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ORIGINAL PAPER

Effect of Thal silica sand nanoparticles and glass fiber reinforcements on epoxy-based hybrid composite

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Abstract Epoxy is a hard, brittle but strong polymeric material and various types of research works are being carried out to exploit its unique properties in commercial service particularly as composite materials. One of these researches is to study the effect of addition of Thal silica sand nanoparticles and glass fiber on epoxy-based hybrid composites. The silica sand was collected from Thal desert situated in Punjab province of Pakistan, milled to nanoparticles using a ball mill. The production of silica sand nanoparticles was verified using a Zeta sizer nanoparticles analyzer and SEM analysis. These silica sand nanoparticles were utilized to develop the epoxy-based composites. The glass fibers were cut into small pieces of 2 cm in length and thoroughly mixed with epoxy along with silica sand nanoparticles. Hand-lay-up fabrication technique was proceeded by room temperature curing which was used to develop the epoxy-based hybrid composites. The tensile and impact specimens were made according to ASTM standard and tested using universal tensile testing and charpy impact testing machines. A Vickers hardness tester, applying 50 g load for 10 s, was used to determine the hardness of the composites. The thermo-gravimetric analysis was carried out to analyze the thermal behavior of the composites particularly to evaluate mass loss or gain due to decomposition and oxidation using TGA apparatus. The interaction of glass fiber and silica sand nanoparticles with epoxy was studied using scanning electron microscopy. It was observed that with increasing silica sand nanoparticles and glass fiber contents, the hardness, tensile, and impact properties of the epoxy-based hybrid composites increased. The TGA results showed that the developed hybrid composites became stable at 300 °C.

Keywords Thal silica sand nanoparticles · Glass fiber · Epoxy-based hybrid composites · Mechanical and thermal properties · Microstructure

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Introduction

Fiber-reinforced polymer composites are mainly used in the aerospace and construction industries. The lightweight, high strength, and stiffness of these composites made them to be utilized in various fields where technical as well as research tasks are needed [1]. Devendra et al. [2] have studied the thermal and fire-resistive properties of E-Glass fiber-reinforced epoxy composites filled with various concentrations of aluminum oxide (Al_2O_3), magnesium hydroxide $Mg(OH)_2$, silicon carbide (SiC), and hematite powder. It was found that Al_2O_3- and $Mg(OH)_2$-filled composites showed lower thermal conductivity, whereas the composites filled with SiC particles which showed low thermal expansion coefficient. The loading of Al_2O_3, $Mg(OH)_2$, and hematite powder increased the time to ignition and reduced the flame propagation rate of the composites as indicated by fire test. Shang et al. [3] have shown that the microstructure of the inter-phase regions of fibers and a bulk polymer matrix can be changed significantly by making different fiber surface modifications. A comparative study of fiber surface topography and local mechanical

