Micro-crack Pinning and Interfacial Fracture in Mixed Metal Oxide Reinforced Epoxy Nanocomposite

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The effects of mixed metal oxides ($\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$) nanoparticle dispersion on the mechanical properties and fracture mechanisms of epoxy polymer matrix and its composite with glass fiber system are reported in this paper. $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles are synthesized using sol-gel method, and its crystallinity is optimized. Epoxy nanocomposites are synthesized by a dispersion technique, and the compressive properties are optimized. The glass transition temperature has been improved. Epoxy with 5 wt.% of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ shows optimal results with an increase of 17.4% in compressive modulus, and an increase of 23.4% in compressive strength with respect to those of neat epoxy. This improvement attributes to higher strength of shearing of polymer during the fracture of the nanoparticle interface. Micro-crack kinks at the interfaces can further delay fracture under compression. E-glass fabric-reinforced 5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ -epoxy nanocomposite also shows improvement in the mechanical properties via nanoscale interface with fibers. This type of ceramic nanocomposites has useful applications in thermal/electrical insulations besides improving the compressive/buckling properties.

Keywords ceramic, glass fabric, interface fracture, micro-crack, nanoparticles, nanocomposite, oxide, zirconia

1. Introduction

Epoxy matrix-based structural components provide excellent mechanical, thermal, and electrical properties. Moreover, the epoxy resins are well-established thermosetting matrices for advanced composites for high stiffness, specific strength, dimensional stability, chemical resistance, and the ease of processing along with strong adhesion to the bonded/embedded reinforcement (Ref 1). The incorporation of inorganic fillers to polymer for improving the performance of the final product has long been an essential industrial activity (Ref 2). Microscale filler particulates have been extensively used in epoxy composites (Ref 3). The resultant composites had enhanced stiffness, strength, and toughness individually or together via various microscale mechanisms. However, the micro-fillers may reduce other important properties, such as the impact resistance, and cause an adverse effect on the processability of the required final material. The nanoparticle-reinforced composite has much higher number of particles per unit area in comparison with the micron-sized particle composite, which causes a small crack propagating through the material, and hence the energy consumption for crack propagation increases, and hence improves the impact resistance of the nanocomposite (Ref 4, 5).

One possible solution for the above problem is to use smaller fillers with dimensions in the range of nanometer scale. The advantages of small fillers are that they can be homoge-

neously distributed within the polymer by various techniques, thereby paving way for an efficient reinforcement effect with enhanced ductility and impact strength and improving the wear resistance and reducing the residual stresses (Ref 6). Suitable nanoparticles can produce good wettability with the thermoset polymer and fill in the small gaps between the cross-linked polymer chains, providing high resistance to deformations under stress. Nanoparticle reinforcements can reduce the thermal expansion coefficient and increase thermal and wear resistance of the host matrix. This is due to the material interfaces that are enhanced by the synergetic effect between the micro-reinforcement and the nanostructure, creating better interfaces and henceforth resulting in interesting improvements in the thermal and mechanical properties (Ref 7-9). On the other hand, previous works have indicated that as a class of porous materials can greatly improve the tribological and mechanical properties of an epoxy matrix composite and to achieve a self-lubricating material (Ref 10, 11).

Mixed metal oxides are known for their high thermal stability and resistance to sintering (Ref 12). Zirconia (ZrO_2) is a known choice for thermal barrier coatings (TBCs) (Ref 13). The use of zirconia in polymer has useful applications in thermal management (Ref 14) and radiation shielding (Ref 15). It is well known that ZrO_2 phases need to be stabilized by doping metal oxides such as CeO_2 , Y_2O_3 , CaO , MgO (Ref 16). Ceria-stabilized zirconia has higher fracture toughness and high thermal stability compared to yttria-stabilized zirconia (Ref 17). In CeO_2 , the replacement of Ce ions by cations of a different size modifies the ion mobility and the lattice structure, resulting in the formation of a defective fluorite structure. Such modifications in the defect structure are able to impart improved properties to the materials, such as better resistance to sintering at elevated temperatures, better thermal and mechanical properties (Ref 18, 19). Recently, some ceramic nanoparticles such as SiC , Al_2O_3 , SiO_2 , WO_3 , CeO_2 , and ZrO_2 have already been used to reinforce polymer matrix (Ref 20-24). All of them have demonstrated their ability to enhance the mechanical behavior of epoxy matrix and in some cases to

