CARACTERIZAREA TRIBOLOGICĂ A MODIFICĂRILOR DE SUPRAFAȚĂ DUPĂ TRATAMENTE TERMICE APLICATE COMPOZITELOR HEMATIT - EPOXIDICE

DRY SLIDING WEAR CHARACTERISTICS OF HEAT TREATED AND SURFACE MODIFIED HEMATITE PARTICLES-EPOXY PARTICULATE COMPOSITE

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In this present work particulate epoxy composite was prepared with thermo assisted surface treated Fe_2O_3fine particles. The principal aim of this work is to improve wear resistance of epoxy resin by reinforcing iron oxide particles. Particle size of 800nm and 200nm were used to fabricate particular composites. Particles were heat treated from 30 º C to 900 º C in a muffle furnace to relive induced stresses which are gained in pre processes and getting magnetite phase. The resultant phase change in iron oxide particles were confirmed by X-ray diffraction. The heat treated particles were again surface treated with a silane coupling agent 3-Aminopropyletriethoxysilane (APTMS). The composites were prepared with reinforcement of 1wt%, 3wt% and 5wt% of iron oxide filler into epoxy resin. All proportions of composites were cured by an aliphatic hardener triethylenetetramine (TETA). Wear characters of epoxy-iron(III)oxide system was studied with pin-on-disc setup. Wear resistance was improved significantly for particle loaded composite in which heat treated siliconized iron oxide-epoxy system gave better result. Scanning electron microscopic images revealed filler dispersion on epoxy matrix.

Keywords: *Particulate composite; APTMS; SEM; Optical microscopy; Pin-on-disc*

1. Introduction

Particles reinforced polymer matrix composites have attractive applications like super hard behavior, Dielectric heating, fluid magnetism, high thermal stability, high wear resistance and good mechanical properties. Adding ceramic fillers like Iron (III) oxide into high strength thermoset polymer like epoxy resin the wear resistance, impact and hardness could be improved [1].When the wear resistance of epoxy composite increases then these materials could be used as a best alternate material for manufacturing high wear resistance plastic gears for precise power transmission purpose. Strengthen the polymers via particle addition is an easy and efficient process where process parameters are minimum [2]. Ball milling could be used to produce low dimension particles where particles are subjected to heavy collision with metal particles and strain hardening leads particle deformation [3]. Heat treatment of iron(III)oxide particles are required to relive residue stresses which are gained in ball milling process and improves oxygen content per unit cell of iron. Getting magnetite phase via chemical reaction (sol-gel) could be a tedious pro - cesses instead the hematite particles could be heat treated to obtain magnetite phase. Particles could be heated up to 900 º C and socked for 1 hour then air cooled to room temperature. In this slow process the hard magnetite could be formed. Magnetite consist of few more extra iron atoms than hematite thus wear rate could be significantly reduced. More uniform dispersion of particles in resin matrix and high adhesion is require to establish high hardness and high wear resistance. To achieve good dispersion and adhesion of iron (III) oxide particles surface modification with an amino functional coupling agent Aminopropyltriethoxysilane (APTMS) could be used. The FT-IR spectra results could be confirmed the attachment of bi functional coupling agent on treated iron (III) oxide particles. Pin-on-disc setup could be used to find the wear resistance of fabricated epoxy composite. Manoj singla.et.al confirmed that the addition of fly-ash particles increased the wear and hardness of composites. Dillini.et.al has concluded that incorporation of particles increased hardness and other mechanical properties of cured resin. Thus hard magnetite particle addition could be a

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most efficient process to improve the tribology properties of epoxy resin.

2. Experimental procedures

2.1 Materials

The epoxy resin used in this study was liquid diglycidyl ether of Bisphenol-A type having viscosity of 12000 cps and density of 1.2g/cm^3 at 25^o C. Triethylenetetramine, a low viscosity aliphatic amine having viscosity of 20cps and density of 0.98g/cm^3 was used as a curing agent. 3-Aminopropyltriethoxysilane (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 used as filler. Figure 1 shows the shape and size of 800 and 200nm iron(III)oxide particles which were scanned using HITACHI S-3400JAPAN.

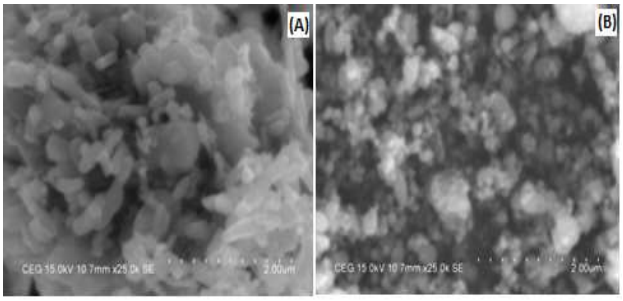

Fig.1 - SEM images of (a) 800nm iron (III) oxide (b) 200nm iron (III) oxide particles.

