Silicon (2020) 12:2533–2544
https://doi.org/10.1007/s12633-019-00347-7

ORIGINAL PAPER

Effect of Silicon Coupling Grafted Ferric Oxide and E-Glass Fibre in Thermal Stability, Wear and Tensile Fatigue Behaviour of Epoxy Hybrid Composite

Arun Prakash V R[1] · **Jayaseelan V**[2] · **Mothilal T**[3] · **Manoj Kumar S**[1] · **Melvin Victor Depoures**[4] · **Jayabalakrishnan D**[5] · **Ramesh G**[6]

Received: 16 August 2019 / Accepted: 1 December 2019 /

Abstract

In this present study the effect of adding silicon coupling grafted ferric oxide and E-glass fibre in thermal stability, wear and fatigue behaviour of epoxy resin hybrid composite was investigated. The principal aim of this research was explicating the importance of silicon coupling grafted E-glass fibre and ferric oxide particle in thermal stability, wear and fatigue properties of epoxy hybrid composite. Ferric oxide particles of 800, 200 and < 100 nm and E-glass fibre of 600 GSM was used as second phase additions in epoxy resin with surface grafted condition. The surface grafting was done using 3-Aminopropyletrimethoxylane via aqueous solution method with acetic acid as pH adjuster. The improvement of 80% was observed in initial thermal stability of surface grafted E-glass fibre epoxy composite on comparing with un-modified glass-epoxy composite. Similar improvements were noted in rapid and final decomposition stages also. The lower specific wear rate of 0.002 was observed for surface grafted E-glass and ferric oxide added composite designation $EGFI_{11}$. The worn surface frcatograph explicated flat and smooth wear track surface for surface grafted composite designations. A highest fatigue life cycle of 18,724 is observed for surface modified composite designation $EGFI_{21}$. These thermally stable and high wear resistance and fatigue strengthened composites could be used in automobile, aircrafts and domestic applications.

Keywords PMC · Silicon coupling · Thermal behaviour · Wear and tensile fatigue

1 Introduction

Synthetic and natural fibre-reinforced particle added epoxy hybrid composite materials are promising materials in structural, automobile and domestic applications due to their lower density, high strength, easy processing methods and cost effective nature [1]. To improve mechanical and thermal properties of virgin epoxy resin, fibre and particle strengthening could be a effective method since these two strengthening mechanisms needs lower process parameters like low operating temperature, no requirements of special atmospheric conditions and low power consumption equipments [2]. Generally the type of fibre and particle could be selected based on the outcome expected in the final composite material. The fibre addition improves the mechanical properties as predominant and the particle addition improves mechanical properties, thermal stability, wear resistance and some time used as filling element when cost reduction is required [3]. When these fibre and particle is added into thermoset resins moisture formation is a documentary issue and it is highlighted by

✉ Arun Prakash V R
vinprakash101@gmail.com

[1] Department of Mechanical Engineering, J.N.N Institute of Engineering, Anna University, Chennai, India

[2] Department of Mechanical Engineering, Prathyusha Engineering College, Anna University, Chennai, India

[3] Department of Automobile Engineering, KCG College of Technology, Anna University, Chennai, India

[4] Department of Mechanical Engineering, Saveetha School of Engineering, Chennai, India

[5] Department of Mechanical Engineering, Sriram Engineering College, Anna University, Chennai, India

[6] Department of Mechanical Engineering, MEA Engineering College, Malapuram, Kerala, India

many researchers [4]. The formation of moisture leads the final composite material become poor in mechanical strength and thermal stability. When tensile or bending load is applied the bounded moisture initiates crack and led the composite fracture at lower loads. Similarly the acquired moisture also provides poor thermal stability while the composites are subjected to heating. More mass loss could occur at lower temperature itself due to moisture. The effect of as-received iron (III) oxide particle in thermal stability of epoxy resin was already explained by the authors in their earlier studies [5]. The authors confirmed that addition of as-received particles reacted with free OH molecule from epoxy resin and produced aqua. This aqua molecule evaporates from composites at lower temperatures thereby higher mass loss could occur. Similarly the tensile, flexural and impact properties of as-received iron (III) oxide particle dispersed epoxy resin composite showed decrement in strength due to particle clustering. Ramesh et al. [6] concluded that adding as-received iron (III) oxide particle into epoxy resin gives higher wear volume than composites made of silane treated iron (III) oxide particles. Dinesh et al. [7] explicated their research findings in thermal stability of synthetic fibre reinforced polymer matrix composites. They confirmed that adding un-modified fibres into epoxy matrix gives lower glass transition temperature and larger mass loss. Thus it is clear that to achieve better mechanical and thermal properties in polymer matrix composites the surface-modified fibre and particles are required to strengthen the virgin matrix. The surface of the reinforcements could be modified by acid, base and silane coupling agent based on the activation mechanism needed on second phase's surface [8]. To improve mechanical behaviour, acid and base treatment could be done on second phase's surface, which may improves inter-locking mechanism between fibre and resin, which could offer higher delamination resistance. But when high concentrated acid or base is utilized for surface modification leaching could happen, which marginally affects the mechanical properties due to lower in cross sectional area [9]. But to improve adhesion of fibre with matrix and dispersion of fine particle in high denser matrix silane surface treatment could be useful. In silane surface treatment the fibre's original cross section never get affected. The silane may cover the surface of fibre and particle without affecting the cross-sectional area. Moreover the silane coupling agent contains reactive functional group (NH_2), which may create possible chemical linking with matrix while curing process takes place, which improve adhesion of fibre and particle with matrix [10]. Most of the researchers have studied the mechanical, thermal and tribological effect of acid and base treatment on fibres and particles and work relating to silane surface modification on both fibre and particle in fatigue behaviour is not explicated. Thus this present study aims to fill the gap by studying the fatigue behaviour of silane treated glass fibre and iron (III) oxide particles. Generally the silane coupling agents could select based on the functional group required and type of matrix used. When thermoset plastics are used as matrix amino silanes are preferred. Since amino silanes contain NH_2 functional group they could react with unsaturated OH molecules of matrix and improves the adhesion between fibre-matrix interfaces [11]. The silane surface modification could be done by aqueous solution method since the productivity is higher compare than other methods. Similarly simple process parameters like low operating temperature, moderate stirring rpm, no atmospheric restrictions and minimal toxicity exposure woos the aqueous solution process as more preferable process to do silane surface modification [12]. The hybrid polymer matrix composites could be prepared using hand lay-up method since this method follow simple process parameters [13]. These thermally enhanced, high wear resistance epoxy composites could be used as alternate material for metallic materials in automobile, domestic and structural applications. Since these composites are lesser in weight and retains high mechanical strength they could be used in air craft, sports bike and sports equipments applications. Similarly, the improvement in wear resistance woos these composites to be placed as brake pads in automobile.

2 Materials and methodology

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 12,000 cps and density of 1.2 g/cm^3 at 25 C. Triethylenetetramine (TETA, Huntsman India Ltd. Mumbai., HY951), a low viscosity aliphatic amine having viscosity of 20 cps and density of 0.98 g/cm^3 was used as a curing agent. 3-Aminopropyltrimethoxysilane (APTMS) was purchased from Sigma Aldrich. E- Glass fiber continuous woven mat (0–90°) with density of 2.54 g/cm^3 was used as reinforcement. Ferric Chloride ($FeCl_3$) of molecular weight 169.8 g/mol and Sodium hydroxide (NaOH) of molecular weight 40 g/mol were taken for Sol-gel process and purchased from Merck India ltd. Ball milled Iron (III) oxide particles with an average particle size of 800 nm, 200 nm and sol-gel prepared average 100 nm with density of 5.2 g/cm^3 were used as a filler to fabricate the hybrid polymer composite.

