature [13].

#### 4.1.2. Surface-modified Fe-O single crystal composites

Fig. 5 shows the dielectric constant and loss of epoxy composites dispersed with surface-modified Fe-O particles. The surface modified Fe-O single crystal particles not altered the dielectric constant of epoxy resin. When amine surface modified Fe-O particles are reinforced in epoxy resin they creates inter-lock between epoxy molecular chains. These inter-locked epoxy molecules are not free enough to rotate and make polarization [14]. Hence, low polarization effect due to immobile epoxy molecule lowering the charge transfer. Figure 5(a) shows the dielectric constant of silane modified Fe-O dispersed epoxy composite. Maximum dielectric constant of 3.2 is observed for composite designation EI<sub>5</sub> at frequency 200 Hz. This value is much smaller than same composite reinforced with as-received Fe-O particle dispersed epoxy composites. This improvement is the result of particle-epoxy interaction and immobile epoxy molecular chains. The surface modified Fe-O particles make very rigid bonds with free OH of epoxy and hence they cannot reorient under external voltage, thus led poor polarization effect, which affect the charge transfer [15].

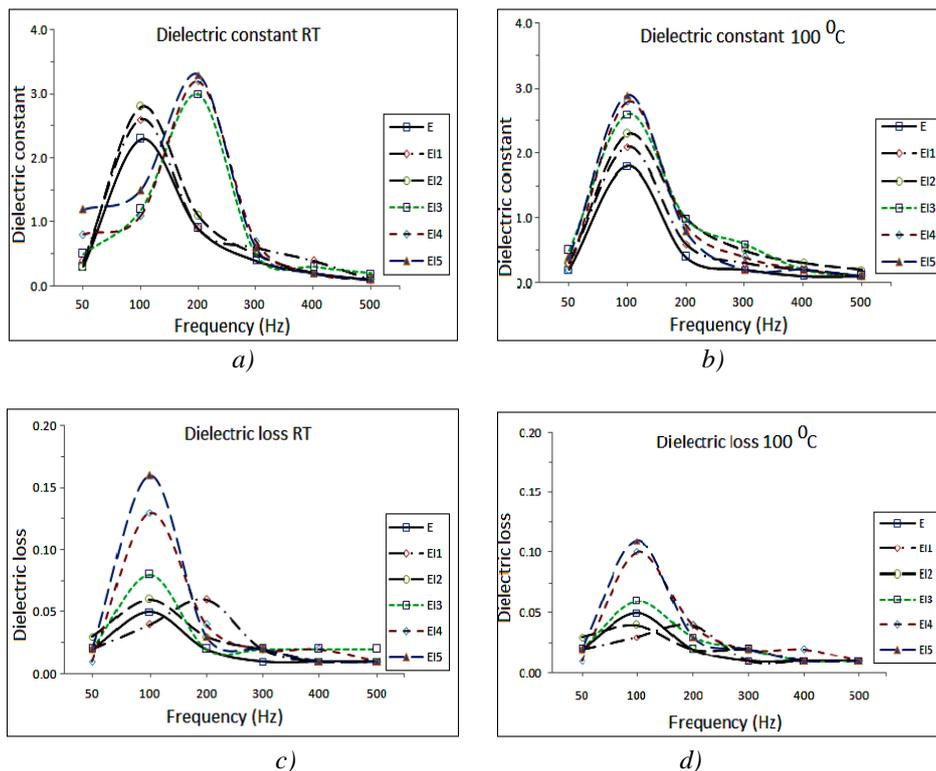


Fig. 5. Dielectric constant and loss of surface-modified Fe-O epoxy composites.

Fig. 6 shows Fe-O epoxy interlocking in surface-modified epoxy composite, which clearly shows the level of tightness in epoxy matrix. The free amine form particle surface, which reacts with epoxy link and form covalent bond. These chemical bonds makes possible link with particle and epoxy and makes the epoxy molecules as immovable. Fig. 5(b) shows the dielectric constant of FeO-epoxy composite under elevated temperature 100 °C. The raise of temperature also not makes any effort in changing of dielectric constant. This improvement is because of silane modified Fe-O particles absorbs more heat thereby increase the heat absorption [16]. Hence the raise of temperature cannot activate the epoxy molecules as maximum level. Maximum dielectric constant of 3 is observed for composite, which consist of 4 vol.% of Fe-O particle in epoxy resin.