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improve their toughness. The superior properties of metal oxides such as hardness, compressive strength, thermal resistance, and wear resistance make them suitable for their application as reinforcement material in polymer matrices (Ref 25-27). Mixed metal oxide nanoparticles due to phase stability, thermal stability, and high surface area-to-volume ratio have increased interfacial interaction between nano-reinforcement and host polymer matrix; thus, better adhesion between resin and filler is achieved. Researchers have used several techniques for dispersing nanoparticles by mechanical agitations, such as ball milling or magnetic stirring, ultrasonic vibration, shear mixing, noncontact mixing, and the use of dispersing agent (Ref 28). In the present investigation, we used shear mixer followed by sonication to prepare all the specimens.

Glass fiber-reinforced polymer (GFRP) composites due to their high specific strength, stiffness, corrosion resistance, and good dielectric properties have become attractive materials in aerospace, automobile industries, marine, armor, microelectronic packaging, electronic circuit board, and civil engineering structures (Ref 29-33). Hence, the use of mixed metal oxide nanoparticles in GFRP composite is a potential way to enhance its thermal, electrical, radiation shielding, and mechanical properties to a large extent.

However, till date, no studies have reported the mechanical performance of mixed metal oxides-incorporated epoxy composite and glass fiber system. In the present research, we report the effect of mixed metal oxides on the mechanical behavior of epoxy nanocomposites with variation in $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ concentrations. Further, we have investigated the effect of an optimally synthesized $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ system on the property improvement of E-glass fabric-reinforced laminates.

2. Materials and Methods

2.1 Mixed Metal Oxide Nanoparticle Optimization

The $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solution powders were prepared using sol-gel method. The solid solution was then dried at 100 °C for 6 h. The dried materials were later milled into fine powders and were calcined at three different temperatures, viz. at 500, 700, and 900 °C, for 8 h to study their crystallinity. Cerium(III) nitrate hexahydrate (Aldrich, USA) and zirconium(IV) oxy-

trihydrate (Aldrich, USA) were used as sources of Ce and Zr, respectively. Ammonium hydroxide (Merck, India) was used as the precipitating agent.

The phases of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles were analyzed using powder x-ray diffraction (XRD, PANalytical X'PERT PRO). The morphology, fracture surface, and interfacial bonding with matrix and E-glass fabric of the tested composites discussed in the later section are observed using FESEM (Ultra 55, Carl Zeiss, GEMINI).

Figure 1(a) shows the XRD patterns of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ powders calcined at 700 °C for 8 h at various positions along x direction. It can be observed that the diffraction peaks were shifted to lower angle with increasing Ce content up to $x = 0.75$ and no peak shift was observed with Ce content higher than $x = 0.75$. As compared to the XRD pattern of CeO_2 alone, the XRD peaks observed for $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solutions become broader, indicating a distortion of the cubic phase of the fluorite structure to a tetragonal one due to the incorporation of ZrO_2 into CeO_2 . Figure 1(b) shows the FESEM micrographs of the calcined $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ powders at 700 °C with average size ranging between 10 and 20 nm. Optimized composition of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ is used for further dispersion in epoxy system due to its better phase stabilization.

2.2 Optimization of Nanoparticle Dispersion in Epoxy Matrix

Commercially available epoxy phenol novolac resin, Araldite LY 5052 (Huntsman Advanced Materials, India), has been used as matrix for the nanoparticle reinforcement. Aradur 5052 CH (India) was used as curing agent for Araldite LY 5052.

The optimized $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticles were added to epoxy resin in an optimal manner (wt.% varying from 0 to 10). The solution was obtained using shear mixer followed by sonication for 15 min. Hardener (38% by weight of epoxy) was then added and mixed to cure the resin. The obtained mixtures were poured into cylinder-shaped molds having dimensions of $12 \times 6 \text{ mm}^2$ and were allowed to cure at room temperature for 24 h with continuous spinning to develop uniform dispersion and avoid any settling of the nanoparticles. It was then cured at 50 °C for 15 h and subjected to vacuum for 24 h to remove trapped air bubbles. The schematic of the fabrication process is shown in Fig. 2.