2.2 Particle Preparation

2.2.1 Ball Milling Process

The un-modified ferric oxide particles of diameter 800 nm were ball milled for 16 Hrs. High energy planetary ball mill was used to reduce particle size by strain hardening principle. 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. The before and after ball milled particle's size and morphology was monitored by particle size analyzer (Malvern 2.0, USA) and scanning electron microscope (HITACHI S-3400, JAPAN). It is noted that the initial particle size was 800 nm it became 200 nm after 16 h ball milling. This reduction is the cause of more strain hardening occurred due to heavy collision of particles. This high strain hardening leads formation of small particles with lower dimensions. Figure 1a, b shows the scanning electron microscopy image of ball milled ferric oxide particles. Figure 1a shows the as-received particle with larger dimension. The particle shows needle morphology in as-received condition. Figure 1b shows the image of 16 h ball milled ferric oxide and it explicit uniform spherical morphology [14].

2.2.2 Sol-Gel Process

In sol-gel ferric chloride ($FeCl_3$) of 1Mol and NaOH of 2 Mol has been taken. The sol of two metal atoms was prepared after constant stirring up to 1 h with 60 C raising the temperature of sol up to 80 C and allowed to evaporate the sol until dark brown gel was formed. The gel was kept in a silica crucible at 300 C in hot oven for 4 h and then furnace cooled to room temperature thus nano scaled ferric oxide particle was formed. Figure 1c shows the transmission electron microscopy image of sol-gel prepared ferric oxide particle. The TEM with EDAX images were analyzed using a high resolution transmission electron microscopy (JEOL JEM 2100 JAPAN). Figure 1d shows The EDAX graph of ferric oxide particle, which explicit oxide state of iron in the absence of other impurity atoms.

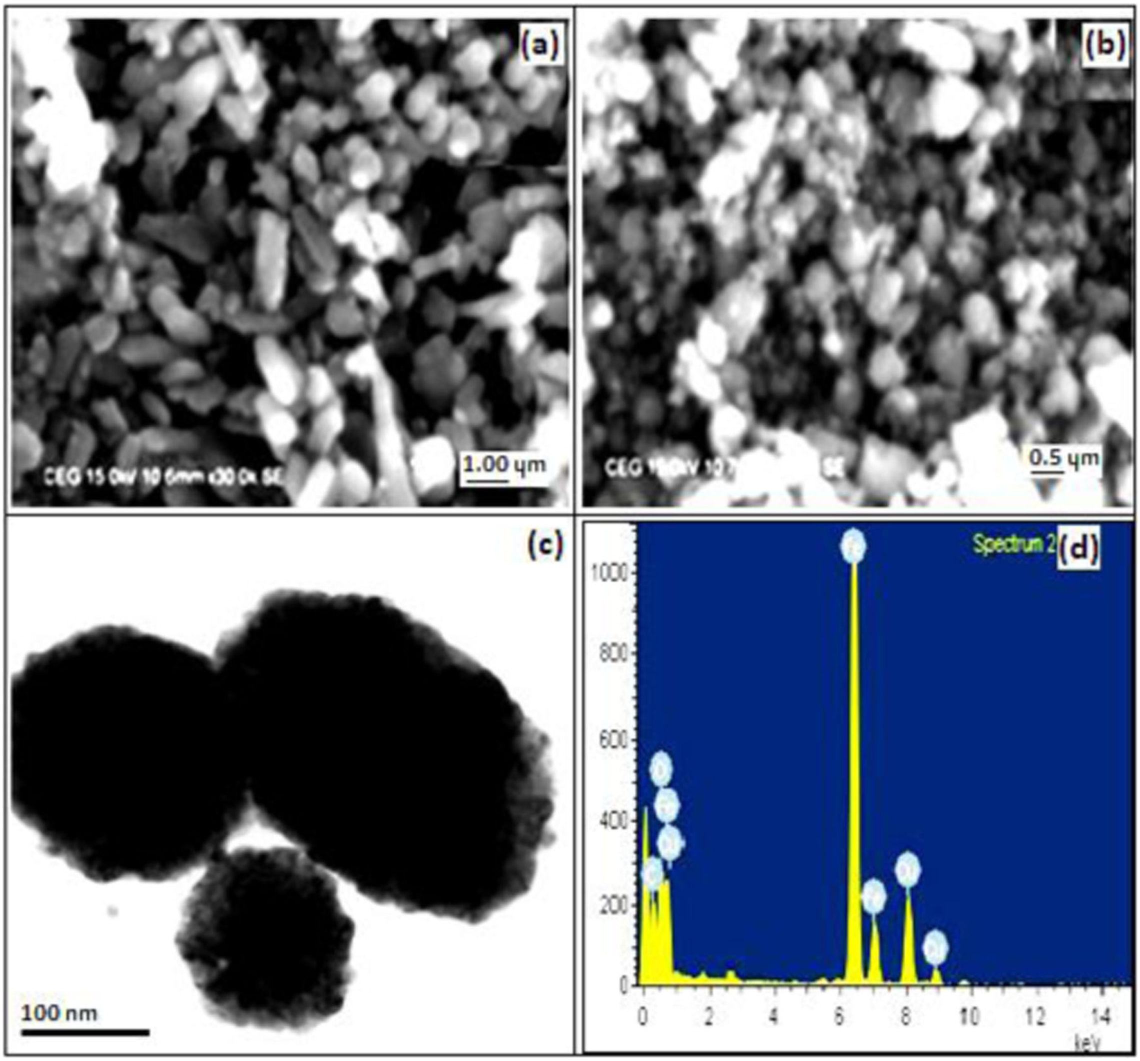
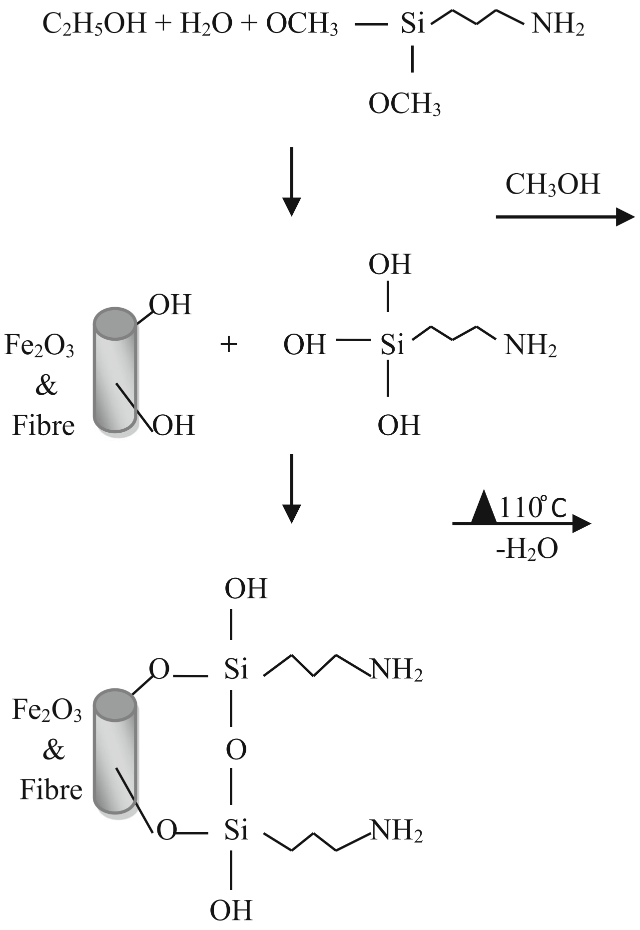