2.2. Sample preparation

2.2.1. Heat treatment process

The ball milled iron oxide particles was heat treated with a muffle furnace having temperature variation from room temperature to 1600 º C. particles were kept in a silica crucible with a lid and the temperature was raised slowly. When the temperature reaches 900 º C heating process was stopped and maintain in the same temperature for about 1 hour. Finally, the iron oxide powder was taken away and kept outside of furnace to reduce the temperature up to room temperature [4]. Crystal structure and form of iron (III) oxide before and after heat treatment was confirmed with x-ray diffraction peaks (Match Phase analyzer, Germany). The Figure 2(a) shows XRD graph of as-received iron (III) oxide particles. The maximum peak of 33.2^o 2 theta reveals the presence of rhombohedra crystal structured alpha-$Fe_2O_3$with 104 lattice pattern and other peaks of $Fe_2O_3$was appeared at 35.1º(110), 49.3º(024), 54.3º(116). The Figure 2(b) shows the XRD peaks of 900 º C heat treated iron oxide particles. The maximum peak intensity was formed at 35.1º (2θ) which indicates formation of magnetite (Fe_3O_4) by more oxidation in heat treatment process. These magnetite molecules are larger in size hence larger 2θ was obtained. Relatively larger intensity peak was formed at 33.2º (2θ) also which indicates the presence of hematite structure (alpha-Fe_2O_3). Crystallite size was found out using Debye-Scherer formula and the value was 44nm for as-received iron(III) oxide particles and 48 Hr heat treated iron(III) oxide particles.

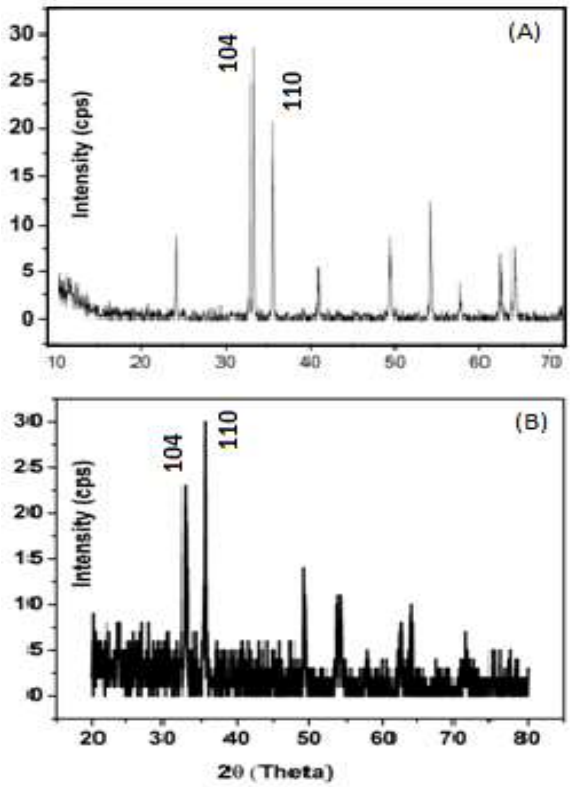

Fig. 2 - XRD patterns of (a) ball milled iron (III) oxide (b) heat treated iron (III) oxide.

2.2.2. Preparation of siliconized iron (III) oxide

The siliconized iron (III) oxide particles were prepared by aqueous solution method [5, 6].. The heat treated particles were immersed in the ethanol – water solution for 10min. Required amount of silane coupling agent generally 2wt% was added into aqueous solution to get homogeneous mixture followed by 5 min gentle stirring. The Figure 3 shows the surface modification reaction.

2.2.3. Preparation of particulate composite

Fixed quantity of resin was mixed with 1wt%, 3wt% and 5wt% of heat treated surface modified iron (III) oxide particles of size 200 and 800nm. Particles were added into resin and stirred thoroughly. Curing catalyst triethelyene tetramine was added by recommended weight ratio and stirred until a homogeneous solution was formed [7, 8]. The resulted suspension was poured into a hallow aluminum cylindrical mold. The curing was done at room temperature for about 24 Hrs. Figure 4 shows reaction between epoxy and siliconized iron (III) oxide particles.

