EFFECT OF SURFACE MODIFICATION AND PARTICLE SIZE ON DIELECTRIC PROPERTIES OF IRON(III)OXIDE-EPOXY COMPOSITE FILM

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In this work surface modified iron(III)oxide particles reinforced epoxy composite warmer material was fabricated. The effect of particle addition on polarization, dielectric properties and heat dissipation was studied. To enhance ionic polarization and electron mobility on epoxy thermoset fine iron(III)oxide filler was selected and utilized as a positive ions. Particle size of 800 and 200nm was used as filler and effectiveness of particle size on dielectric behavior was studied. Uniform distribution of fillers on matrix favors desirable outputs hence the particles were surface treated with an amine functional coupling agent (APTMS).Siliconization process was done by thermo assisted aqueous solution method. Epoxy particulate composite was fabricated by reinforcing 0.25, 0.5, 1.0, 2.0, 4.0 vol% of siliconized iron(III)oxide followed by hand layup method. Crystalline and functional groups of siliconized iron(III)oxide particles were characterized by XRD and FTIR spectroscopy analysis. All proportions of composites were cured by an aliphatic hardener triethylenetetramine (TETA). The scanning electron microscopy images revels the shape and size of iron(III)oxide particles in different milling time and dispersion quality in epoxy matrix. Dielectric properties of iron(III)oxide reinforced composites were investigated with parallel plate capacitor method. Dielectric loss and constant was analyzed as a function of frequency and temperature. Dielectric loss was increased when particle loading was increased. The as-received iron(III)oxide particles gives little effect on dielectric loss, whereas surface functionalized iron(III)oxide particle gives maximum because of good dispersion and more active site for electron mobility in epoxy matrix. The increased temperature affects the dielectric loss and constant because of supplied internal energy that was studied at 100ºC. Dielectric constant of epoxy was increased significantly when particle loading increases and reduced when temperature and frequency was increased.

1. Introduction

Particles reinforced polymer matrix composites have attractive applications like conducting polymer, Dielectric heating, fluid magnetism, high thermal stability, and good mechanical properties. Adding fillers like Iron(III)oxide into high strength thermoset polymer like epoxy special properties like electromagnetic shielding and dielectric loss can be improved [1].Generally epoxy resins are good insulators because of non polar molecular structure [2]. This high insulation can be reduced by reinforcing conductive or semi conductive metallic fillers. Making epoxy as a polar may improve charge mobility hence desirable properties can be achieved. When epoxy contains di-pole molecules (OH and Fe) they may attracted by external frequency hence ionic polarization occurs. Iron(III)oxide was chosen as a filler because of its ease of availability, processing, more stable in room temperature rather than other oxides of iron and good mechanical strength. Epoxy consists of plenty of free OH group in its secondary link so its

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negative ionic character will not motivate charge mobility. Whereas adding iron(III)oxide particle creates more positive domains hence polarization occur easily. This phenomenon helps the epoxy to transfer electron by ionic polarization but the same will be converted as a heat when frequency is increased. When dielectric loss is increased these materials can be used as a heating element. This heat dissipation concept can be used in dielectric heater on food containers and storage tanks to maintain warm up of food without other heat sources. Particle dispersion quality is very important when consistent and desirable dielectric properties are needed. Modification of particle surface by a surfactant (3-Aminopropyltrimethoxysilane) helps uniform distribution in epoxy matrix [3]. Surface modification process could be done by aqueous solution method since it is easy and cheap method to produce large volume of treated particles. On surface treatment iron(III)oxide particles are surrounded by silane substance and creates NH_2 functional group. Theses functional groups could be reacted with epoxy resin and form a clear network [4]. Controlled size of particles is very much important to acquire better output, in these aspect different particle sizes of 800nm and 200nm was used for fabrication. To achieve less dimension (200nm)ball milling process could be used. The particle sizes could be confirmed by particle size analyzer. High energy planetary ball milling could be used since it is a cheaper way of producing low dimensioned particles