Fig. 1 **a**, **b** SEM images of ferric oxide particle and **c**, **d** shows TEM images of ferric oxide particle

2.3 Preparation of Silicon Coupling Grafted Ferric Oxide Particle and E-Glass Fiber

Silicon coupling grafted ferric oxide particle and E-glass fibre were prepared via hydrolysis process; in this the particle and fibre are immersed 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 was then added drop by drop followed by 5 min gentle stirring. The particles and fiber were dipped in the ethanol water solution for 10 min. The isolated ferric oxide and fiber was separated from aqueous solution by decanting excess solution manually. The precipitated particles and fiber were washed with ethanol to remove excess silane and dried at 110 C for 10 min in a hot air oven to forms silanol structures [15]. Scheme 1 shows the silane surface-modification done on E-glass fibre and iron (III) oxide particles.

Figure 2 shows the NMR peaks of silicon coupling grafted ferric oxide particles. A Bruker AVANCE III HD, 400 MHz, NMR spectro-meter was used to analyze the surfaces of ferric oxide to confirm the functional group attachment. A strong peak at 4.1 ppm indicates the presence of C-H and N-H groups on silane treated ferric oxide surface, which is attached with propyle group. The weak peak at 5.7 ppm indicates the presence of C=C-H groups, which may be formed during the acid hydrolysis process of silane. Thus the silane treatment modifies and activates the surfaces of ferric oxide, which may ensure better dispersion and adhesion in high denser matrix [16].



Scheme 1 Silane surface-modification process on E-glass fibre and particle

2.4 Preparation of Hybrid Composite

A fixed quantity of resin was mixed with varying volume percentage of ferric oxide particles (0.5 and 1.0) at room temperature and stirred thoroughly until complete mixing takes place. A homogeneous mixture of resin and particle was produced at the end of stirring process. Curing catalyst (TETA) was then added by 10:1 weight ratio and stirred until a homogeneous solution formed. The viscous colloidal suspension was then poured into a rubber mould with wax coating and 30 volume percentage of E- Glass woven mat (3- ply) was laid with epoxy resin matrix and entrapped air bubbles were removed by cotton roller. The excess resin was wiped out manually to get uniform thickness of composite. The curing was done at room temperature for about 24 h and post cured for 48 h [17].

2.5 Specimen Preparation

The prepared E-glass fiber–particle dispersed epoxy composites were taken out from mould and cleaned neatly. Specimens of suitable dimensions according to ASTM standards were cut by abrasive water jet machining (Maxiem water jets 1515, KENT, USA) with garnet size of 80 Mesh; abrasive flow rate of 0.30 Kg/min, maximum pressure of 225 MPa and nozzle diameter of 1.1 mm [18]. The designation and composition of hybrid composites are presented in Table 1.

2.6 Characterization

2.6.1 Thermal Analysis

The thermal behavior of composite was analyzed with a thermo gravimetric analyzer (NETZSCH STA Jupitar 409 PL Luxx, Germany) under N_2 atmosphere. Samples were scanned from 0 to 600 C at the heating rate of 10 C/min with crucible material as Al_2O_3. The thermo gravimetric analysis was performed to study the mass loss of polymer composite with rise in temperature.

2.6.2 Wear Characteristics

The wear properties of E-glass fibre-reinforced ferric oxide particle added epoxy resin hybrid composite was tested in a pin-on-disc set up (Magnum Engineers India Pvt. Ltd). The

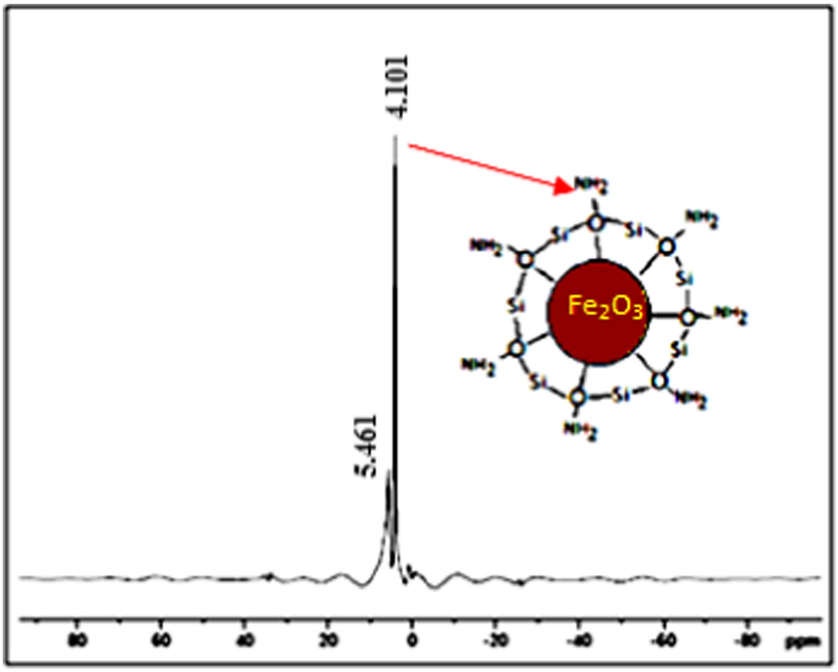


Fig. 2 1-H Proton NMR spectra of silicon coupling grafted ferric oxide

pin-on-disc has a wear disc of diameter 165 mm, disc speed of 100–2000 rpm and a normal load of 5–200 N. But in this present study, a load of 5 N, sliding speed of 800 rpm and sliding distance of 400 m was maintained as process parameters. Flat specimen of 3 mm thick and 5 mm width was used to check the wear resistance of hybrid composites.

2.6.3 Fatigue Behaviour

The fatigue behaviour of un-modified and surface-modified E-glass fibre-reinforced ferric oxide particle dispersed epoxy resin hybrid composites were investigated by a tension-tension fatigue machine (MTS Landmark 370 load frame, USA) with hydraulic power actuated mechanical grippers. Dumbbell shaped specimens of five identical test samples were tested followed by ASTM D 3479 to compute average fatigue life in cycles. Loading frequency of 5 Hz, stress ratio of 0.1, maximum load of 1.28KN (50% of maximum tensile load, since 25% feels under stress and 75% lead over stress), elastic modulus of 6.00 GPa, and working ambience of 23 °C were set as process parameters.

3 Results and Discussions

3.1 TGA Analysis

Tables 2 and 3 shows the initial, rapid and final mass loss of pure epoxy, as-received and surface-modified E-glass fibre-reinforced epoxy resin composite. It is observed that the pure epoxy resin gives mass loss of 4.09, 74 and 4.48% at initial, rapid and final phase. The initial phase starts at 315 °C and end up at 355 °C. The temperature raise of 40 °C was utilised to perform this mass loss. It is observed that addition of as-received E-glass fibre of 30 vol.% reduced the initial thermal stability.