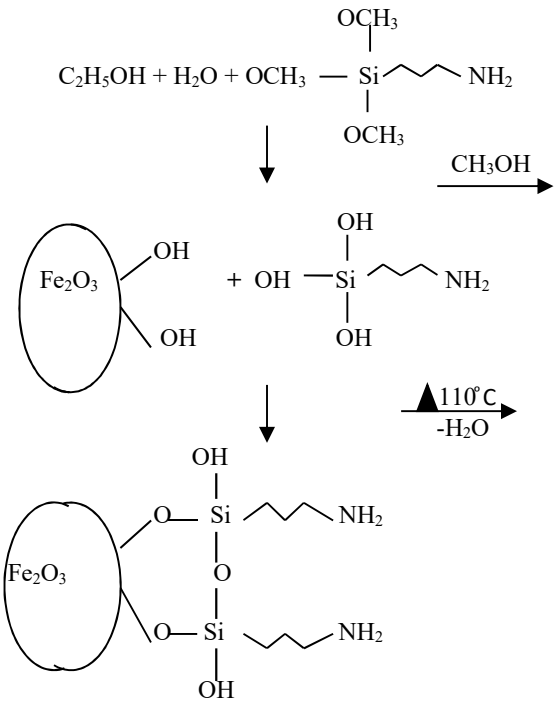

Fig.3-Surface modified reaction of (3- aminopropyle)trimethoxysilane on iron(III) oxide surface [5].

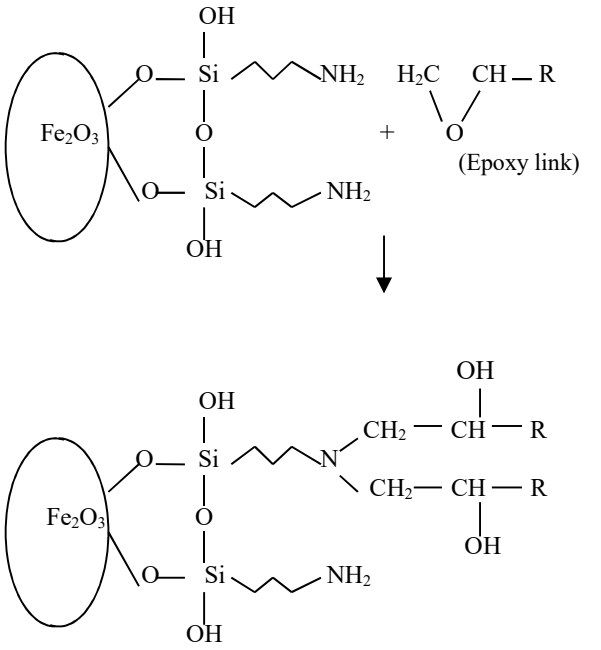

Fig. 4 - Reaction between epoxy to surface modified iron (III) oxide particles [5].

2.3. Specimen preparation

The prepared iron(III)oxide filler reinforced epoxy composite specimens were checked for dimensions based on pin-on-disc experimental requirements. Suitable dimensions, length 30mm and diameter 8mm was prepared by post machining process. The designation and composition of hybrid composites are presented in Table 1.

Table 1

Composition and designation of composites

Material Designation	Epoxy (wt %)	Fe_2O_3 (wt%)	Fe_2O_3size (nm)
R	100.0	0.0	-
RI_1	99.0	1.0	800
RI_{11}	97.0	3.0	800
RI_{12}	95.0	5.0	800
RI_2	99.0	1.0	200
RI_{21}	97.0	3.0	200
RI_{22}	95.0	5.0	200
RIh_1	99.0	1.0	800
RIh_{11}	97.0	3.0	800
RIh_{12}	95.0	5.0	800
RIh_2	99.0	1.0	200
RIh_{21}	97.0	3.0	200
RIh_{22}	95.0	5.0	200
RIs_1	99.0	1.0	800
RIs_{11}	97.0	3.0	800
RIs_{12}	95.0	5.0	800
RIs_2	99.0	1.0	200
RIs_{21}	97.0	3.0	200
RIs_{22}	95.0	5.0	200

R- Resin; RI_h- heat treated Fe_2O_3; RI_S- siliconized Fe_2O_3.

2.4. Mechanical characterization

Wear characters of heat treated and silane modified iron oxide-epoxy system was unveiled by a pin-on-disc setup (Ducom instruments pvt.Ltd, India).The pin-on-disc has wear track diameter of 50-100mm, wear disc diameter up to 165mm, disc speed of 100-2000 rpm and normal load of 5-200N.The wear test was carried out based on ASTM standard G99 and set variables. The load applied 10N; sliding speed of 1000rpm and sliding time of 5min was selected as a process parameter. The hardness of composites was tested using Durometer (Shore-D) as per ASTM-D 2240.