2. Experimental procedures

2.1 Materials

The epoxy resin used in the present study was a liquid diglycidyl ether of Bisphenol-A type (Huntsman India Ltd. Mumbai, Araldite LY556) with an equivalent weight per epoxide group of 195 g/mol having viscosity of 12000 cps and density of $1.2g/cm^3$ at $25^{\circ}C$. Triethylenetetramine (TETA, Huntsman India Ltd. Mumbai., HY951), a low viscosity aliphatic amine was having viscosity of 20cps and density of $0.98g/cm^3$ was used as a curing agent. Surface modifier 3-Aminopropyltrimethoxysilane (APTMS) was purchased from Sigma Aldrich. Ball milled Iron(III)oxide particles with an average particle size of 800nm, 200 nm with density of $5.2g/cm^3$ were usedas a filler to fabricate the particulate composite. All the chemicals and materials were used in as received condition without any post process treatments.

2.2. Sample preparation
2.2.1 Ball milling process

Iron(III)oxide particles of diameter 800nm were ball milled for 16 Hrs. High energy planetary ball mill was used to reduce particle size by strain hardening principle [5]. The powder to ball ratio was maintained as 1:15 and ball material used was tungsten carbide. The planetary mill speed was setup with 300 rpm throughout the milling time. Particle size and morphology of particles were monitored by particle size analyzer and scanning electron microscope for intervals (1Hr, 2Hr, 4Hr, and 8Hr) respectively. The size of ball milled iron(III)oxide particles were measured with a particle size analyzer (Malvern V 2.2, Germany). Ball milled powder samples of refractive index 2.91 were dispersed in distilled water of refractive index 1.333, viscosity of 0.88 and ultrasonically stirred for 10 min with 70Hz before testing.
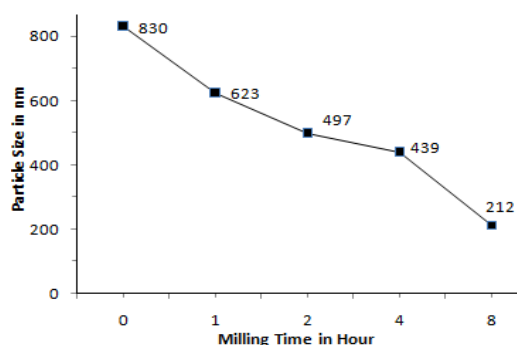

Fig.1. Effect of milling time on particle size

Surface morphology of ball milled iron(III)oxide particles was analyzed using scanning electron microscope (HITACHI S-3400 JAPAN). The fractured surface of the samples was coated with gold before scanning. The SEM images of ball milled iron(III)oxide particles in Figure 2 reveals that when milling time increases the size and shape of particles changed. It was observed that in Figure 2(a, b) the particles were in needle structure and irregular, where as in Figures 2(c, d) reduced size of particles and uniform spherical shape has been observed because of high milling time up to 8 hr.
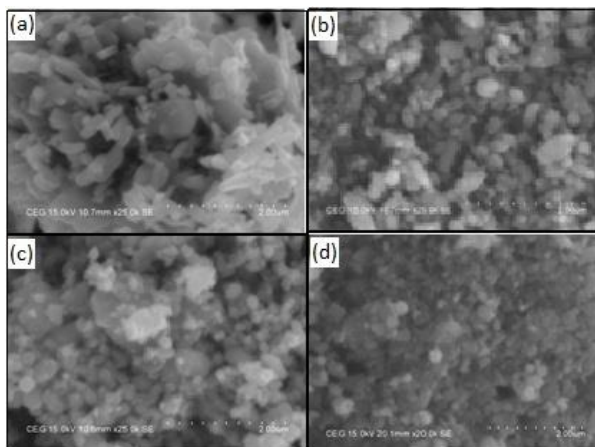
Fig.2.SEM images of (a) 0 hr, (b) 2 hr, (c) 4 hr, (d) 8 hr ball milled iron(III)oxide particles.