property change at the inter-phase of E-glass fiber reinforced in the epoxy, and E-glass fiber reinforced modified polypropylene matrix composite was carried out using tapping mode phase imaging and nano-indentation test using atomic force microscopy (AFM). It was observed that the higher the inter-phase modulus and trans-crystalline microstructure, the higher will be the tensile strength and impact toughness of the composite. Denture base composites with various fiber reinforcements were prepared and investigated by Katja et al. [4]. The deflection fatigue test having a maximum of 100,000 cycles was applied on the composite specimens. The test specimens of polymethylmethacrylate (PMMA) with uniform fiber distribution through the cross-section showed better properties. A higher number of loading cycles were observed in PMMA-preimpregnated glass-fiber than polyethylene fiber ribbon composites [5, 6]. Boger's et al. [7] studied the modification of the fatigue properties of glass-fiber reinforced epoxy laminate with small amounts of nanoparticles of fumed SiO_2 and multiwall carbon nanotubes using static and dynamic fatigue tests. An increase in interfiber fracture strength up to 16 % and high-cycle fatigue life by several orders were observed. The improved fatigue behavior was correlated with the increased inter matrix-fiber fracture strength. The load and damage state were monitored by the conductivity measurements of multiwall carbon nanotubes (MWCNT)-modified composite. It was observed that the onset of matrix cracking and increase in electrical resistivity were correlated which could be used in enabling self-sensing capabilities. Xiaolong et al. [8] studied the multistate reinforcement and interfacial strengthening of epoxy-based composites. They prepared the composites using nano-scale complex constituting the zero-dimensional silica nanoparticles and one-dimensional multiwall carbon nanotubes and characterized them using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM) techniques. This resulted in significant improvement of mechanical properties rather than simple functionalized MWCNT epoxy composite due to the synergy reinforcing effect of SiO_2_MWCNT. The chemically bonded nano-scale interfacial area between the glass fiber and matrix showed the strong interfacial adhesion resulting in an effective stress transfer. It also showed an impression of bridge generated by SiO_2_MWCNTs resulting in higher mechanical properties and high chemical reactivity with matrix. The effect of addition of the phosphorus-containing reactive amine on an aliphatic and an aromatic epoxy resin system with carbon fiber as reinforcement was studied by Toldy's et al. [9]. The performance of flame retardancy of the resins was characterized by the relevant tests and mass loss-type cone calorimeter and tensile tests, bending tests, and interlinear shear strength. The simultaneous amelioration of flame retardancy and mechanical properties of the epoxy resins were found better. Ashraf et al. [10] have prepared novel conjugated polymer/nanodiamond nanocomposites using in situ oxidative polymerization. The fibrillar morphology of resulting nanocomposites with granular arrangement of nanofiller in matrix was observed by FESEM. This study also revealed that new conducting nanocomposites may act as useful contenders in significant industrial applications such as polymer Li-ion battery. Chen et al. [11] have synthesized biphenyl diol formaldehyde resin (BPFR) and glycidyloxypropyl polyhedral oligomeric silsesquioxane (G-POSS) and used them for the modification of fiber-glass reinforced composites of epoxy resin (ER). The results showed that the addition of G-POSS to the composites increased their T_g. It was also found that 5 wt% addition of G-POSS to the hybrid composites increased the tensile and impact strength up to 249.87 MPa and 63.83 kJ/m^2, respectively. Hesami et al. [12] prepared epoxy/glass composites containing carbon nanotubes (CNTs) and ammonium polyphosphate (APP) as a microfiller and montmorillonite (MMT) as a nanofiller to enhance thermal stability and flame retardancy of the developed composites. It was observed from the TGA analysis that the combination of 0.5 wt% CNTs with either 5 wt% MMT or 15 wt% APP can increase the initial thermal decomposition temperature up to 62 °C for the former polymer composite and 47 °C for the latter.

Bahramian et al. [13] prepared epoxy-based composites by adding polyethylene glycol (PEG) as phase change materials (PCM) and montmorillonite nanoclay as a thermal property modifier. The thermal protection performance of nanocomposites was also studied. The results showed that the thermal protection performance was improved by increasing PCM content; however, the thermal diffusivity of nanocomposites was lower than that of the epoxy.

Rajabi et al. [14] prepared epoxy-based nanocomposites reinforced with boehmite, salicylate alumoxane (Sal-A), and *p*-hydroxybenzoate alumoxane (PHB-A) and studied their curing behavior, thermal stability, hardness, and fracture surface morphology by varying the amounts of these reinforcements. The results showed that the existence of the functionalized nanostructures improved the thermal stability and hardness of the nanocomposites.

Tahir et al. [15, 16] have studied the effect of Tronoh silica sand nanoparticles on the mechanical and thermal properties of HDPE and epoxy-based composites. It was found that the addition of Tronoh silica sand nanoparticles improved the mechanical and thermal properties of the developed composites but that composites were only a binary system not hybrid composites such as Thal silica sand and glass fiber epoxy-based composites.

From the above cited literature, it is evident that researchers utilized glass or carbon fibers in combination

with or without synthetic SiO_2 particles as reinforcement in different polymer matrix hybrid composites, but still no attempt was made to evaluate the effect of natural silica sand nanoparticles in combination with glass fiber on the properties of epoxy-based composites. Therefore, this research is focused on the development of Thal silica sand nanoparticle–glass fiber–epoxy-based hybrid composite and its characterization in terms of tensile, hardness, and thermal properties.