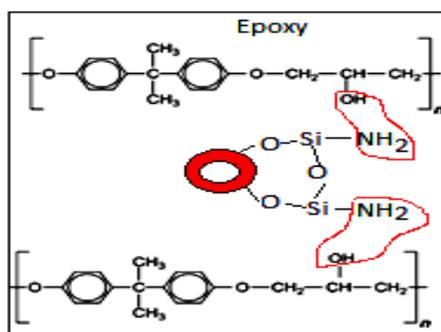


Fig. 6. Shows Fe-O epoxy interlocking.

Fig. 5(c) shows the dielectric loss of various composites fabricated. The silane modified Fe-O particles in epoxy matrix not produced higher heat dissipation. The maximum heat dissipation of 0.16 was observed for composite designation EI5. This improvement is because of surface modification process created bond with epoxy molecular chain and enables better

adhesion. Thus improvement in frequency moderates the polarization and ensures better charge flow. Similar improvements were noted in high temperature also in Figure 5(d). When temperature increases the molecules tries to move out from primary C-C chain and easily oriented to be polarized. But the surface modified Fe-O particles not allowed the epoxy molecules to disperse freely and ensure lower heat dissipation [17].

#### 4.2. Mechanical properties

Fig. 7 (a, b, c & d) shows the mechanical properties of as-received and surface-modified fabricated Fe-O epoxy composites under mechanical loading. The pure epoxy measures the tensile, flexural, impact and hardness behaviour of 65 MPa, 110 MPa, 0.42 J and 82 Shore-D respectively. The addition of Fe-O single crystal into epoxy resin modified the tensile, flexural, impact and hardness behaviour. The reduction of Tensile, flexural, impact and hardness values in FeO-epoxy composite is the results of as-received FeO particles in epoxy, which makes particle cluster. These clusters increase the stress concentration and reduce the strength of composites [18].

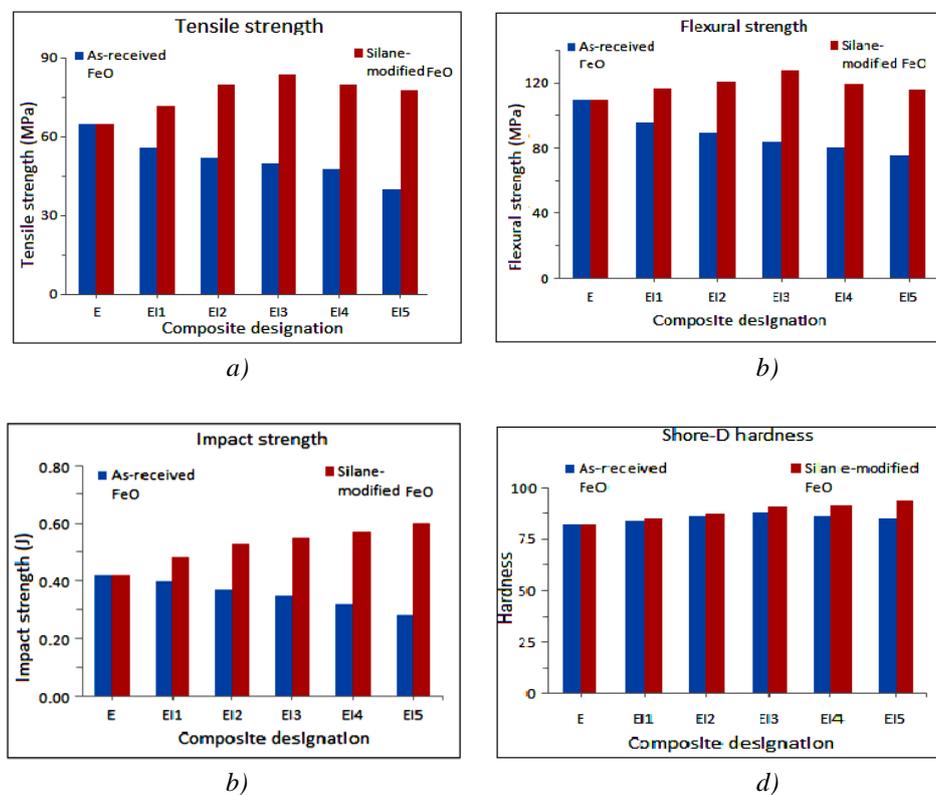


Fig. 7. Shows Mechanical properties of composites fabricated.