2.2.2 Preparation of siliconized iron(III oxide

The siliconized iron(III)oxide particles were prepared by hydrolysis process; in this the particles are briefly dipped in the ethanol – water solution. A 95 % of ethanol and 5 % of water were taken and mixed gently for 10 min. required amount of silane coupling agent generally 2 % concentration was added drop by drop to get homogeneous mixture followed by 5 min gentle stirring. Minimum surface coverage amount of silane has been calculated based on formula [6]. The particles were dipped in the ethanol - silane solution for 10 min. The precipitated iron(III)oxides were separated from aqueous solution by decanting excess solution manually. The precipitated particles were washed briefly with ethanol to remove excess silane and dried with 110℃ for 10 min in furnace to remove moisture and forms Si-O-Si structures [7].Figure 4 shows FTIR spectra of both silane and siliconized iron(III)oxide. The samples were analyzed by a FTIR spectroscopy (Bruker alpha ATR mode, Germany). Samples were kept in KBr pellet holder and reference spectra were recorded. The spectra was revealed that the siliconized iron(III)oxide contains absorbance peak at $3432cm^{-1}$ which indicate amine(NH_2) functional group on iron(III)oxide surface. Similarly wave lengths at $2900cm^{-1}$, $1470cm^{-1}$ and $998cm^{-1}$ revealed the presence of silane on particle surface. Thus siliconization process introduced silane functional group on particle surface. Figure 3(a and b) shows XRD graph of as-received and siliconized iron(III)oxide particles. The crystal structure analysis of iron(III)oxide powders were recorded with a XRD analyzer (Match phase analyzer, Germany). The radiation source used was Cu-Ka 1 and wave length was 1.54° Angstrom. The strong peak of (2θ) at 33.2° and 35.1° reveals the presence of rhombohedra α-fe_2o_3 with [h,k,l] pattern of (104) and (110).This data reveals that surface modification does not affect the crystal structure and phase ofiron(III)oxide particles.
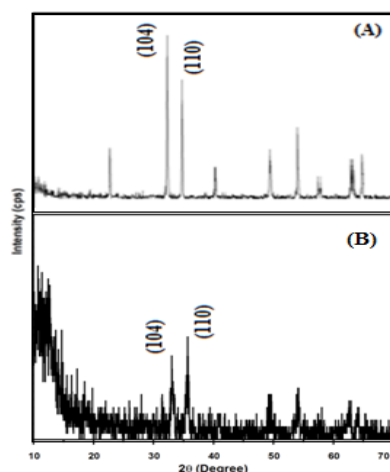
Fig. 3. XRD graphs of (a)as-received iron(III)oxide, (b)siliconized iron(III oxide particles.

2.2.3 Preparation of particulate composite

A fixed quantity of resin with varying volume percentage of siliconized iron(III)oxide particles (0.25, 0.5, 1.0, 2.0 and 4.0v%) were added to the resin at room temperature and stirred thoroughly until degassing process completed. A homogeneous mixture of resin and filler was produced at the end of stirring process. Curing catalyst (TETA) was then added by 10:1 weight ratios and stirred until a homogeneous solution was formed. The viscous colloidal suspension was poured into a rubber mould with wax coating and entrapped air bubbles were removed by cotton roller. The curing was done at room temperature for about 24 Hrs. Scheme 1 shows siliconized iron(III)oxide reaction with epoxy resin matrix. The **Table I** gives composition and designation for fabricated composites.
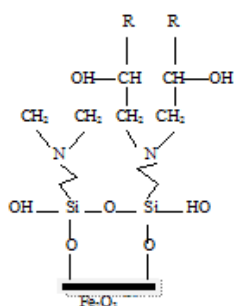
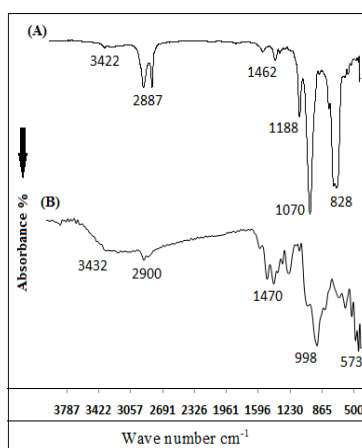*Scheme 1- Siliconized iron(III)oxide reaction with epoxy resin matrix.*

