Original Article

Silane coupling agent for enhanced epoxy-iron oxide nanocomposite

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In this study, silane-treated Fe$_2$O$_3$ nanoparticles were successfully prepared using (3-amino propyl) triethoxysilane (APTES). The chemical structure and morphology of the obtained nanoparticles were investigated by several analysis techniques including FTIR, XRD, TEM and DLS. Both of untreated Fe$_2$O$_3$ (IO) and silane-treated Fe$_2$O$_3$ (SIO) nanoparticles were used in the preparation of epoxy nanocomposites with 5% by weight fraction. FTIR and XRD approved that SIO was successfully prepared with highly crystalline structure. TEM and DLS indicated the good dispersion of treated nanoparticles in the nanocomposite matrix, also the average particle size of nanofiller decreased to ∼200 nm after silane treatment. The dynamic properties for the prepared nanocomposites were studied using DMA and confirmed by nanoindentation technique. The results indicated that silane-treated nanoparticles can improve the hardness and $T_g$ by 87.5 and 5 °C respectively at 5% weight fraction.

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1. Introduction

Epoxy is considered as one of the greatest desired thermoset polymers. This results from its high mechanical and physical characteristics and highly cross-linked nature. Extensively, epoxy is being applied in several areas such as “constructions, car accessories, electrical insulators, marine and aerospace applications” [1]. Whilst the neat crosslinked epoxy has a brittle nature, low fatigue resistance and low toughness manner, this can restrain the growth of its applicable domain. Several attempts were actually suggested to enhance the physical, mechanical and thermal characteristics of epoxy through filling epoxy matrix with different nanofilling materials. Concerning this, nanofilbers with many types and different grades such as “SiO$_2$, CNT, Al$_2$O$_3$, natural and synthetic nanofibrils, MMT and TiO$_2$” were loaded within epoxy matrix with different ratios to obtain improved nanocomposites [2]. For example, Phong et al. successfully fabricated micro and nano bamboo fibers using mercerization treatment followed by “mechanical extraction” technique that called “micro-grinding”. When epoxy matrix was filled by 0.8 wt.% treated nanofibers, the obtained nanocomposite achieved enhanced “fracture toughness” by 84.6% [3].

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In fact, the two factors of “high viscous matrix” and “large specific surface area of nanofiller” can lead to bad dispersion of nanofiller within matrix. In this case, the collected and agglomerated nanofillers cannot enhance the different characteristics of the resulted nanocomposite. As well, these agglomerated ones may help and increase the start of cracking process that leads to premature deformation. Some attempts such as chemical and physical treatments have been studied to overcome this disadvantage. Adding of suitable coupling agents, using of surface coating and addition of some surfactants are some of these common treatments [4].

Actually, the surface treatment using a suitable coupling agent helps and improves the combination between the matrix and its filling material, the reinforcement process in this case will be highly effective [5]. The silane coupling agent, for example, such as methyltrimethoxysilane and aminopropyltriethoxysilane, has inorganic and organic ends. Silane reacts with the inorganic filler through its easily hydrolysable group meanwhile it attaches with the matrix through its organic end. So, silane can attach both organic matrix and inorganic filler together resulting in new filler-matrix interface [6,7]. The influence of chemical treatment for “aluminum powder” with “3-aminopropyltriethoxysilane” coupling agent on the epoxy characteristics was reported by Kim et al. [8]. In this study, the “tensile strength and modulus” for chemically treated composite were respectively enhanced by 12 and 9%, compared with neat epoxy.

Concerning current study, epoxy-iron oxide nanocomposites were formulated through filling epoxy matrix with iron oxide and silane-modified iron oxide nanoparticles. For studying the effect of treatment of filler with silane on the overall composite; microstructural, physical and mechanical characterizations were performed using FTIR, XRD, TEM, DLS, nanoindentation and DMA techniques.

2. Materials and methods

2.1. Materials

Epoxy matrix (635-Thin epoxy resin-US Composites) with viscosity of 600cps was used with its amine hardener as 2:1. Iron oxide (IO) nanoparticles, Fe₂O₃, was used as filler and aminopropyltriethoxysilane (APTES) was used as coupling agent; both were purchased from Sigma Aldrich.