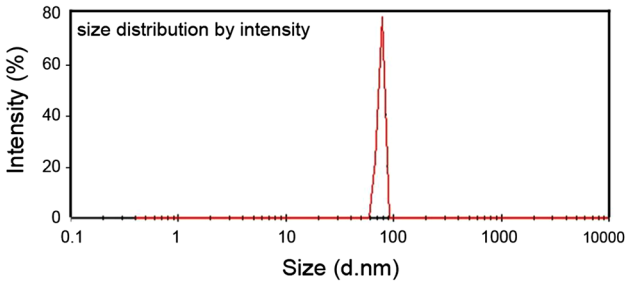

Fig. 1 Silica sand nanoparticles with average particle size of 74.83 nm

Experimental

The silica sand was collected from Thal desert near district Khushab, in Punjab province of Pakistan. This silica sand was washed with distilled water, then dried, and sieved using sieve shaker. The silica sand particles maximum retained on 212 μm was milled to nanoparticles using a ball mill at room temperature with 100 rpm speed for 6 h. The nanoparticles production was verified using Zetasizer nanoparticles analyzer and SEM analysis. The average particles size was found to be 74.83 nm as shown in Fig. 1. At nano-level, there is a large tendency to agglomeration and segregation of particles as observed at higher magnification of field emission electron microscope (FESEM) analysis as shown in Figs. 2a, b. The chemical composition of Thal silica sand and the silica sand nanoparticles was measured using X-rays fluorescence (XRF) and found that the milling process increased the weight percent of silica and silica sand as shown in Table 1. Thal silica sand contained major oxide impurities of Al_2O_3 and CaO. These oxides which were liberated during sieve analysis were harder as compared to SiO_2.

Zinc-coated steel mold with approximate thickness of 0.5 cm was used for hand-lay-up process. The mold was made like a tray with the dimension of 30 × 15 cm to hold the composite part firmly in position during curing process. Commercially available chopped strand mats (300 g/m^2) of glass fibers were further cut down into small pieces as short fibers of approximate 2 cm in length. The mold was completely dried, cleaned, and treated with wax which acted as releasing agent. The mold was also treated with a release agent of polyvinyl alcohol (PVA). The epoxy was mixed together with its respective hardener ratios of 1:1 by wt % and was carefully applied into the mold. Different weight percentages of Thal silica sand nanoparticles and glass fibers were added to the epoxy and properly mixed manually and stirred mechanically and the composites were left for 24 h at room temperature for curing process. The compositions of the developed composites are shown in Table 2.

Each sample of the developed composites was cut into tensile samples, according to ASTM D 638–97 standards.

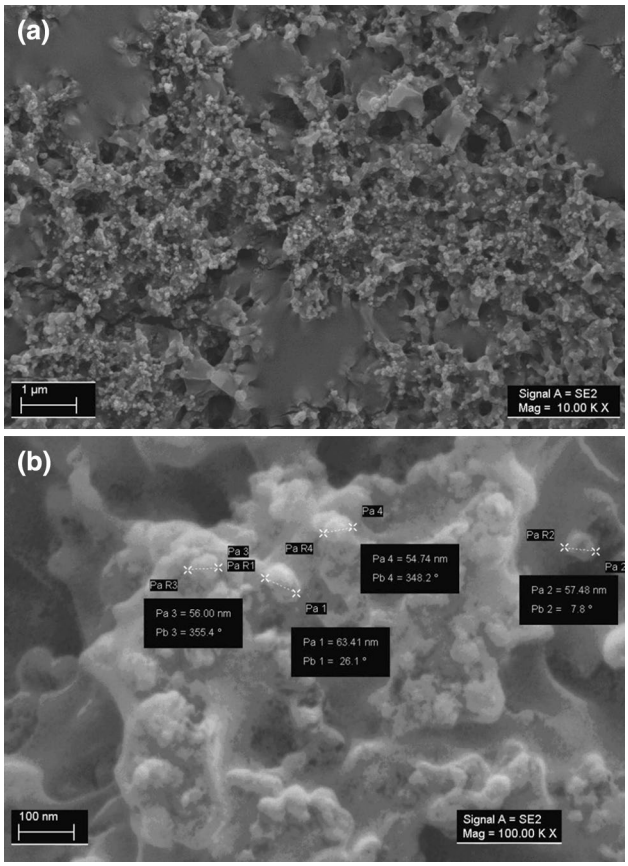

Fig. 2 **a** FESEM micrograph of silica sand nanoparticles (10kX), **b** FESEM micrograph of silica sand nanoparticles (100kX)

A Vickers hardness test was carried out on the surface of the composites using 50 g load for 10 s. The morphology of the fracture surfaces of the tensile samples was studied using scanning electron microscopy (SEM). The fracture surfaces of the tensile samples were coated with a gold–palladium layer to make them conductive using vacuum sputtering process. Charpy impact test was carried out according to ASTM Standard 6110 D (08.03) to determine the impact strength.