Fig.4. FTIR spectra of (a) pure silane (b) siliconized iron(III)oxide.

Table 1. Composition and designation of composites

Material Designation	Epoxy (vol %)	Fe_2O_3 (vol%)	Fe_2O_3size (nm)
R	100.00	0.0	-
RIa1	99.75	0.25	200
RIa2	99.50	0.50	200
RIa3	99.00	1.00	200
RIa4	98.00	2.00	200
RIa5	96.00	4.00	200
RIb1	99.75	0.25	800
RIb2	99.50	0.50	800
RIb3	99.00	1.00	800
RIb4	98.00	2.00	800
RIb5	96.00	4.00	800

R- Resin; Ia-200nm of Fe_2O_3; I_b-800 of Fe_2O_3

2.3. Dielectric Characterization
2.3.1 Dielectric characterization
The Dielectric property of composites were measured with a LCR Hi-TESTER 3532-50 (HIOKI – Japan) with operating range varies from 42Hz - 5MHz as per standard ASTM D 150. Samples were cut out as suitable rectangular pieces and dimensions were noted. The prepared samples were kept between parallel conductors and kept inside the heating chamber. Five identical samples were tested for each designation. Results were taken out as room temperature (28 ° C) and elevated temperature (100 ° C).

3. Results and discussion

3.1 Dielectric constant (ε)
The dielectric constant (relative permittivity) of epoxy resin was increased when adding more volume of filler this is because of charge mobility when polarization occurs. It is observed that polarization occurs when frequency was 100Hz at this region charge mobility is high. Introduction of more iron(III)oxide fillers increased the ability of effective polarization and charge carrier. Figure5 shows graph of dielectric constant to frequency. It is noted that dielectric constant was decreased gradually when frequency was increased. This is because of very high frequency affects relaxation time of dielectric to be polarized. Figure 6 shows the graph of dielectric constant (vs) frequency at 100º C from graph it is noted that increased temperate and frequency greatly affects the charge mobility in epoxy resin [8]. The increased temperature collapse the molecular structure of epoxy since glass transition temperature of epoxy is near 70º C at this temperature epoxy molecules gain enough energy and start rotate about primary C-C chain hence molecules orientation was affected.
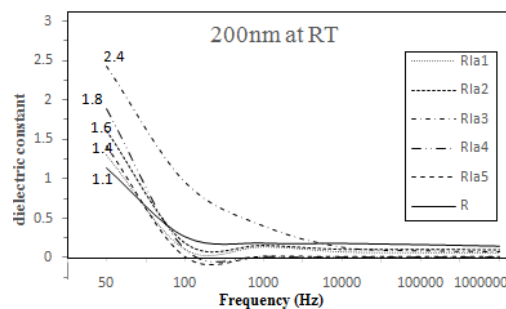