The compressive mechanical and thermal properties of the composites were determined using universal testing machine (UTM, Makron-Biss) and Dynamical Mechanical Analyzer

Fig. 1 (a) XRD patterns of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solution and (b) FESEM micrograph of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ solid solution powders calcined at 700 °C for 8 h

Fig. 2 Schematic diagram showing ceramic-epoxy nanocomposite synthesis steps

Fig. 3 Schematic diagram of epoxy-5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ /glass fabric laminate fabrication process

(DMA, MetraVib). Burnout testing was performed in a muffle furnace. Specimens as well as crucibles were initially cleaned using acetone and dried in the vacuum for a day to eliminate any moisture/impurities. Specimens were then placed in the weighed crucible, and the weight was recorded along with the crucible. The specimens were then heated at different temperatures (25-350 °C) with a half-hour holding at constant temperature till the specimens were charred. The weight difference at each temperature was recorded. All the compression tests were carried out in accordance with ASTM 695, and the specimen dimensions were kept as $12 \times 6 \text{ cm}^2$ for the test. For all the specimens the dimensional tolerance was ensured by polishing the sample within 2- μm variation to avoid generation of stresses at the sample edges.

2.3 Dispersion of Nanoparticle-Epoxy Matrix in Glass Fabric

The optimized nanocomposite matrices (5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$) were infused into the unidirectional $[0^0]_5$ GFRP laminates by hand lay-up technique as shown in Fig. 3. The specimens are cured in the vacuum at room temperature for 24 h. Tensile specimens are thereafter laser-cut and polished to the desired dimensions. In order to achieve better performance, the composites were then post-cured at 50 °C for 15 h and subjected to vacuum for 24 h, as discussed in the previous section. Unidirectional E-glass fabric with fiber size of 9 μm , yarn size of 66 TEX, fabric thickness of 0.3 mm and GSM of 260 is used as the fiber reinforcement phase.

Fig. 4 FESEM micrographs of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$: (a) 1 μm , (b) 100 nm, (c) 20 nm; (d) compressive stress–strain curves of corresponding particle size variation; and (e) compressive strength vs. particle size of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$

Fig. 5 FESEM micrographs of (a) pure epoxy and epoxy– $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ with (b) 1 wt.%, (c) 3 wt.%, (d) 5 wt.%, and (e) 10 wt.%

3. Results and Discussion

3.1 Effect of Nanoparticle Structure and Properties on Nanocomposite Matrix

Enhancements of the mechanical properties of the epoxy due to the mixed metal oxides were studied systematically. Figure 4(a), (b) and (c) shows the FESEM micrographs of varying particle sizes of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$. The effect of particle size on the composite strength of epoxy– $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanocomposites is shown in Fig. 4(d) and (e), where the average size is 1 μm , 100 nm and 20 nm, respectively. It can be seen that the particle size effect clearly enhanced the compressive stress–strain behavior of the epoxy– $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanocomposite. The addition of nanoparticles into epoxy polymer increases the strength due to higher surface area, which can promote stress transfer from matrix to nanoparticles.

In contrast, the presence of microparticles, the reduction in strength, and failure strain demonstrated that the load transfer between matrix and microparticles is insufficient and the interface is weak (Fig. 4d). This suggests that smaller particles introduce additional mechanisms of energy absorption during compression.

Dispersion of nanoparticles in polymers is a crucial factor in determining the final properties of the nanocomposites. In this study, we have followed (section 2.2) different approaches to achieve very good particle distribution at the nanoscale. Figure 5(a), (b), (c), (d) and (e) shows the FESEM micrographs of pure epoxy and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticles (Fig. 1b) dispersed in epoxy with varying wt.%. It can be seen that the proposed fabrication steps produced excellent particle dispersion at 5 wt.% in the matrix system (Fig. 5d). There is no agglomeration of nanoparticles for 5 wt.%, although at the highest concentration of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticles a small

Fig. 6 (a) Compressive stress–strain curves of different wt.% of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ in the epoxy matrix nanocomposites. (b) Compressive strength vs. wt.% of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$

Table 1 Sample weight ratios and compression properties of epoxy– $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanocomposites

Compressive property	$\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ dispersed in epoxy				
	Pure epoxy	1%	3%	5%	10%
Compressive modulus, GPa	1.66 ± 0.3	1.45 ± 0.13 (12.6%↓)	1.21 ± 0.1 (27.1%↓)	1.95 ± 0.8 (17.4%↑)	1.75 ± 0.7 (5.4%↑)
Compressive strength, MPa	184.34 ± 3.4	193.40 ± 2.4 (4.9%↑)	202.32 ± 6.2 (9.7%↑)	227.55 ± 7.6 (23.4%↑)	208.47 ± 0.6 (13.1%↑)
Compressive yield, MPa	90.09 ± 0.4	82.03 ± 4.3 (8.9%↓)	82.29 ± 5.1 (8.6%↓)	91.40 ± 1.3 (1.5%↑)	89.51 ± 0.3 (0.6%↓)
Compressive failure strain, %	45.14 ± 0.6	47.64 ± 0.2 (5.5%↑)	47.43 ± 0.3 (5%↑)	47.59 ± 0.3 (5.4%↑)	43.53 ± 0.8 (3.5%↓)

degree of agglomeration is observed. This is because the presence of more van der Waals forces between the nanoparticles would limit its dispersion (Fig. 5e). This is subsequently used as an optimal concentration for dispersion in the epoxy–ceramic–GFRP system.

The effect of nano- $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ on the compressive stress–strain response of the epoxy polymer is illustrated in Fig. 6(a). Compression tests reveal that the increase in the compressive strength of epoxy matrix takes place with an increase of up to 5 wt.% of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$. Compressive strength of pure epoxy is 184.3 MPa, which increased to 227.6 MPa for 5 wt.% of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$. Compressive modulus and compressive strength are shown in Table 1. An increase in the compressive strength with an increase in the concentration of up to 5 wt.% is a result of high strength and hardening behavior of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticles dispersed uniformly in the resin with very high interfacial area between matrix and nanoparticles, thus enhancing the resistance to interfacial fracture. The presence of 5 wt.% of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ improved ductility and promoted higher plastic hardening behavior after yielding. The property enhancement is due to homogeneous dispersion nanoparticles in the matrix as shown in Fig. 5(d) (Ref 34). The compressive strength and modulus decreased upon increasing the 5 wt.% (Table 1). This decrease can be due to the agglomeration of nanoparticles, thus reducing the interfacial area for stress transfer from matrix. Regions around the agglomerated nanoparticles develop thermal stresses during curing cycle due to the mismatch of thermal expansion coefficient between epoxy matrix and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ aggregate.

Other than that, agglomerates in the matrix cause a propagation crack and induce the initiation of the final failure. Therefore, the particle dispersion optimization conditions and size of the particles are playing role for mechanical property improvements.

To understand the mechanical behavior of the epoxy– $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ nanocomposites, compression tests were carried out for all samples along the various positions along x direction. It is observed from Fig. 7 that the compressive strength of the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticle epoxy system is higher than that of all other samples. This confirms the higher stiffness and all other mechanical characterization of that composition in correlation with the phases shown in the XRD patterns in Fig. 1. This is because ceria-stabilized zirconia has higher fracture toughness and high thermal stability (Ref 17). Moreover, the stabilized cubic structure with zirconia content enhances ($\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$) the mechanical properties. It is clear that the infusion of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticles also resulted in uniform dispersion of nanoparticles over the entire volume of epoxy resin and there are no adverse reactive effects. These results indicate the overall improvement of compressive behavior of epoxy– $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ system (see Table 2). Compressive strength of pure ZrO_2 sample was 188.4 MPa which increased to a 227.5 MPa for $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ sample. An increase in Ce concentration up to pure (CeO_2) caused a decrease in compressive strength, and the trend is shown in Fig. 7.

In order to study the fracture mechanism of mixed metal oxide nanoparticles in the epoxy, a controlled fracture tough-

Fig. 7 (a) Compressive stress–strain curves of different concentrations of epoxy– $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ nanocomposites, (b) compressive strength vs. different concentrations of epoxy–5 wt.% $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$

Table 2 Sample weight ratios and compressive properties of epoxy– $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ nanocomposites