Table 1 Chemical Composition of Thal Silica Sand Nanoparticles

Compound	SiO_2	Al_2O_3	K_2O	CaO	TiO_2	Cr_2O_3	Fe_2O_3	MnO
Natural silica sand	86.60	3.30	1.30	6.51	0.80	0.23	1.10	0.18
Silica sand nanoparticles	95.52	1.71	0.52	1.30	0.44	0.23	0.56	0.11

Table 2 Composition of the developed hybrid Composites

Composites name	Wt% ratio of reinforcement
Pure Epoxy (PE)	Pure epoxy
2 wt.% (SG)	1 wt.% of silica sand nanoparticles and 1wt %. of glass fiber
4 wt.% (SG)	2 wt.% of Thal silica sand nanoparticles and 2wt. % glass fiber
6 wt.% (SG)	3 wt.% of Thal silica sand nanoparticles and 3wt. % glass fiber
8 wt.% (SG)	4 wt.% of Thal silica sand nanoparticles and 4wt. % glass fiber

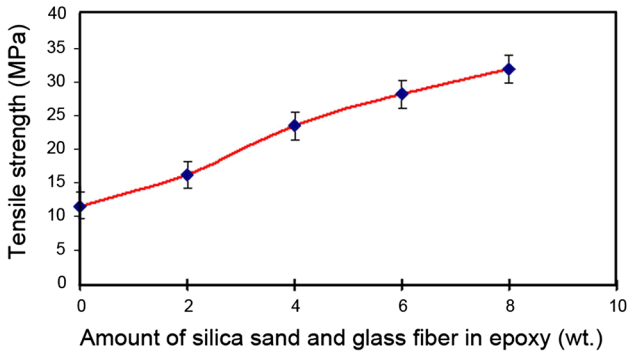

Fig. 3 Tensile strength of silica sand nanoparticle–glass fiber (SG)–epoxy composites

Thermo-gravimetric analysis was carried out to analyze the thermal behavior of the composites particularly to evaluate mass loss or gain due to decomposition, oxidation, calculation of organic component, degradation mechanism, and kinetics of reactions if any.

Results and discussion

Tensile strength of the epoxy-based silica sand nanoparticle–glass fiber (SG) hybrid composites

An increasing trend of tensile strength of the hybrid composites was observed with increasing content of glass fibers and silica sand nanoparticles in epoxy-based composites as shown in Fig. 3. This shows that when we increase the content of silica sand nanoparticles and glass fiber in the matrix the load bearing capacity of the composites increases because the strength of both fiber and silica sand nanoparticles is higher than that of epoxy. A maximum strength of 31.65 MPa was observed with 8 wt % of silica sand nanoparticles and glass fiber in hybrid composites.

When Thal silica sand nanoparticles are trapped into the epoxy matrix, the strength is increased. On the other hand, the fiber content increment leads to increasing the strength. Therefore, the matrix not only withstands the applied load but also stops the initiated cracks to propagate further. The addition of silica sand nanoparticle–glass fiber to epoxy also improved the ductile behavior of the hybrid composites as shown in Fig. 4. As the fibers are pulled out from the epoxy matrix during tensile testing so it delays the fracture of the samples. The addition of silica sand nanoparticles, as they fix in the network of epoxy during preparation