Whereas additions of silane modified Fe-O particles in epoxy increased the mechanical behaviour of epoxy composite. This improvement is the result of addition of silane-modified Fe-O particles in epoxy resin and improved dispersion and adhesion of the same. The good dispersed Fe-O particles evenly shared the load thereby increases the mechanical strength. The maximum tensile strength of 92 MPa, flexural strength of 128 MPa, Impact strength of 0.54 J and shore-D hardness of 92 were observed for composite which contain silane-modified Fe-O particles. Thus addition of silane modified Fe-O particles increase the mechanical properties of epoxy resin composite [19].

### 4.3. Morphology

Fig. 8 shows the SEM image of particle dispersed epoxy composite. Fig. 7(a) shows particle cluster due to as-received Fe-O particles. When the as-received particles are dispersed in matrix they form hydroxide state immediately. These hydroxide states have maximum tendency to react with neighbouring particles results cluster. But Fig. 7(b) shows uniform dispersion of Fe-O particles in epoxy matrix. The surface modification on particle surface favours uniform dispersion of particles in epoxy resin. When the surface-modified particles are dispersed in matrix the capped silane agent prevents the hydroxide state formation. There is no particle cluster is visible thus indicates uniform dispersion of particles [20].

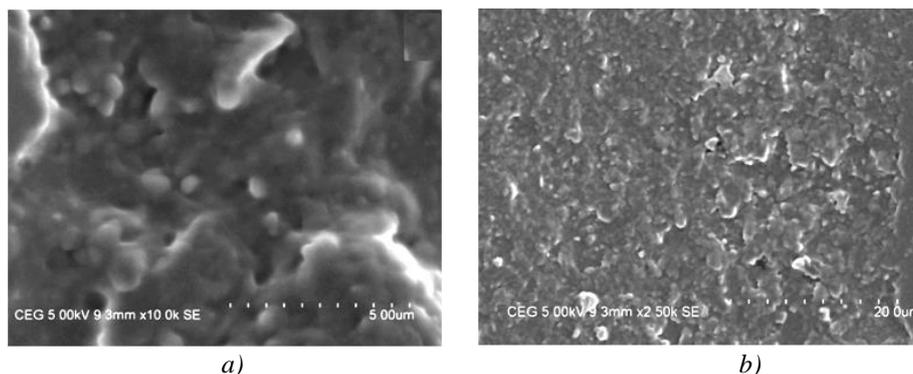


Fig. 8. SEM images of (a) As-received Fe-O particle in matrix and (b) Silane-modified Fe-O particle in matrix.

## 5. Conclusions

The Fe-O single crystal dispersed epoxy composites were prepared and analyzed for their effectiveness. The Fe-O single crystal particles are prepared via simple techniques and confirmed using XRD. The composites were prepared with variable volume of Fe-O particles with as-received and surface modified condition. The Dielectric results confirm that addition of as-received particles in epoxy resin abruptly increased the dielectric constant and loss at room temperature and also in elevated temperature. Whereas the silane capped Fe-O particles not altered the dielectric values much.

The raise of temperature directly affected the dielectric values of as-received Fe-O epoxy composite but the silane capped Fe-O in epoxy resin not changed the values much. The mechanical result shows that as-received Fe-O in epoxy gives poor mechanical properties, whereas the silane capped Fe-O particles increases the mechanical strength of composite. The SEM morphological images revealed the uniform dispersion of Fe-O single crystal in epoxy resin. Thus the silane capped Fe-O particles increases the mechanical properties without altering the insulation properties of epoxy resin.

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