Table 1 Composition and designation of composites

Material designation	Epoxy (Vol%)	Fiber (Vol%)	Fe$_2$O$_3$ (Vol%)	Fe$_2$O$_3$ size (nm)
E	100	0.0	0.0	–
EGF	70	30.0	0.0	–
EGFI$_1$	69.5	30.0	0.5	800
EGFI$_{11}$	69.5	30.0	0.5	200
EGFI$_{12}$	69.5	30.0	0.5	100
EGFI$_2$	69.0	30.0	1.0	800
EGFI$_{21}$	69.0	30.0	1.0	200
EGFI$_{22}$	69.0	30.0	1.0	100

E- Epoxy; GF- glass fiber; I$_1$–0.5 vol.% Fe$_2$O$_3$ and I$_2$–1.0 vol.% Fe$_2$O$_3$ particle

Table 2 Thermogravimetric analysis of as-received E-glass fibre-reinforced ferric oxide particle added epoxy composites

Material designation	As-received second phase additions											
	Mass Loss (%)			Temperature (°C)								
	Initial phase	Rapid phase	Final phase	Initial phase			Rapid phase			Final phase		
				Start	End	Range	Start	End	Range	Start	End	Range
E	4.09	74.00	4.48	315	355	40	355	395	40	395	600	205
EGF	7.53	27.47	19.36	275	340	65	340	375	35	375	600	225
EGFI$_1$	3.00	36.50	9.57	300	340	40	340	400	60	400	600	200
EGFI$_{11}$	4.31	45.70	13.40	325	353	28	353	422	69	422	600	178
EGFI$_{12}$	3.15	44.20	17.00	310	330	20	330	362	32	362	600	238
EGFI$_2$	5.74	40.40	8.50	280	320	40	320	410	90	410	600	190
EGFI$_{21}$	3.26	30.50	27.80	325	345	20	345	385	40	385	600	215
EGFI$_{22}$	5.70	37.26	11.44	320	350	30	350	420	70	420	600	180

E- Epoxy; GF- glass fiber; I_1–0.5 vol.% Fe_2O_3 and I_2–1.0 vol.% Fe_2O_3 particle

A highest mass loss of 7.53% was observed in initial decomposition zone, which is 45% of decrement on comparing with pure epoxy resin. The initial decomposition starts at 275 °C itself and it is near 14% of decrement on comparing with pure epoxy resin. This reduction in initial thermal stability is the reason of formation of aqua molecules by the reaction between E-glass fibre surface and unsaturated OH molecules from epoxy resin [19]. Whereas in silane grafted E-glass fibre-reinforced epoxy resin composite, an improved thermal stability is observed. The initial decomposition starts at 330 °C and end up at 350 °C. The temperature range of 20 °C is the net improvement by the addition of silane grafted E-glass fibre into epoxy resin. This improvement is because of silane coverage on E-glass fibre surface, which could absorb more heat before the fibre start absorbs the heat energy. Thus a positive shift in initial decomposition temperature was found. Similar improvements were found in rapid and final decomposition phases.

It is observed that further addition of silane grafted ferric oxide particle into E-glass epoxy composite improved the thermal stability of hybrid composite. A very lower mass loss of 2.14% was observed in EGFI$_1$ composite designation, while the other composites give significantly higher mass loss at early temperate. The on-set and off temperature of EGFI$_1$ composite designation at initial decomposition stage is 330 °C and 343 °C. Similarly the rapid and final temperatures are 343 °C, 368 °C and 368 °C, 600 °C respectively. Whereas the as-received epoxy composite designation of EGFI$_1$ gives significantly lower thermal stability. An initial, rapid and final mass loss of 3.00, 36.5 and 9.57% were observed. Similarly

Table 3 Thermogravimetric analysis of as-received E-glass fibre-reinforced ferric oxide particle added epoxy composites

Material designation	Surface-modified second phase additions											
	Mass Loss (%)			Temperature (°C)								
	Initial phase	Rapid phase	Final phase	Initial phase			Rapid phase			Final phase		
				Start	End	Range	Start	End	Range	Start	End	Range
E	4.09	74.00	4.48	315	355	40	355	395	40	395	600	205
EGF	2.72	42.55	15.00	330	350	20	350	382	32	382	600	218
EGFI$_1$	2.14	30.00	4.78	330	343	13	343	368	25	368	600	232
EGFI$_{11}$	2.93	48.50	4.57	320	343	23	343	370	27	370	600	230
EGFI$_{12}$	2.91	62.22	11.61	332	340	8	340	378	38	378	600	222
EGFI$_2$	3.30	55.37	6.36	320	342	22	342	370	28	370	600	230
EGFI$_{21}$	2.37	39.00	5.95	320	340	20	340	362	22	362	600	238
EGFI$_{22}$	3.44	47.61	5.83	328	345	17	345	378	33	378	600	222

E- Epoxy; GF- glass fiber; I_1–0.5 vol.% Fe_2O_3 and I_2–1.0 vol.% Fe_2O_3 particle the on-set and off set temperature of EGFI$_1$ composite designation at initial decomposition stage is 300 °C and 340 °C. It is near 5% decrement on comparing with silicon coupling grafted ferric oxide particle in E-glass-epoxy composite (EGFI$_1$). This improvement in surface-modified epoxy composite is because of silicon coupling grafting on particle and fibre surface. At first the aqua formation along the fibre/particle-epoxy interface reduced significantly and also the amount of energy to be spent to break the silicon coupling layer (graft) on fibre and particle surface is high. Thus higher thermal stability is observed for surface-modified E-glass fibre ferric oxide particle dispersed epoxy hybrid composite [20].

It is observed that the particle size of 200 nm with 1.0 vol.% (EGFI$_{12}$**)** gives higher stability on comparing with other composite designations whereas other composites, which contains 800 nm and 100 nm gives marginally lower thermal stability at initial, rapid and final phase. This improvement is because of effective dispersion of 200 nm ferric oxide particles in epoxy molecular voids and arresting the degree of rotation of secondary molecules while heating. When free volume is reduced by the addition of particles, the energy required to activate the secondary molecular chains are higher. Thus large amount of energy is observed. It is further noted that the composites with 800 and 100 nm with 1.00 vol.% gives decreased thermal stability. This reduction in thermal stability is because of particle agglomeration in high denser epoxy matrix. In 800 nm the 1.00 vol.% of ferric oxide particles felt over dozing and in 100 nm with 1.0 vol.% the degree of clustering increases, which leads agglomeration [21].