Fig.5. Dielectric constant (vs) frequency at room temperature 200nm siliconized iron(III) oxide
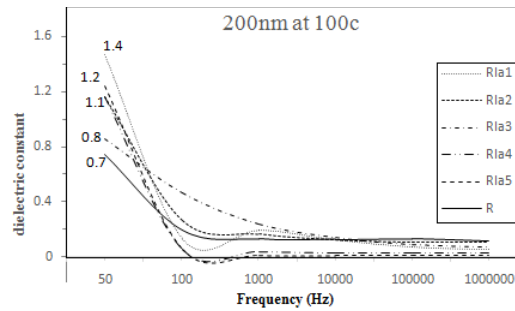
Fig.6. Dielectric constant (vs) frequency at 100 ºC 200nmsiliconized iron (III)oxide
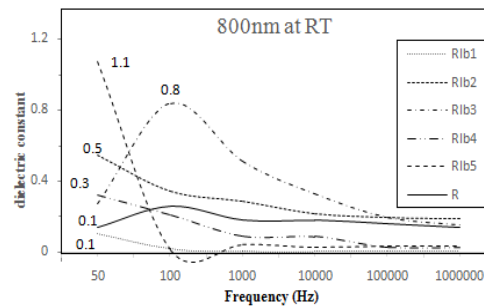

Fig.7. Dielectric constant (vs) frequency at room temperature 800nm siliconized iron(III)oxide
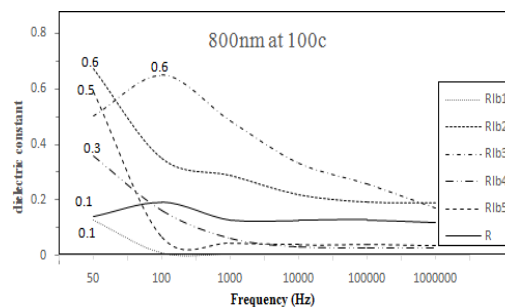

Fig.8. Dielectric constant (vs) frequency at 100 ºC 800nm siliconized iron(III) oxide

Figure 7 shows dielectric constant values against frequency for composites made up of 800nm siliconized iron(III)oxide with different volume ratios. The graph indicates relative permittivity of composites increased at lower frequency because of incorporated fillers, when frequency increases there is drop in relative permittivity. The particle size of 800nm filled composites gives lesser permittivity value than composites consist of 200nm. This is because of cluster formation of 800nm particles on resin matrix due to random filling affects chain network. Figure 8 shows the value of relative permittivity of 800nm filled composites at 100º C against to frequency. It is noted that when temperature increases free volume increases hence epoxy molecules randomly oriented this would be affected the polarization which leads lesser relative permittivity [9]. Figure 9shows the effect of particle dimension on dielectric constant of epoxy composite at 100Hz. It is observed that the dielectric constant was increased at the maximum (0.95) for RIa_3 when particle dimension was 200nm. This is because of less dimensioned particles filled in matrix evenly and forms a chain network []. Whereas 800nm particles formed as clumsy and overlapped this phenomenon affected the chain network of particles and affected charge mobility. Figure 10 shows effect of particle size on dielectric constant at 100ºC. Peak dielectric constant value of 0.64 was noted for composite which consist of 800nm particles (RI_{b3}). This is because of increased free volume. When volume increases these large dimensioned particles settle

down in proper epoxy molecular chain voids thus particles overlapping was reduced significantly. Since Iron content is directly proportional to charge mobility maximum dielectric constant was observed.
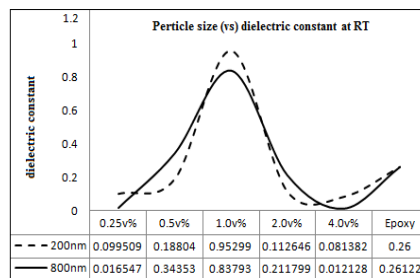

	0.25v%	0.5v%	1.0v%	2.0v%	4.0v%	Epoxy
200nm	0.099509	0.18804	0.95299	0.112646	0.081382	0.26
800nm	0.016547	0.34353	0.83793	0.211799	0.012128	0.26122

Fig.9. Dielectric constant at 100Hz (vs) siliconized iron (III)oxide particle size at RT