Compressive property	Nano- $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ filled with epoxy					
	Pure epoxy	$\text{Ce}_0\text{Zr}_1\text{O}_2$	$\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$	$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	$\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$	$\text{Ce}_1\text{Zr}_0\text{O}_2$
Compressive modulus, GPa	1.66 ± 0.3	1.62 ± 0.7 (2.4%↓)	1.53 ± 0.4 (7.8%↓)	1.76 ± 0.4 (6.0%↑)	1.95 ± 0.8 (17.4%↑)	1.77 ± 0.3 (6.6%↑)
Compressive strength, MPa	184.34 ± 3.4	188.4 ± 2.4 (2.2%↑)	197.65 ± 1.6 (7.22%↑)	208.42 ± 3.1 (13.0%↑)	227.55 ± 7.6 (23.4%↑)	224.3 ± 0.6 (21.7%↑)
Compressive yield, MPa	90.09 ± 0.4	87.77 ± 4.3 (2.5%↓)	88.25 ± 1.3 (2.0%↓)	88.36 ± 2.12 (1.9%↓)	91.40 ± 1.3 (1.45%↑)	90.31 ± 2.4 (0.2%↑)
Compressive failure strain, %	45.14 ± 0.5	41.87 ± 0.2 (7.2%↓)	47.16 ± 0.3 (4.4%↑)	43.55 ± 0.25 (3.5%↓)	47.88 ± 0.33 (6.0%↑)	48.23 ± 0.78 (6.8%↑)

Fig. 8 Bilayer fracture of epoxy– $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanocomposites under compression

ness test was performed using a compression bilayer cylindrical specimen as shown in Fig. 8(a). The cylindrical specimen under compression has an outer layer of pure epoxy and the nanocomposite in the inner core. Under compression, the crack opens due to hoop stress and the crack enters from the outer

layer to the inner layer. Fracture surfaces were observed using FESEM to examine the fractured surface morphology. Figure 8(b) shows the FESEM image of the crack tip area. As shown in Fig. 8(b, A), the fracture surface of neat epoxy is featureless with a smooth surface, consistent with its typical

brittle fracture behavior. The characteristic brittleness and low fracture toughness of cured epoxy are the result of high cross-link density of cured epoxy, which causes low absorption of energy during fracture. With the addition of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticles, the fracture surface shows more irregular, coarse and multi-plane surface features as seen in Fig. 8(b, B), consistent with higher fracture toughness of nanocomposites compared to neat polymer matrix. As shown in Fig. 8(c), the increase in crack kinking around the nanoparticle can be clearly observed from surface of the nanocomposite, which is a possible reason for the increase in the fracture toughness along the bilayer cylindrical surface. Also we can see the internal crack regions in higher-magnification images, which show the debonding process during fracture due to nano-sized particles. However, debonding is important because this reduces the restriction at the crack tip and hence allows the matrix to deform plastically via a void growth mechanism. Figure 8(b, B) shows the evidence of voids around the nanoparticles debond during fracture, which we cannot observe in pure epoxy shown in Fig. 8(b, A). This is expected to be a combined effect of nanocomposite geometry for crack kinking, void growth mechanism. Also due to inhibitory effect of the nanoparticle in the matrix cross-linking and presence of oxide to the polymer cross-linking showed in Energy Dispersive Spectroscopy (EDS) mapping.

The burnout test results reported in Fig. 9(a) clearly suggest the minimum oxidation of 10 wt.% in $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ -epoxy composite due to high vapor pressure of ceria. A significant degradation occurred between 300 and 325 °C. This is due to oxidation reactions involving aliphatic bridges that bonded the aromatic rings of the matrix and breaking of bonds between rings and aliphatic bridges/phenolic hydroxyl groups. The elastic modulus and loss factor versus temperature for the cured pure epoxy and epoxy nanocomposite filled with 5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ are shown in Fig. 9(b). It shows the elastic modulus of epoxy-5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ composite which is little higher than pure epoxy. Figure 9(b) shows a slight increase in the glass transition temperature T_g of the epoxy-5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ composite compared to that of pure epoxy. The glass transition temperature of cured pure epoxy and epoxy with nanocomposite reinforced with $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticle loading of 5 wt.% is 127.8 °C, which is 4.1 °C higher than that of cured epoxy (123.7 °C). Increased T_g is associated with the increased cross-linking degree of the

materials, which means $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticle could restrict the mobility of the polymer chain and promote the curing process (Ref 35, 36).