3.2 Wear Behaviour

Table 4 shows the sp. wear rate and coefficient of friction values of epoxy hybrid composites. It is observed that the pure epoxy resin gives sp. wear rate and COF of 0.012 mm^3/Nm and 0.84 respectively. This higher wear rate and coefficient of frication is the cause of soft epoxy molecules and absence of wear resistance mechanism. It is observed that addition of 30 vol.% of E-glass fibre into epoxy resin improves the wear resistance. The lower sp. wear rate of 0.010, 0.007 and 0.75, 0.65 were observed for un-modified and surface modified EGF composite designation. This improvement in wear resistance is the cause of presence of E-glass fibre in epoxy matrix. The glass fibre in matrix reduces the effective direct contact of bare epoxy resin to abrasion disc, thus lowering the chances of getting wear of pure epoxy resin [22]. Moreover the presence of E-glass fibre absorbs large heat, which is produced while abrasion takes place. This phenomenon increases the resistance against erosion of pure epoxy molecules due to heat. Moreover addition of E-glass fibre of 30 vol.% decrease the adhesion between abrasion disc and composite material. This phenomenon increases the wear resistance by reducing the adhesion wear of composite material. It is observed that the silane surface grafted E-glass fibre into epoxy resin gives improved wear resistance and lowering coefficient of friction than un-modified E-glass fibre into epoxy resin. This improvement is because of improved adhesion between fibre and matrix. When the composite material is touch with the abrasion disc, shear force is generated due to sliding. The silane surface-modified E-glass fibre offers higher resistance for the external shear force due to high interfacial bonding with matrix. The incurred load is effectively transferred to matrix and maintains very high stability against abrasion, adhesion and erosion wear mechanisms [23].

It is noted that further addition of un-modified ferric oxide nano particle into epoxy resin along with E-glass fibre increase the wear loss. The increase in the wear loss is attributes to the abrasion and erosion wear phenomenon. When the un-modified ferric oxide particles are dispersed with epoxy resin they were not chemically linked. These poorly bonded ferric oxide particles are evicted out when sliding takes place. Moreover the evicted ferric oxide particles are present in between the composite and rubbing disc and produced large volume loss via three body abrasion. Thus reduced wear resistance is observed for composite designations dispersed with un-modified ferric oxide particles whereas the addition of

Table 4 Wear values of hybrid composites

Composite designation	Un-modified E-glass fibre and ferric oxide		Surface-grafted E-glass fibre and ferric oxide	
	Sp. Wear rate (mm^3/Nm)	COF	Sp. Wear rate (mm^3/Nm)	COF
E	0.012	0.84	0.012	0.84
EGF	0.008	0.60	0.007	0.65
EGFI$_1$	0.009	0.66	0.003	0.40
EGFI$_2$	0.010	0.70	0.005	0.68
EGFI$_{11}$	0.009	0.69	0.002	0.32
EGFI$_{21}$	0.010	0.71	0.003	0.37
EGFI$_{12}$	0.011	0.75	0.005	0.58
EGFI$_{22}$	0.010	0.70	0.006	0.54

silane surface-modified ferric oxide particle into glass-epoxy composite improved the wear resistance. The improvement of 75, 58.3, 83.3, 75, 58.3 and 50% is observed in sp. wear rate and 53, 19, 62, 56, 31 and 36% were observed for COF in composite designations EGFI$_1$, EGFI$_{11}$, EGFI$_{21}$, EGFI$_{12}$ and EGFI$_{22}$ respectively. This improvement is because of improved adhesion of silane surface grafted ferric oxide particle with epoxy matrix. The adhesion improved ferric oxide particles are bonded tight with matrix and reduce the direct contact of soft epoxy to expose on the abrasion disc. Instead of epoxy molecules the hard ferric oxide particles are exposed to abrasion disc and resist the abrasion wear. Moreover the fine ferric oxide particles maintain very high adhesion with epoxy matrix, even though large shear force is applied on the surface during sliding takes place. This phenomenon reduces the eviction of fine ferric oxide particles form matrix and reduces the chances of three body abrasion [24, 25].

It is observed that the very fine particle of size 200 nm with 0.5 vol.% gives highest wear resistance than other composite designations. This improvement is because of effective surface area of very fine ferric oxide particles, which could reduces the void content of matrix thereby decreasing the abrasion wear phenomenon. It is noted that the particle volume of 1.0% gives larger sp. wear rate than 0.5 vol.% in all composite designation. This reduction is because of clustering of particles due to large volume and chances of more wear loss [26]. More over the particles of dimensions 800 and 100 nm also gives lower wear resistance. This is because of poor void filling of 800 nm particle and high rate of agglomeration of ultra fine 100 nm particles in matrix [27].

Figure 3 shows the optical microscope worn surfaces of pure epoxy and its composites. The images were captured by using an optical microscope with 25 X magnification capability (Motic L 312, 25 X, China). Figure 3a shows worn surface of pure epoxy resin. The image revealed marginal rough surface, which indicates adhesion wear mechanism. Figure 3b shows the worn surface of un-modified ferric oxide particles in epoxy resin matrix (EGFI$_{22}$). The image revealed that poorly bonded ferric oxide particles are evicted from the rubbing surface during sliding and produced more dimple portions on surface [28].

Figure 3c, d shows the worn surface of silane surface grafted ferric oxide particles in EGFI$_{22}$ composite designation. The image revealed that the worn surface is very smooth without any dimples. This result indicates improved adhesion of ferric oxide particles with epoxy matrix. The silane surface modification activates the NH$_2$ functional group on particle surface, which in-turn improves the chemical bonding between matrix and particle. Thus the chances of two body and three body abrasion wear mechanisms get reduce and maintain higher wear resistance. Figure 4 shows the EDAX report of debris collected from the worn surfaces. The report confirms that the debris contains presence of iron (III) oxide particles, which indicates poor bonding of particles with matrix. Figure 5 shows the SEM micrographs of worn surfaces of pure resin, resin with fibre and particle toughened fibre-reinforced epoxy resin hybrid composite. It is observed that the pure epoxy resin has the clean and flat wear track, which indicates high brittle nature of epoxy resin. Figure 5b shows fibre patches on the wear track, which indicates reduction in direct contact of epoxy molecules to the abrasion disc. This presence of E-glass fibre batches reduced the three body abrasion and reduces the COF. Similarly, 5(b) shows both particles and fibre patches on worn surface. It indicates high adhesion improved fibres and particles presence on matrix and reduced the COF. Thus improved wear resistance is observed in silane surface treated reinforcements epoxy composite.

3.3 Fatigue Behaviour

Table 5 shows the fatigue behaviour of pure epoxy resin and un-modified and surface-modified E-glass fibre-reinforced epoxy composite. It is observed that the pure epoxy resin gives very lower fatigue life cycle of 320 counts. This lower fatigue strength is the reason of absence of load sharing micro constituents in matrix. When repeated load is applied, the cured epoxy molecules stretched as minimum level and gain residual stress. These acquired stresses further developed as micro crack and propagates rapidly, which causes plastic deformation. Whereas in E-glass fibre-reinforced epoxy composite improved fatigue strength is observed. The as-received E-glass fibre-reinforced epoxy composite gives maximum fatigue life cycle of 3100 counts. On comparing with pure epoxy the fatigue life increases 89%. This improvement is because of high load sharing ability of E-glass fibre, which reduces the stress intensity factor (state of stress at crack tip) in matrix thereby giving improved fatigue strength. When load applied the load can uniformly transferred through matrix via improved bonding and suppressing the micro-cracks production. Thus improved fatigue strength is observed. It is observed that the addition of surface-modified E-glass fibre in epoxy resin gives improved fatigue life cycle of 3850 counts. Compare than as-received E-glass fibre in epoxy the surface-treated fibre in epoxy resin gives improved fatigue strength of 19%. This improvement is the reason of improved adhesion of fibre with matrix and restricts the interfacial crack development [29].