3. Results and Discussion

3.1. Mechanical

The wear rate, wear volume and frictional force for particulate composites were listed in **Table II**. The addition of iron(III)oxide was increased the wear resistance when compare with virgin epoxy resin [9]. Whereas the heat treated iron(III)oxide served substantial increment in wear resistance when compare with as-received iron(III)oxide filled composite, this is because of formation of magnetite in heat treatment. In heat treatment process above 900ºC favors more oxidation thus oxygen per unit cell increases. Due to increases of oxygen content the regular shape rambohedra become unusual structure and creates vacant in unit cell. The extra acquisition of oxygen in every unit cell reacts with extra iron atoms, thus iron per unit cell increases. More iron content directly proportional to strength of composite. It is observed that the particle size of 200nm was worked well with epoxy matrix to share the load due to high surface area. The wear resistance was increased for composite designations RI_1, RI_{11}, RI_{12}, RI_2, RI_{21}, and RI_{22} is (58%, 60.5%, 73%, 66%, 72% and 82%)

Table 2

Mechanical properties of composites

Material Designation	wear (microns)	applied load (N)	wear volume (cubic microns)	Frictional force (N)	Wear rate (m/s)	Hardness (shore-D)
R	578	10	14.5	0.5	4.81	85
RI_1	241	10	6.1	1.4	2.01	87
RI_{11}	228	10	5.7	0.3	1.90	88
RI_{12}	156	10	3.9	1.8	1.30	90
RI_2	197	10	4.9	0.9	1.64	86
RI_{21}	159	10	4.0	3.0	1.32	88
RI_{22}	103	10	2.6	1.3	0.85	89
RIh_1	210	10	5.2	2.7	1.75	87
RIh_{11}	197	10	4.6	1.2	1.66	89
RIh_{12}	111	10	2.9	0.1	0.92	91
RIh_2	158	10	3.9	0.8	1.31	86
RIh_{21}	149	10	3.4	1.9	1.21	88
RIh_{22}	91	10	2.4	0.9	0.74	91
RIs_1	190	10	4.4	1.0	1.58	87
RIs_{11}	174	10	3.8	0.8	1.49	89
RIs_{12}	96	10	2.6	0.1	0.76	90
RIs_2	120	10	3.0	0.1	1.00	88
RIs_{21}	107	10	2.7	0.9	0.90	89
RIs_{22}	88	10	2.2	0.1	0.73	91

respectively. The heat treated particles greatly withstand against of frictional force applied. The increased value of wear resistance for heat treated particle loaded composites RI_{h1}, RI_{h11}, RI_{h12}, RI_{h2}, RI_{h21}, and RI_{h22} is (63%, 66%, 80%, 77%, 74% and 84%) respectively. The heat treated cum silane treated iron oxide particles shows better improvements in wear resistance. Even dispersion and interfacial attachment between resin and filler yield maximum wear resistance.

The increased wear resistance was noted for composite designation RI_{s1}, RI_{s11}, RI_{s12}, RI_{s2}, RI_{s21}, and RI_{s22} is (67%, 70%, 83%, 79%, 81% and 85%) respectively. Thus processes like heat treatment and surface modification of fillers improve mechanical behavior of virgin epoxy polymer when it serves high surface contact applications. The hardness values of iron oxide reinforced epoxy resin shows better improvements. Table 2 provides Shore-D micro hardness values of particulate composite. The maximum hardness value of 91 Shore-D was absorbed for material designation RI_{h12}, RI_{h22} and RI_{s22}.This is because of high density of iron atoms packed in every unit cell [10]. The improved value of hardness for composite designations RI_1, RI_{11}, RI_{12}, RI_2, RI_{21}, and RI_{22} is (2.3%, 3.5%, 5.5%, 1.1%, 3.5% and 4.5%) respectively.

The heat treated iron oxide particles shows better improvements in hardness. The improved values for composite designation RI_h1, RI_{h11}, RI_{h12}, RI_{h2}, RI_{h21}, and RI_{h22} is (2.3%, 4.5%, 6.6%, 1.1%, 3.5% and 6.6%) respectively. The particles which were treated with both heat and silane shows refined results in hardness. The hardness values of composite designation RI_{s1}, RI_{s11}, RI_{s12}, RI_{s2}, RI_{s21}, and RI_{s22} is (2.3%, 4.5%, 5.5%, 3.5%, 4.5% and 6.6%) respectively.

3.2. Morphology

Morphology of pure (Fig.5a) and particle reinforced composite system shows, the as-received iron oxide particles were formed a cluster structure in epoxy matrix (Fig.5b).This is because of dipole attraction of OH molecules from epoxy resin and Fe atoms from iron oxide [11, 12, and 13]. But in silane treated particles, even dispersion could be seen because of silane attachment on particle surface (Fig. 5c and 5d). The silane treatment ensures reaction with epoxy matrix and iron oxide via NH_2functional group [14and 15].