3.2 Effect of Nanocomposite Matrix in GFRP Laminate

From last few decades, the development of polymer nanocomposites such as epoxy nanocomposites delivers new opportunities to explore new fracture behavior and multi-functionality beyond those found in conventional FRP composites. The mechanisms for increasing their modulus of elasticity, tensile strength, ductility, and fracture toughness of polymers via incorporation of micro-/nano-sized particles have been extensively studied (Ref 37). In addition, most studies attributed the role of the enormous surface area of nanofillers; however, most of polymer nanocomposites exhibited partly agglomerated dispersion of nanofillers, and few systems could achieve full dispersion. Here we intended to characterize the fiber-reinforced composite with a matrix modified with uniformly dispersed mixed metal oxide nanoparticles to improve mechanical properties, particularly interfacial bonding between fiber and matrix. It is observed that for the 5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticles in the epoxy matrix, the tensile modulus and strength of the epoxy composite improved slightly

Fig. 10 Tensile stress-strain graphs of pure epoxy and epoxy-5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanocomposite

Fig. 9 (a) Burnout results for epoxy-(x wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$) composites compared to epoxy, (b) dynamic elastic property of pure epoxy and epoxy-5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$

Fig. 11 FESEM images of (a) epoxy/GFRP and (b) $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ /GFRP nanocomposites after tensile fracture

(Fig. 10). This may be due to the strong interface between metal oxide and matrix to fiber. To further understand the enhancing mechanism, the failure surfaces of the samples were examined using SEM. Figure 11 shows the morphology of the tensile-fractured GFRP matrix composite with 5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$. It is evident from Fig. 11(a) that the layers of polymer and glass fibers stacked one over another formed good bonding. It is clear that glass fibers are well embedded in epoxy, which improves the mechanical properties of the composites with usual fracture initiated from matrix cracking. In optimized 5 wt.% of the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ nanoparticles interfaces which are formed inside the composite and are close to fibers are shown in Fig. 11(b). No or very little micro-cracks are observed with a small amount of shear bonding as compared to that at epoxy, which suggests a relatively strong interfacial bonding, control of the local stress concentration, and good compatibility of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ particles with the fiber interface. From the SEM observations, it appears that the nanocomposites possess better interfacial bonding than the conventional one. Finally, it is concluded that the influence of mixed metal oxide nanoparticle reinforcements indicates that the interfacial bonding between matrix/fiber enhances the final structure of the mechanical properties.

4. Conclusions

XRD study shows, except pure ZrO_2 all other samples are well crystalline and cubic fluorite phase with the composition $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ is observed with optimal influence on mechanical properties of the epoxy matrix system. Average particle size ranged between 10 and 20 nm, which confirms the monodispersed system of 5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ particles. The overall mechanical properties of the nanocomposite matrix are improved with 5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$. With the addition of 5 wt.% $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, the fracture toughness enhancement due to the toughening mechanisms via crack kinking, void growth mechanism and interface addition are confirmed. The elastic modulus, glass transition temperature and loss factor of the nanocomposite were improved. Tensile strength and modulus of nanocomposite/GFRP system show a marginal increase. Micro-cracks are minimized at the fiber interface of GFRP, which suggests a relatively strong interfacial bonding, control of the local stress concentration, and good compatibility of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ particles.