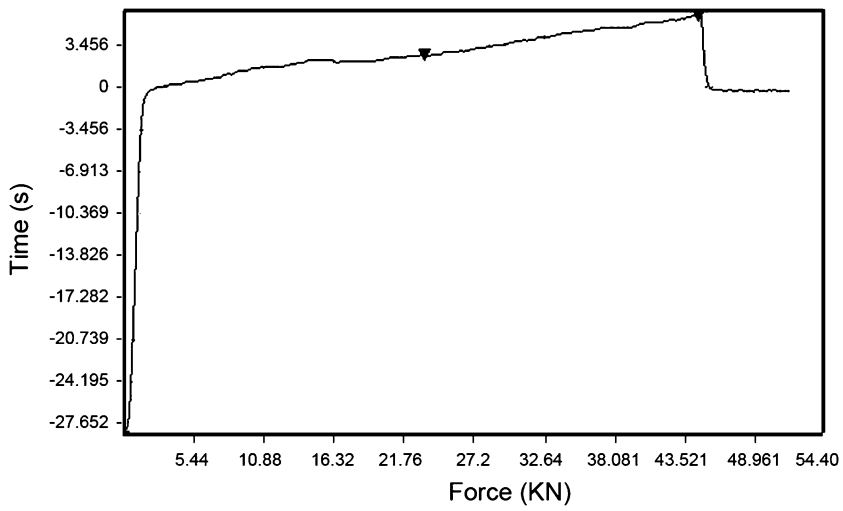

Fig. 4 Time load-curves for silica sand nanoparticle–glass fiber–epoxy (SG) composites

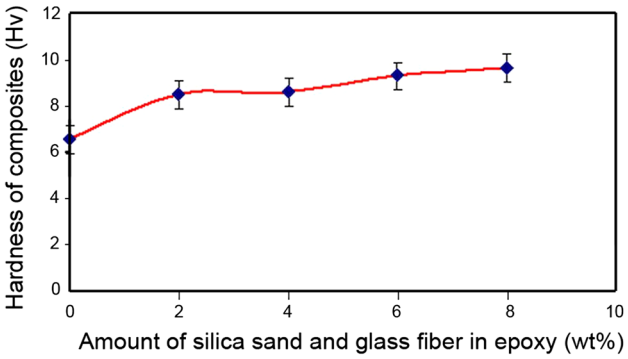

Fig. 5 Hardness of silica sand nanoparticle–glass fiber–epoxy-based hybrid composites

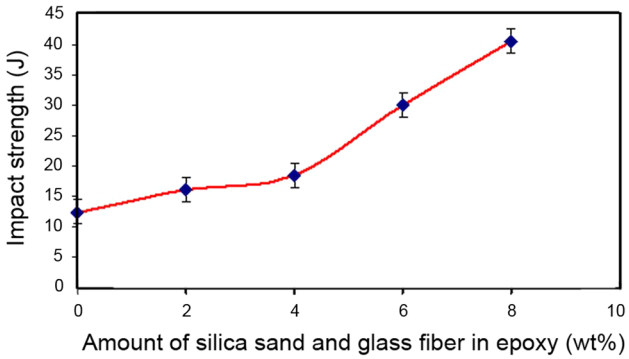

Fig. 6 Impact strength of silica sand nanoparticle–glass fiber–epoxy-based hybrid composites

improves the ductility and tensile strength of the composites. A high degree of sensitivity is often displayed by reinforced polymeric materials toward straining rate, so these specimens were also tested over a broad load-time scale to access the improvement of their applications which were found to be reliable in service. The silica sand nanoparticles also moved the stress to transfer and redistribute in the epoxy matrix. Stress concentrations and cavities filling by nanoparticles are helpful in making the epoxy composites to show ductile behavior [17, 18].

Hardness behavior of the silica sand nanoparticle–glass fiber–epoxy-based composites

The hardness behavior of the hybrid composites was studied and found an increasing trend in hardness with increase in reinforcement of the hybrid composites. A maximum hardness of 9.5Hv was observed with 8 wt% addition of both silica sand nanoparticles and glass fiber in the epoxy-based composites. This is because silica sand and glass fibers, as ceramic materials, when added to the epoxy made improvement in the hardness of the hybrid composites. The silica sand addition and glass fibers did not allow indentation to go deeper in the epoxy-based composites. At least five readings were recorded for each sample and the averages are presented in Fig. 5.

Impact behavior of silica sand nanoparticle–glass fiber–epoxy-based composites

A small increment in the weight percentage of the reinforcement can create a significant increase in the strength and can improve the properties of the epoxy-based composites with respect to their applications and the same situation can be observed in their impact strength. It was observed that the increasing trend of the reinforcement in the epoxy would improve the impact strength of the hybrid composites as shown in Fig. 6. The maximum impact strength was found up to 40.28 J with addition of 8 wt% of both silica sand nanoparticles and glass fibers to the epoxy-based composites.