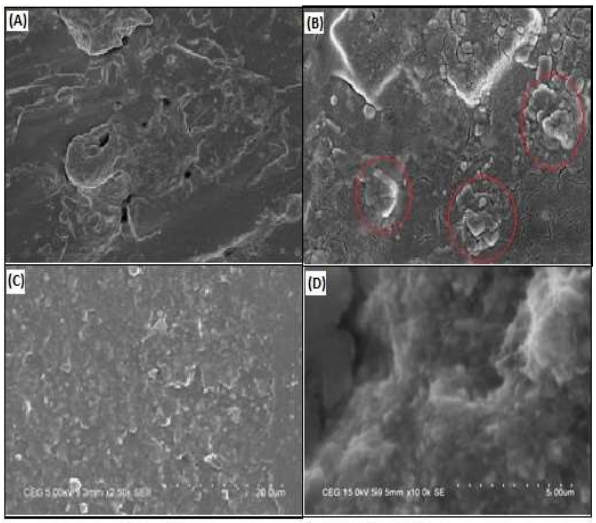

Fig. 5 - SEM images of (a) pure resin (b) as received iron oxide in matrix (c and d) siliconized iron oxide in matrix.

The surface morphology of wear surface shows that the pure epoxy (Fig.6a) had a smooth surface without any porous surface. This is because of no filler was added in epoxy matrix whereas in iron oxide particles loaded epoxy composite

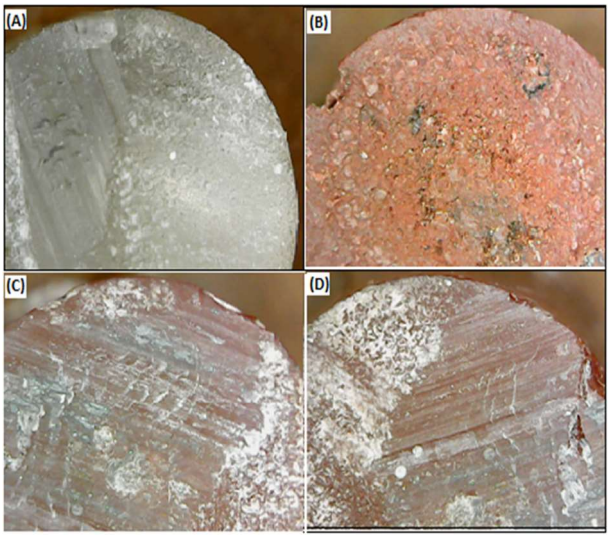

Fig. 6 - Optical macroscopic images of (a) pure resin (b) as received iron oxide in matrix (c) heat treated iron oxide and (d) HT cum siliconized iron oxide in matrix.

(Fig.6b) shows that the surface was highly rough and more porous. It indicates that the presence of iron oxide particles before wear test and same was fled away when friction force is applied. Wherever the particles were present before wear test those areas shows more porous. The Fig. 6c shows surface morphology of heat treated iron oxide reinforced epoxy composite. It is very clear that the surface is smooth like a pure epoxy since the reinforced particles were eventually removed, there is no particle fled off hence less porous is observed. The Fig. 6d shows heat treated cum surface modified iron oxide-epoxy composite. The color of iron oxide is changed because of phase change during heat treatment [16].

4.Conclusion

Based on the results following conclusion could be made. The particle addition is an easy and efficient way to increase wear resistance and hardness of polymers. To obtain greater wear resistance for polymer composites the fillers would be heat treated and processed. Iron is an allotropy material hence it is a noteworthy selection as iron oxide will be a filler material. Heat treatment up to 900 ºC and slow cooling of iron oxide particles rendered phase change and conversion of magnetite phase from hematite phase. Magnetite is harder than hematite hence better wear resistance was achieved. The maximum wear resistance achieved by heat treatment process was 84%. Uniform dispersion of iron oxide fillers has been achieved by surface modification process. The heat treated and surface modified iron oxide particles served substantial improvements in wear resistance of epoxy polymer. The maximum wear resistance of 85% was obtained for the epoxy composite which was filled with 5wt% of heat and surface treated . particles. In hardness the particle addition shows better improvements. The maximum increased hardness of 91 Shore-D (6.6%) was noted for 5wt% of particles filled epoxy composite. Thus iron(III)oxide particles addition followed by heat treatment and surface modification is a pivoting rule to obtain good wear resistance value of any polymer materials.

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