It is observed that further additions of as-received and surface-modified ferric oxide particles of 800, 200 and 100 nm in to E-glass fibre epoxy composite gives significant improvements in fatigue life cycle of composite. The improved fatigue life cycles of 4255 counts was observed for composite, which contain 0.5 vol.% of 800 nm ferric oxide particle. This is near 92% of improvement on compared with pure epoxy resin. This improvement is because of presence of 800 nm ferric oxide particle, which hinder initiation of cracks

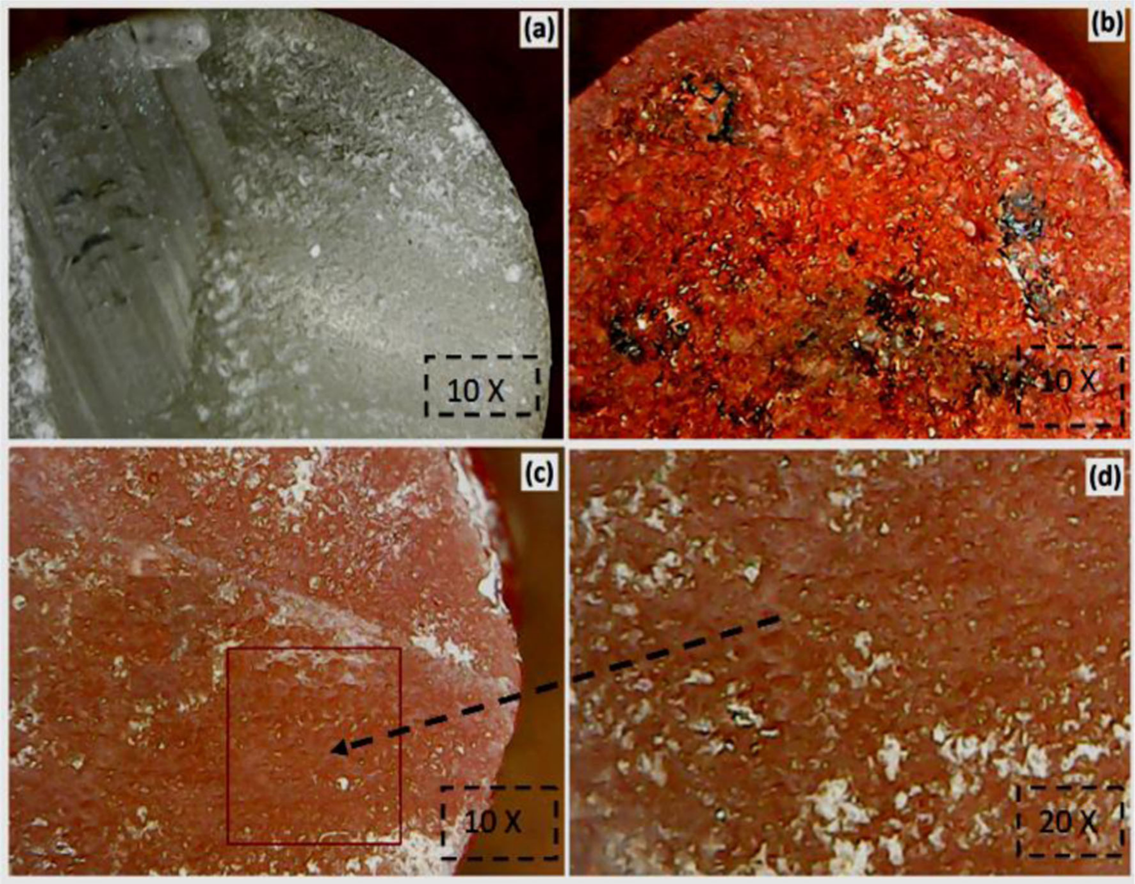
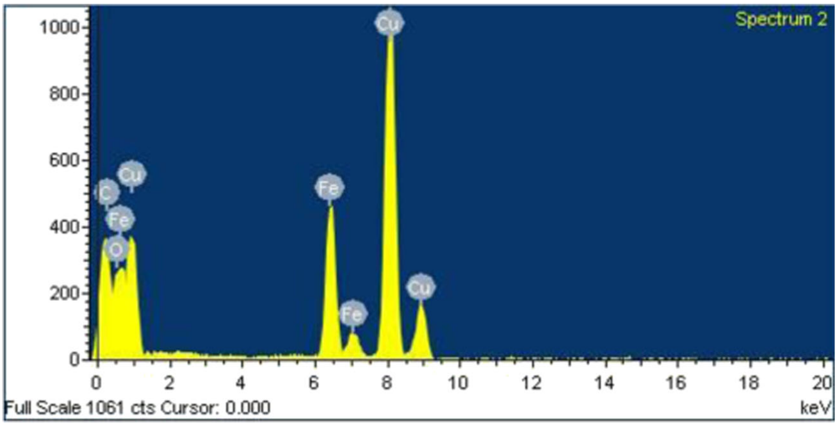


Fig. 3 Optical microscopy images of **a** pure epoxy resin, **b** Un-modified $EGFI_{22}$, **c** Silane surface-modified $EGFI_{22}$ in 10 X and **d** Silane surface-modified $EGFI_{22}$ in 20 X

from voids. The ferric oxide particle of 800 nm particles further restricts the propagation of crack at voids thereby showing improved results. It is observed that adding more volume of (1.00 vol.%) 800 nm ferric oxide particle into epoxy resin reduces the fatigue cycle counts. This reduction is the cause of improved brittleness due to agglomeration of large volume of particle in high denser matrix. The presence of large volume of iron (III) oxide particles formed cluster and induce large number of micro-cracks. These micro-cracks subsequently propagates and developed as a full crack and creating interfacial delamination, fibre pullout and plastic deformation [30, 31].

It is observed that lower dimension particle of 200 and 100 nm in E-glass fire-reinforced epoxy composite gives improved fatigue strength than 800 nm ferric oxide particle. The improved fatigue life cycle counts of 11,675 and 18,724 were observed for surface-modified composite designation $EGFI_{12}$ and $EGFI_{22}$ respectively. This