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References

1. I.A. Al Ajaj, M.M. Abd, and H.I. Jaffer, Mechanical Properties of Micro and Nano TiO_2 /Epoxy Composites, *IJMMME*, 2013, **2**, p 2320–4060
2. B. Bittmann, F. Hauptert, and A.K. Schlarb, Preparation of TiO_2 /Epoxy Nanocomposites by Ultrasonic Dispersion and Their Structure Property Relationship, *Ultrason. Sonochem.*, 2011, **18**, p 120–126
3. Y. Zheng, Y. Zheng, and R. Ning, Effects of Nanoparticles SiO_2 on the Performance of Nanocomposites, *Mater. Lett.*, 2013, **57**, p 2940–2944
4. A. Omrani, L.C. Simon, and A. Rostami, The Effects of Alumina Nanoparticle on the Properties of an Epoxy Resin System, *Mater. Chem. Phys.*, 2009, **114**, p 145–150
5. T.R. Prabhu, S. Basavarajappa, R.B. Santhosh, and S.M. Ashwini, Tribological and Mechanical Behaviour of Dual-Particle (Nanoclay and CaSiO_3)-Reinforced E-Glass-Reinforced Epoxy Nanocomposites, *Bull. Mater. Sci.*, 2017, **40**, p 107–116
6. V. Arrighi, I.J. McEwen, H. Qian, and M.B. Serrano Prieto, The Glass Transition and Interfacial Layer in Styrene-Butadiene Rubber Containing Silica Nanofiller, *Polymer*, 2003, **44**, p 6259–6266
7. Z. Guo, K. Lei, Y. Li, H.W. Ng, S. Prikhodko, and H.T. Hahn, Fabrication and Characterization of Iron Oxide Nanoparticles Reinforced Vinyl-Ester Resin Nanocomposites, *Compos. Sci. Technol.*, 2008, **68**, p 1513–1520
8. Z. Guo, T. Pereira, O. Choi, Y. Wang, and H.T. Hahn, Surface Functionalized Alumina Nanoparticle Filled Polymeric Nanocomposites with Enhanced Mechanical Properties, *J. Mater. Chem.*, 2006, **16**, p 2800–2808
9. H.J. Kim, D.H. Jung, I.H. Jung, J.I. Cifuentes, K.Y. Rhee, and D. Hui, Enhancement of Mechanical Properties of Aluminium/Epoxy Composites with Silane Functionalization of Aluminium Powder, *Composites B*, 2012, **43**, p 1743–1748
10. G. Zhang, G. Xie, J. Wang, L. Si, D. Guo, S. Wen, and F. Yang, Controlled Friction Behaviors of Porous Copper/Graphite Storing Ionic Liquid through Electrical Stimulation, *Adv. Eng. Mater.*, 2017, **20**(5), p 1700866
11. G. Zhang, G. Xie, L. Si, S. Wen, and D. Guo, Ultralow Friction Self-Lubricating Nanocomposites with Mesoporous Metal–Organic Frameworks as Smart Nanocontainers for Lubricants, *ACS Appl. Mater. Interfaces*, 2017, **9**, p 38146–38152
12. T.M. Pollock, D.M. Lipkin, and K.J. Hemker, Multifunctional Coating Interlayers for thermal-Barrier Systems, *MRS Bull.*, 2012, **37**, p 923–931
13. P. Nitin, G. Maurice, and H.J. Eric, Thermal Barrier Coatings for Gas-Turbine Engine Applications, *Science*, 2002, **296**, p 280–284
14. L. Yves, Durability of Nanosized Oxygen-Barrier Coatings on Polymers, *Prog. Mater. Sci.*, 2003, **48**, p 1–55