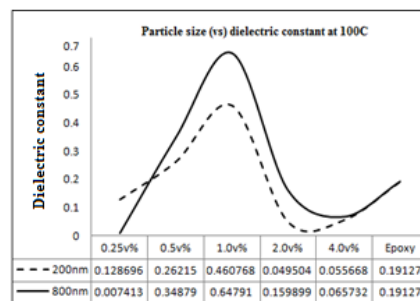|	0.25v%	0.5v%	1.0v%	2.0v%	4.0v%	Epoxy
200nm	0.128696	0.26215	0.460768	0.049504	0.055668	0.19127
800nm	0.007413	0.34879	0.64791	0.159899	0.065732	0.19127

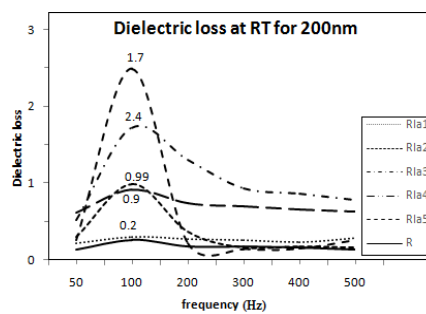*Fig.10. Dielectric constant at 100Hz (vs) siliconized iron(III) oxide particle size at 100ºC*

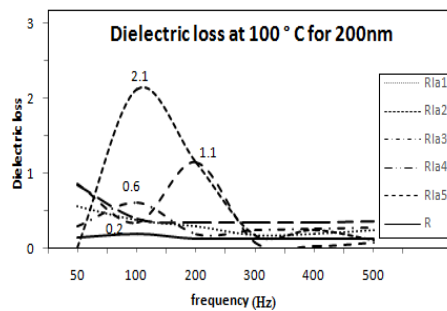*Fig.11. Dielectric loss (vs) frequency at RT 200nm siliconized iron (III)oxide.*

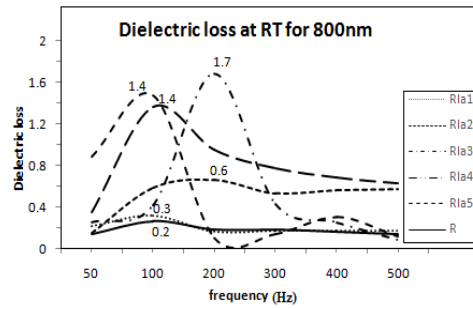*Fig.12. Dielectric loss (vs) frequency at 100ºC200nm siliconized iron(III)oxide.*

Fig.13. Dielectric loss (vs) frequency at RT 800nm siliconized iron (III)oxide.
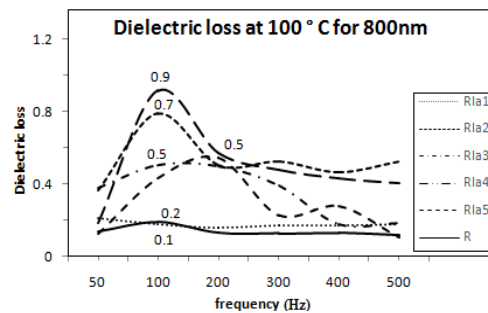

Fig.14. Dielectric loss (vs) frequency at 100ºC 800nmsiliconized iron (III)oxide.