Thermal gravimetric analysis (TGA) of silica sand nanoparticle–glass fiber–epoxy-based composites

Thermo-gravimetric analysis test was carried out to examine the stability of the test specimen at temperature range 30–300 °C. Every specimen showed good stability behavior and with the increase in the temperature the decomposition rate of the specimen was observed. However, an increase in the stability behavior of the specimen was found with the increase in the weight percentage ratio of silica sand nanoparticles and glass fibers in the epoxy-based composites. This means that with the increase in the weight percentage of Thal silica sand nanoparticles-fiber glass, the stability of all composites also increases at that temperature range as shown in Table 3. The TGA behavior of the hybrid composites is shown in Fig. 7.

SEM analysis of the fractured surfaces of tensile samples of glass fiber–silica sand nanoparticle–epoxy-based composites

The SEM analysis was performed to observe the dispersion of reinforcements, their interface, and interaction with the matrix and fracture behavior. The dispersion of

Table 3 Wt. % loss of composites during TGA analysis at 300 °C

Composites name	Weight loss (%)
Pure Epoxy (PE)	3.483
2 wt.% (SG)	3.012
4 wt.% (SG)	2.489
6 wt.% (SG)	2.41
8 wt.% (SG)	2.22

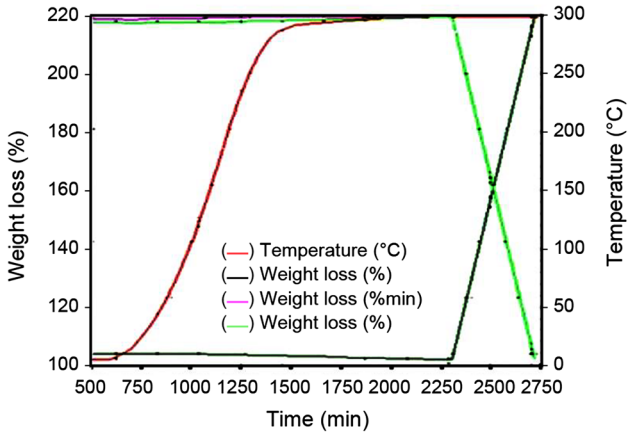

Fig. 7 TGA analysis of silica sand nanoparticle–glass fiber–epoxy-based hybrid composites