15. C.P.F. Crissia, T.B.N. Annibal, P.S. Adelina, and O.F. Luiz, P(VDF-TrFE)/ZrO₂ Polymer-Composites for X-Ray Shielding, *Mater. Res.*, 2016, **19**, p 426–433
16. B. Ma, Y. Li, and K. Su, Characterization of Ceria-Yttria Stabilized Zirconia Plasma-Sprayed Coatings, *Appl. Surf. Sci.*, 2009, **255**, p 7234–7237
17. S.K. Tadokoro and E.N.S. Muccillo, Physical Characteristics and Sintering Behavior of Ultrafine Zirconia–Ceria Powders, *J. Eur. Ceram. Soc.*, 2002, **22**, p 1723–1728
18. W. Huang, C. Wang, J. Yang, B. Zou, X. Meng, Y. Wang, X. Cao, and Z. Wang, Effect of Zr/Ce Molar Ratio on the Structure of Powders and Zr_{1-x}Ce_xO₂ Coatings on Quartz Fiber Reinforced Polyimide Matrix Composites via Sol–Gel Process, *J. Sol Gel Sci. Technol.*, 2012, **61**, p 213–223
19. K.V. Pochiraju, G.P. Tandon, and G.A. Schoeppner, *Long-Term Durability of Polymeric Matrix Composites*, 1st ed., Springer, Berlin, 2012, p 1–677
20. X.F. Yao, H.Y. Yeh, D. Zhou, and A.H. Zhang, The Structural Characterization and Properties of SiO₂-Epoxy Nanocomposites, *J. Compos. Mater.*, 2006, **40**, p 371–381
21. V.K. Rangari, T.A. Hassan, Q. Mayo, and S. Jeelani, Size Reduction of WO₃ Nanoparticles by Ultrasound Irradiation and Its Applications in Structural Nanocomposites, *Compos. Sci. Technol.*, 2009, **69**, p 2293–2300
22. S. Datta, B.M. Nagabhushana, and R. Harikrishna, A New Nano-ceria Reinforced Epoxy Polymer Composite with Improved Mechanical Properties, *IJARET*, 2012, **3**, p 248–256
23. R. Medina, F. Hauptert, and A.K. Schlarb, Improvement of Tensile Properties and Toughness of an Epoxy Resin by Nanozirconium-Dioxide Reinforcement, *J. Mater. Sci.*, 2008, **43**, p 3245–3252
24. S.M. Mirabedini, M. Behzadnasab, and K. Kabiri, Effect of Various Combinations of Zirconia and Organoclay Nanoparticles on Mechanical and Thermal Properties of an Epoxy Nanocomposite Coating, *Composites A*, 2012, **43**, p 2095–2106
25. P. Dittanet and R.A. Pearson, Effect of Silica Nanoparticle Size on Toughening Mechanisms of Filled Epoxy, *Polymer*, 2012, **53**, p 1890–1905
26. M. Sudheer, K.M. Subbaya, D. Jawali, and T. Bhat, Mechanical Properties of Potassium Titanate Whisker Reinforced Epoxy Resin Composites, *J. Miner. Mater. Charact. Eng.*, 2012, **11**, p 193–210
27. H.J. Kim, D.H. Jung, I.H. Jung, J.I. Cifuentes, K.Y. Rhee, and D. Hui, Enhancement of Mechanical Properties of Aluminium/Epoxy Composites with Silane Functionalization of Aluminium Powder, *Composites B*, 2012, **43**, p 1743–1748
28. H. Faleh, R. Al-Mahaidi, and V. Shen, Fabrication and Characterization of Nanoparticle Reinforced Epoxy, *Compos. B Eng.*, 2012, **43**, p 3076–3080
29. A. Toldy, B. Szolnoki, and G.Y. Marosi, Flame Retardancy of Fibre-Reinforced Epoxy Resin Composites for Aerospace Applications, *Polym. Degrad. Stab.*, 2011, **96**, p 371–376
30. S. Lu, J. Ban, and K. Liu, Preparation and Characterization of Liquid Crystalline Polyurethane/Al₂O₃/Epoxy Resin Composites for Electronic Packaging, *Int. J. Polym. Sci.*, 2012, **2012**, p 728235
31. Y. He, B.E. Moreira, and A. Overson, Thermal Characterization of an Epoxy-Based Under Fill Material for Flip Chip Packaging, *Thermochim. Acta*, 2000, **357–358**, p 1–8
32. D. Ratna, T.K. Chongdar, and B.C. Chakraborty, Mechanical Characterization of New Glass Fiber Reinforced Epoxy Composites, *Polym. Compos.*, 2004, **25**, p 165–171
33. B. Kchaou, C. Turki, and M. Salvia, Dielectric and Friction Behaviour of Unidirectional Glass Fibre Reinforced Epoxy (GFRE), *Wear*, 2008, **265**, p 763–771
34. C.S. Tiwary, S. Kishore, R. Vasireddi, D.R. Mahapatra, P.M. Ajayan, and K. Chattopadhyay, Electronic Waste Recycling via Cryo-Milling and Nanoparticle Beneficiation, *Mater. Today*, 2017, **20**, p 67–73
35. M. Abdalla, D. Dean, M. Theodore, J. Fielding, E. Nyairo, and G. Price, Magnetically Processed Carbon Nanotube/Epoxy Nanocomposites: Morphology, Thermal, and Mechanical Properties, *Polymer*, 2010, **51**(7), p 1614–1620
36. Y. Pan, Y. Xu, L. An, H. Lu, Y. Yang, and W. Chen, Hybrid Network Structure and Mechanical Properties of Rodlike Silicate/Cyanate Ester Nanocomposites, *Macromolecules*, 2008, **41**(23), p 9245–9258
37. J. Njuguna, K. Pielichowski, and S. Desai, Nanofiller-Reinforced Polymer Nanocomposites, *Polym. Adv. Technol.*, 2008, **19**(8), p 947–959