Fig. 4 EDAX report of debris of worn surface



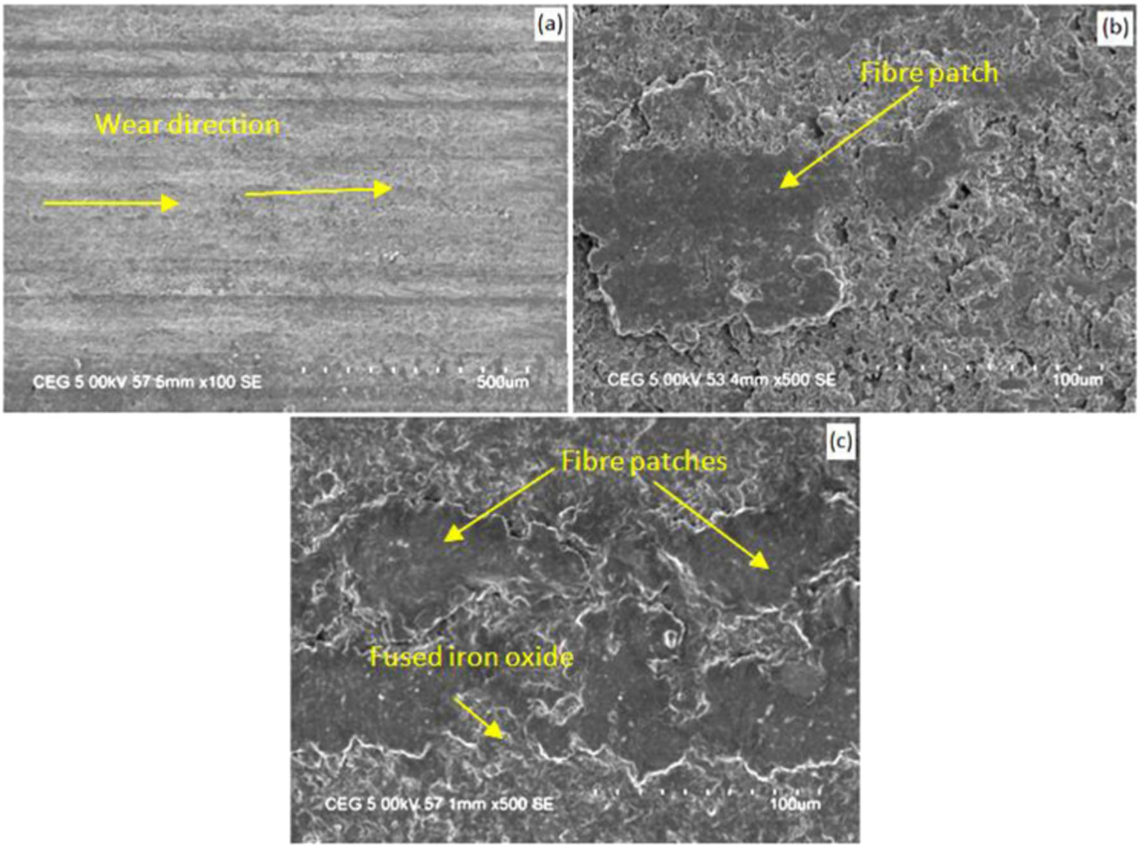


Fig. 5 SEM Worn surfaces of **a** pure resin, **b** E-glass fibre reinforced epoxy composite and **c** Iron (III) oxide particle toughened E-glass fibre-reinforced epoxy hybrid composite

improvement is because of uniform dispersion of fine ferric oxide particles of dimensions 200 and 100 nm, which effectively suppress the crack initiation and propagation in void and fibre-matrix interface [30]. Similar with surface-treated E-glass fibre in epoxy resin the surface-modified ferric oxide particle gives improved fatigue strength. This improvement is the cause of improved dispersion and adhesion of particle in matrix, which, reduce the crack propagation. Figure 6 shows the fractograph of failure sample of un-modified and surface-modified $EGFI_{21}$ under tension-tension cyclic load.

It is observed that the as-received reinforcements in epoxy resin hybrid composite (Fig. 6a) shows fibre pullout and interfacial delamination. Poor adhesion and bonding strength between fibre and matrix caused this failure under repeated loading. Whereas in surface-treated E-glass fibre-reinforced ferric oxide particle added epoxy composite (Fig. 6b) no such failure occurs. There is no fibre pullout and vast interfacial delamination explicated during repeated tension loading. This improvement is because of amine functionalized surface treated fibre and ferric oxide particle greatly improved the adhesion and ensures uniform dispersion of particle with

Table 5 Fatigue values of hybrid composites

Material designation	Un-modified E-glass and ferric oxide Fatigue life cycle (counts)	surface-modified E-glass and ferric oxide Fatigue life cycle (counts)
R	320	320
RF	3100	3850
RFI_1	4255	5100
RFI_{11}	3601	4010
RFI_{12}	9720	11,675
RFI_2	8762	10,076
RFI_{21}	15,218	18,724
RFI_{22}	12,880	15,315

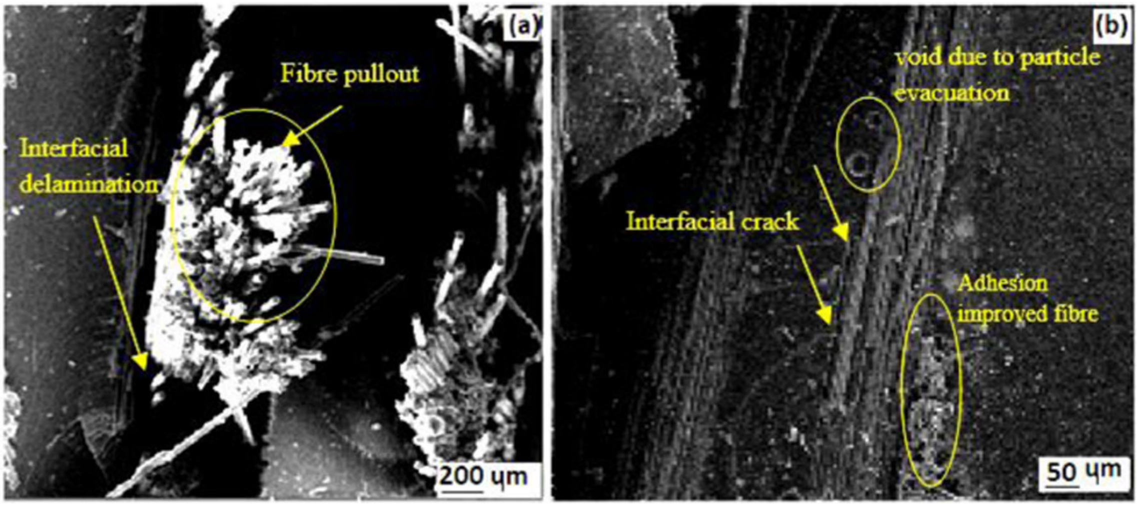


Fig. 6 SEM fractograph of fatigue specimen EFGI$_{21}$ **a** un-modified and **b** surface-modified

matrix. These adhesion improved reinforcements may able to transfer the tension load effectively and reduces the stress concentration thereby increased the fatigue strength [32, 33].

4 Conclusion

Epoxy hybrid composites were fabricated using un-modified and silane surface grafted glass fibre and ferric oxide nanoparticles and characterized.

1. The thermogravimetry results showed that the un-modified E-glass fibre and ferric oxide particle in epoxy resin gives large mass loss at early temperature itself whereas in silane surface-grafted E-glass fibre and ferric oxide particle-dispersed epoxy composite gives very high thermal stability with lower mass loss.
2. The wear behaviour of silane surface modified E-glass fibre and ferric oxide particle shows significant wear resistance. The two body and three body abrasion resistance is typically lower compared to un-modified E-glass fibre and ferric oxide particles.
3. The optical microscope image for worn out surface revealed flat and smooth surface for silane surface modified E-glass fibre and ferric oxide reinforced epoxy composite. There is no dimple and particle evacuation pit marks were seen. But un-modified composite's worn surface unveiled very high porous and high particle evacuated dimples.
4. The fatigue behaviour of silane surface modified epoxy hybrid composites shows remarkable fatigue life. Higher fatigue life cycle of 18,722 was counted for composite designation EGFI$_{21}$ but in un-modified condition the same composite gives lower fatigue strength.
5. Thus in the process of high strength and performance hybrid composites formation the reinforcements like fibres and fillers are sought to be surface modified with the help of silanes. These silanes just cover the surface of the reinforcements without affecting their physical and dimensional properties.
6. These high thermal, wear and fatigue resistance epoxy composites could be used in automobile, structural and domestic appliances manufacturing.