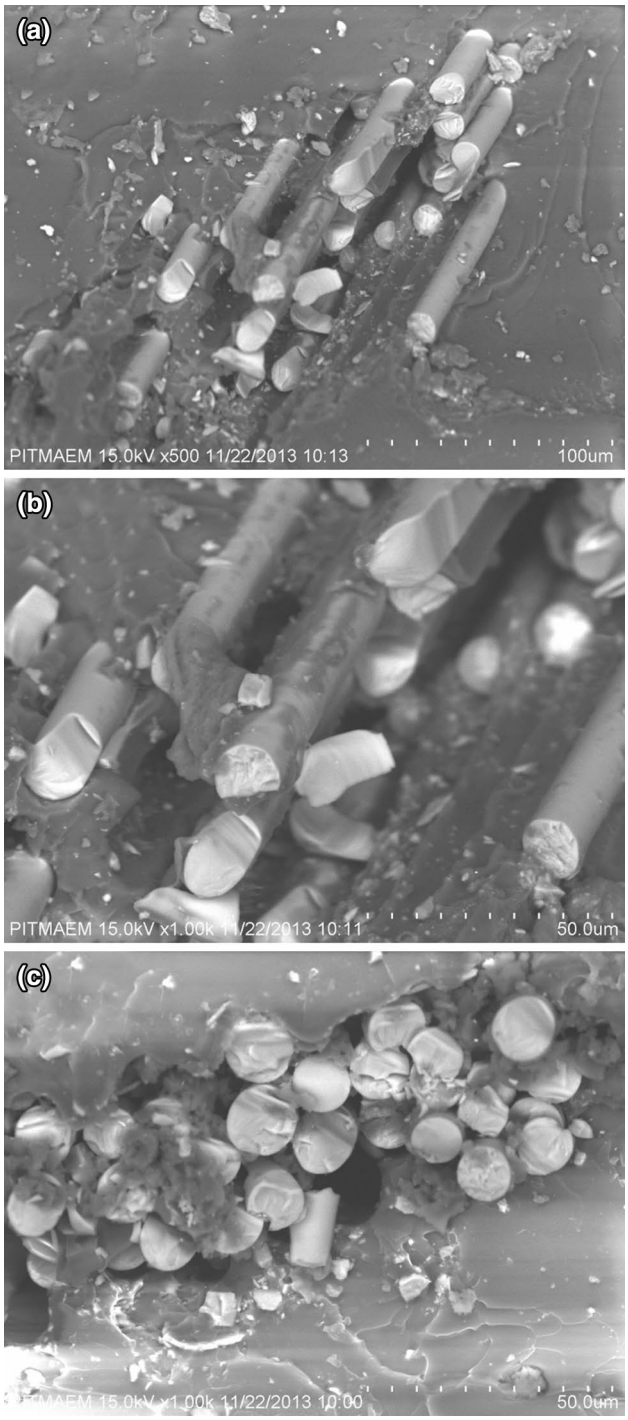

Fig. 8 **a** Fibers pulled out from epoxy matrix during tensile test, **b** Breaking of fiber during tensile test, **c** Coherency of the fibers with epoxy matrix

reinforcements greatly affects the physical and mechanical properties of the epoxy matrix. The pull out behavior of the glass fiber is also supported in the morphology study by SEM as shown in Figs. 8a, b. The coherency of the fibers with the epoxy matrix is shown in Fig. 8c. It was observed that increase in the weight percentage of the reinforcement increases the strength of the hybrid composites. During preparation of the composites, mechanical stirring was preferred to manual stirring for proper mixing of Thal silica sand nanoparticle–glass fiber and epoxy. For engineering design purposes, material tensile properties play a vital role in providing the useful data. The specimen of Thal silica sand nanoparticle–glass fiber reinforced epoxy-based composite fractured in ductile manner. The fracture surfaces of the composites specimens are shown in Fig. 8, showing the interface between epoxy and Thal silica sand nanoparticle–glass fiber. The glass fibers are seemed as small bars coming out of the epoxy matrix as shown in Figs. 8a, b. When the tensile stress is applied these glass fibers are pulled out from the matrix, during pulling, the silica sand nanoparticles resist the pull out of the fibers by filling the pores generated due to the applied tensile stress. The better dispersion and adhesion of silica sand nanoparticles support to increase the strength of epoxy matrix as shown in Fig. 8, while the glass fibers show a mixed behavior. In some areas, the complete coherency of the glass fibers in the matrix is observed as shown in Fig. 8c which has resulted in stronger hybrid composites. On the other hand, in some areas the fibers were pulled out from the matrix during tensile test. When the load is applied, two types of debonding occur for silica sand nanoparticles. First, these nanoparticles are debonded from the matrix and then from the short fibers as shown in Figs. 8b, c. Also the addition of silica sand nanoparticles play two roles in the fracture mechanism by improving the fracture toughness and relieving the overload near to the fiber ends in front of the crack tip via the above matrix-related failure events [16]. Jiin et al. [19] studied the epoxy matrix filled with silicate clay nanoparticles and their final properties were related to the microstructure achieved in the processing of these materials. It

was observed that the full state of ideal exfoliation, dispersion, and orientation was not achieved. The dispersion and intercalation of nanoparticles into the matrix play very important role for the mechanical properties of the nanoparticles. Similar study was carried out by Tahir et al. [16] who used silica sand nanoparticles in epoxy and found that improper mixing of the nanoparticles in the matrix resulted in decrease in the mechanical properties. It was concluded that the agglomeration, segregation, and adherence of the nanoparticles result in improper mixing and can lead to weaker mechanical properties of the composites.

Conclusion

Thal silica sand nanoparticles were developed using a ball mill and they were used to fabricate the epoxy-based hybrid composites with glass fiber using hand-lay-up process by curing at room temperature. The SEM studies revealed the homogeneous mixing of both silica sand nanoparticles and glass fibers in the epoxy matrix. The reinforcement of silica sand nanoparticles and short glass fiber improved both the tensile and impact strengths of the hybrid composite up to 31.65 MPa and 40.28 J, respectively. An improvement of hardness was also observed with the increase in the weight percentage of the reinforcements. The ductile type fracture behaviors under tensile loading due to the mechanism of pulling and breaking of the fibers from the epoxy matrix were verified by the SEM analysis. SEM also revealed the adherence of silica sand nanoparticles with the fibers and a uniform distribution of the reinforcement in the epoxy matrix. The TGA results of the hybrid composites showed improved stability of the composites at 300 °C.