3.2 Dielectric loss (D)

The dielectric loss of particulate epoxy composite was investigated with respect to frequency and temperature. When polarization occur electrons tends to mobile but fails and converted as a heat loss due to high band gap [10]. Figure 11 shows dielectric loss against to frequency (50Hz- 500Hz). It is noted that maximum dielectric loss was observed at 100 Hz this is because of exact relaxation time given to dielectric to be polarized. When frequency increases dielectric loss is decreased this is because of unresponsive nature of epoxy molecules. At higher frequencies epoxy molecules cannot response for every cycles of external field. Thus polarization got depleted which leads low mobility of charges. Figure 12 shows values of dielectric loss for composites which was filled with 200nm particles against to frequency at 100ºC. It is observed that dielectric loss was decreased by increasing frequency. The maximum dielectric loss was observed for composite designation RI_{b4} which is loaded with 2vol% of siliconized iron(III)oxide. Figure 13 and 14 shows dielectric loss values of 800nm particles reinforced epoxy composites. It is absorbed that all the composites got polarized around 100Hz and allows the charges to flow [11& 12]. At room temperature dielectric value is more and lesser at 100ºCbecause of rise in temperature affects molecule orientation and chain network. The figure 15and 16 shows the effectiveness of particle dimension on dielectric loss at 100Hz. It is noted that maximum dielectric loss was observed for 200nm particles reinforced epoxy composites. This is because of fine particles dimension favors even distribution and network formation [13, 14 & 15].
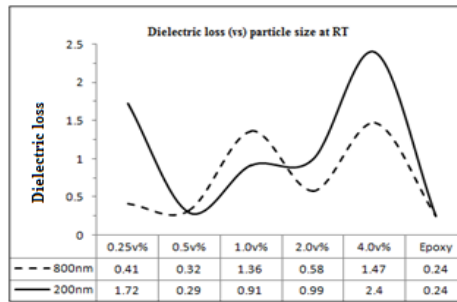
Fig.15. Dielectric loss at 100Hz (vs) siliconized iron (III)oxideparticle size at RT
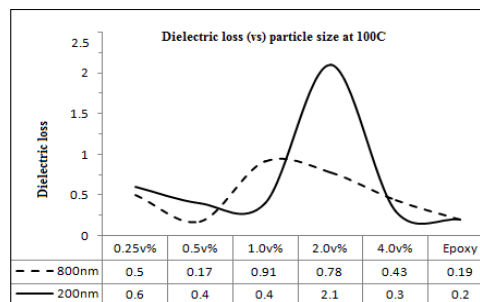

Fig.16. Dielectric loss at 100Hz (vs) siliconized iron oxide particle size at 100ºC

3.3 Morphology

The morphology of as received and surface treated iron(III)oxide particles reveals that particles were formed as a cluster (rounded portion) in figure 17(a)this is because of ionic attraction between free OH^- of epoxy and Fe^+ of iron oxide. Figure 17(b) shows even distribution of particles in matrix. This is because of surface treated particles reacted with epoxy chain and distributed evenly. Hence surface treatment on particle surface improved chain network of particles in polymer matrix thus enhanced maximum charge mobility.
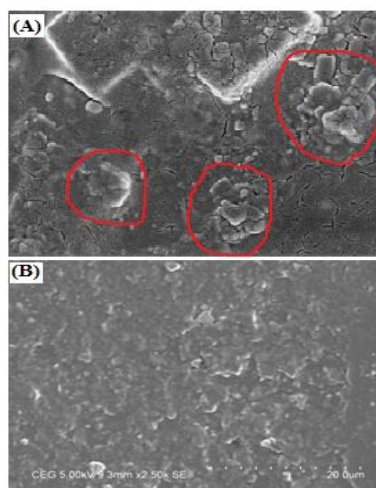

Fig.17. SEM images of (a) As-received iron(III)oxide and (b)siliconized iron(III)oxide particles in epoxy matrix.

4. Conclusions

From results the following conclusions have been made. Additions of siliconized iron(III)oxide particles changes the dielectric behavior epoxy resin composite. The as-received particles did not change the dielectric properties as much as effective. Whereas additions of surface modified iron(III)oxide particles increased the dielectric constant and dielectric loss.

The temperature plays effective role in improving the dielectric constant and dissipation factor. The dissipation factor found to be high due to large charge conversion. The SEM images revealed that the as-received particles formed cluster whereas surface modified particles increased the dispersion effectiveness on matrix. Thus these composites could be used in warm up of polymer material under external frequency.

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