References

1. Arun Prakash VR, Rajadurai A (2016) Thermo-mechanical characterization of siliconized E-glass fibre/hematite particles reinforced epoxy resin hybrid composite. Appl Surf Sci 384(16):99–106
2. Senthil Kumar R, Senthil Kumar A, Asha Melba V (2014) Processing of 45 degree stitched mat GLARE laminate and analyzing tensile and flexural properties. J Appl Chem 7:54–62
3. Domun N, Hadavinia H, Zhang T, Sainsbury T, Liaghat GH, Vahid S (2015) Improving the fracture toughness and the strength of epoxy using nanomaterials – a review of the current status. Nanoscale 7:10294–10329
4. Arunprakash VR, Jaisingh J (2018) Mechanical strength behaviour of silane treated E-glass fibre/Al6061 & SS-304 wire mesh-reinforced epoxy resin hybrid composite. Silicon 10:2279–2286
5. Arun PVR, Rajadurai A, Jayaseelan V, Dass SJ, Murali M (2019) Role of silanized magnetic Fe$_2$O$_3$ particle in heat dissipation and microwave shielding behavior of E-glass fibre-reinforced epoxy resin composite. Mater Res Express 6:076113
6. Ramesh C, Manickam C, Maridurai T, Arun Prakash VR (2017) Dry sliding wear characteristics of heat treated and surface modified hematite particles-epoxy particulate composite. Romanian Journal of Materials 47(3):401–405
7. Dinesh T, Kadirvel A, Arunprakash (2018) Effect of silane modified E-glass fibre/Iron (III) oxide reinforcements on UP blended epoxy resin hybrid composite. Silicon 10(3):1–12
8. Manikandan V, Jappes JTW, Kumar SMS, Amuthakkannan P (2012) Investigation of the effect of surface modifications on the mechanical properties of basalt fibre reinforced polymer composites. Compos Part B 43:812–818

9. Sokolova OA, Kuhn M, Palkowski H (2012) Deep drawing properties of light weight steel/polymer/steel sandwich composites. Arch Civ Mech Eng 12:105–112
10. Bandyopadhyay A (2011) Molecular modeling of cross-linked epoxy polymers: the effect of crosslink density on thermomechanical properties. Polymer 52(11):2445–2452
11. Vincent A, Ramesh G, Kumar SM (2018) Microwave shielding behaviour of surface treated MWCNT-epoxy composites in I & J band-A note. Colloid Interfac Sci Commun 24:89–92
12. Guo Z, Lei K, Li Y, Hahn T (2008) Fabrication and characterization of iron oxide nanoparticls reinforced vinyl-ester resin nanocomposites. Compos Sci Technol 68:1513–1520
13. Julyes Jaisingh S, Selvam V, Suresh Chandra Kumar M, Thigarajan K (2013) Thermomechanical behaviour of unsaturated polyester toughened epoxy silane treated iron (III) oxide nano composite. Indian J Eng Mater Sci 1:241–245
14. Arun Prakash VR, Viswanathan R (2018) Microwave shielding behavior of silanized Cu and Cu-Fe3O4 compound particles reinforced epoxy resin composite in E, F,I and J band frequencies. Polym Bull 75:4207. https://doi.org/10.1007/s00289-017-2262-1
15. Ramesh G, Jayabalakrishnan D, Rameshkumar C (2018) Mechanical and thermal characterization of heat/surface treated egg shell particle diffused natural rubber green composite. J Optoelectron Biomed Mater 10(1):21–28
16. Saravanan R, Suresh Babu A, Maridurai T (2016) Influence of surface-modified MWCNT on mechanical and thermal properties of carbon fibre/epoxy resin hybrid nano composite. Digest J Nanomater Biostruct 11(4):1303–1309
17. Parivendhan I, S R (2017) Mechanical, wear and thermal behaviour of hemp fibre/egg shell particle reinforced epoxy resin bio composite. Trans Can Soc Mech Eng. https://doi.org/10.1139/tcsme-2017-0079
18. Arunprakash VR, Viswanathan R (2019) Fabrication and characterization of Echinoidea spike particles and Kenaf natural fibre-reinforced Azadirachta-Indica blended epoxy multi-hybrid bio composite. Composites: A 118:317–326
19. Chakradhar KVP, Venkata Subbaiah K, Ashok Kumar M, Ramachandra RG (2011) Epoxy/polyester blend nano composites: effect of nano clay on mechanical, thermal and morphological properties. Malays Polym J 6:109–118
20. Arun Prakash VR, Rajadurai A (2016) Mechanical, thermal and dielectric characterization of Iron oxide particles dispersed glass fiber epoxy resin hybrid composite. Digest J Nanomater Biostruct 11(2):373–380
21. Peerapan D, Pearson Raymond A, Paisan K (2017) Thermomechanical behavioursand moistureabsorption of silica nanoparticle reinforcement in epoxy resin. Inter J Adhesion Adhes 78:74–82
22. Suresha B, Chandramohan G, Prakash JN, Balusamy V, Sankaranarayanasamy K (2006) The role of particles on friction and slide wear characteristics in glass-epoxy composite systems. J Min Mater Character Eng 5(1):87–101
23. Shalwan A, Yousif B (2014) Influence of date palm fibre and graphite particle on mechanical and wear characteristics of epoxy composites. Mater Des 59:264–273
24. Singla M, Chawla V (2010) Mechanical properties of epoxy resin – Fly ash composite. Journal of composite 9(3):199
25. Suresha B, Chandramohan C, Jawali ND, Siddaramaiah (2007) Effect of short glass fiber content on three-body wear behaviour of polyurethane composites. J Compos Mater 41:2701–2713
26. Poomali, Siddaramaiah BS, Lee J-H (2008) Mechanical and three body abrasive wear behavior of PMMA/TPU blends. Material Sci Eng A:1–5
27. Kishore P, Sampathkumaran S, Seetharamu PT, Janardhana M (2005) A study on the effect of the type and content of filler in epoxy-glass composite system on the friction and wear characteristics. Wear 259(1–6):634–641
28. Suresha B, Chandramohan G, Sampathkumaran P, Sethuramu S (2007) Investigation of the friction and wear behavior of glass-epoxy composite with and without graphite filler. J Reinf Plast Comp 26:81
29. Maragoni L, Carraro PA, Peron M, Quaresimin M (2016) Fatigue behavior of glass/epoxy laminates in the presence of voids. Int J Fatigue 95:18–28
30. Manjunatha CM, Taylor AC, Kinloch AJ (2010) The tensile fatigue behavior of a silica nanoparticle-modified glass fibre-reinforced epoxy composite. Compos Sci Technol 70:193–199
31. Navaneetha Krishnan G, Selvam V, Saravanan C (2015) Effect of CNTs-Fe2O3 hybrids on mechanical studies of glass fibre/epoxy nanocomposites. J Chem Pharm Sci 6:196–201
32. Jumahat A, Kasolang S, Bahari MT (2015) Wear properties of nanosilica filled epoxy polymers and FRP composites. J Tribol 6: 34–36
33. Karsli NG, Yesil S, Aytac A (2014) Effect of hybrid carbon nanotube/short glass fibre-reinforcement on the properties of polypropylene composites. Compos Part B 63:154–160