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References

1. Tamer S, Egemen A, Mustafa OB, Onur C (2011) A review: fiber metal laminates, background, bonding types and applied test methods. Mater Des 32:3671–3685
2. Devendra K, Rangaswamy T (2012) Evaluation of thermal properties of E-glass/epoxy composites filled by different filler materials. IJCER 2:1708–1714
3. Gao Shang-Lin, Madre Edith (2002) Characterization of interphase nano-scale property variation in glass fiber reinforced polypropylene and epoxy resin composites. Compos Part A: Appl Sci Manuf 33:559–576
4. Katja KN, Lippo VJ, Lassila, Vallittu PK (2005) Flexural fatigue of denture base polymer with fiber-reinforced composite reinforcement. Compos Part A: Appl Sci Manuf 36:1275–1281
5. Vallittu PK (1997) Glass fiber reinforcement in repaired acrylic resin removabledentures: preliminary results of a clinical study. Quint Int 28:39–44
6. Narva K, Vallittu PK, Helenius H, Yli-Urpo A (2001) Clinical survey of acrylic resin removable denture repairs with glass–fiber reinforcement. Int J Prosthodont 14:219–224
7. Boger L, Sumfleth J, Hedemann H, Schulte K (2010) Improvement of fatigue life by incorporation of nanoparticles in glass fiber reinforced epoxy. Compos Part A: Appl Sci Manuf 41:1419–1424
8. Jia Xiaolong, Li Gang, Liu Baiyang, Luo Yuming, Yang Gang, Yang Xiaoping (2013) Multiscale reinforcement and interfacial strengthening on epoxy-based composites by silica nanoparticle-multiwalled carbon nanotube complex. Compos Part A: Appl Sci Manuf 48:101–109
9. Toldy B, Szolnoki Marosi Gy (2011) Flame retardancy of fiber-reinforced epoxy resin composites for aerospace applications. Polym Degrad Stab 96:371–376
10. Ashraf R, Kausar A, Siddiq M (2014) High-performance polymer/nanodiamond composites: synthesis and properties. Iran Polym J 23:531–545
11. Chen s, Gao J, Han H, Wang C (2014) Mechanical and thermal properties of epoxy-POSS reinforced-(biphenyl diol formaldehyde/epoxy hybrid resin) composites. Iran Polym J 23:609–617
12. Hesami M, Bagheri R, Masoomi M (2014) Combination effects of carbon nanotubes MMT and phosphorus flame retardant on fire and thermal resistance of fiber-reinforced epoxy composites. Iran Polym J 23:469–476
13. Bharamian AR, Sadat Ahamdi L, Kokabi M (2014) Performance evaluation of polymer/clay nanocomposite thermal protection systems based on polyethylene glycol phase change material. Iran Polym J 23:163–169
14. Rajabi L, Marzban M, Ashraf Derakhshan A (2014) Epoxy/alumoxane and epoxy/boehmite nanocomposites: cure behavior, thermal stability, hardness and fracture surface morphology. Iran Polym J 23:203–215
15. Tahir A, Othman M (2011) The development and characterization of HDPE- silica sand nanoparticles composites, IEEE CHUSER 5–6th December, Penang
16. Tahir A, Othman M, Rafiq A (2013) Studying the effect of adding silica sand nanoparticles epoxy based composites. J Nanoparticles 2013:1–5
17. Ke YC, Stroeve P (2005) Polymer–layered silicate and silica nanocomposites. Elsevier, Oxford
18. Zhang G, Rasheva Z, Karger J, Burkhart T (2011) Synergetic role of nanoparticles and micro-scale short carbon fibers on the mechanical profiles of epoxy resin. Express Polym Lett 5:859–872
19. Luo Jyi-Jiin, Isaac MD (2003) Characterization and modeling of mechanical behavior of polymer/clay nanocomposites. Compos Sci and Technol 63:1607–1616