2.2. Treatment of Fe₂O₃ nanoparticles

Firstly, 0.5 g of IO nanoparticles was dispersed into 400 ml of ethanol using ultrasonication for 10 min. The chemical treatment of iron oxide with silane was started by adding 2 ml of APTES dropwise to the dispersed solution of IO. Powerful stirring has been applied for this system and maintained for 24 h. The obtained treated material was then centrifuged, washed with ethanol-distilled water solution (1:1) three times and finally dried at 80 °C to obtain SIO as illustrated in Scheme 1.

Scheme 1 – Formation of silanated iron oxide nanoparticles.

2.3. Preparation of Fe₂O₃-epoxy nanocomposite

Epoxy matrix was filled with loading percentage of 5% using both IO and SIO nanofillers. Separately, IO and SIO were firstly mixed well into epoxy base and then were dispersed using ultrasonication for 10 min in ice bath. After addition of the hardener, the epoxy-IO and epoxy-SIO nanocomposites were kept for curing at room temperature for 7 days in teflon molds to avoid stacking.

2.4. Characterizations

2.4.1. Fourier transform-infrared

The spectral data of Fourier transform-infrared (FTIR) were detected within a wave number range of 400–4000 cm⁻¹ using Nicolet IS-10 FTIR spectrophotometer-Thermo Fisher Scientific. The specimens were finely grinded followed by mixing along with KBr in the form of pellets.

2.4.2. X-ray diffraction

The crystallinity of treated and untreated samples was characterized using X-ray diffraction (wide angle XRD) analysis. The diffraction patterns were measured by Panalytical-X’pert-PRO with the Cu K-alpha source. The analysis was run though “1.54 Å wavelength, 40 kV voltage and 40 mA current”. The 2θ range was 4–80° with a rate of 1°/min.

2.4.3. Transmission electron microscopy

The morphological features were examined by transmission electron microscopy (TEM) using high resolution JEOL-2100F TEM at 200 kV.

Measurements were conducted by preparing the sample in a diluted ethanol colloidal mixture which was sonicated for 15 min. A droplet of the dispersed solution has been positioned on the TEM grid. After drying, the grid was connected to the microscope and images were captured.

2.4.4. Dynamic light scattering

The “particle size distribution” for IO and SIO was statistically measured using Malvern dynamic light scattering (DLS). The specimen was firstly well dispersed and sonicated in deionized-water 10 min. The obtained dispersed solution was then subjected to DLS at 23 °C with a scattering angle of 90°.
2.4.5. Nanoindentation
Load-depth, hardness, modulus and creep were identified for the different nanocomposites using YL-Nanotest Vantage-Micromaterials based on the standards for instrumented indentation, “ASTM E-2546”. For each specimen, a matrix of 25 indents were performed using the Berkovich diamond tip through a grid of five indents in Y-axis and five indents in Z-axis. The applied load was gradually reached to 100 mN with a loading rate of 10 mN/s. The maximum load was held for 10 s followed by unloading with the same rate.

2.4.6. Dynamic mechanical analysis
“Glass transition temperature” (Tg) and “storage modulus” (E’) were measured for different nanocomposites by dynamic mechanical analyzer (DMA) using Triton Technology-TTDMA following “ASTM D-4065” standards. Using three point bending mode with frequency of 1 Hz, the specimens with “25 mm length, 10 mm width and 3 mm thickness” subjected to 100°C by heating rate of 5°C/min.

3. Results and discussion

3.1. Fourier transform-infrared
Silane grafting on IO nanoparticles has been assured through FTIR analysis as shown in Fig. 1. In IO spectrum, a broad band and another weak one were observed near 3350 and 1620 cm⁻¹ that characteristic for stretching and bending of “O-H” groups [9]. The peak at 560 cm⁻¹ is characteristic to “Fe-O” [10]. In the FTIR spectrum of SIO compared with that of IO, it is clear that the band near 3350 cm⁻¹ disappeared. This is due to consuming of hydroxyl groups through reaction with silane that attached to iron oxide surface. In addition to 560 cm⁻¹–570 cm⁻¹ band that characterized for “Fe-O-Si”, a group of new three bands are observed at 2920, 1600 and 1150 cm⁻¹ which respectively refer to “C-H, N-H and Si-O-C” groups, respectively [11]. These absorption bands confirm that silane coupling agent was covalently bonded to the surface of iron oxide. The obtained FTIR spectra approve successful grafting of iron oxide with silane yielding SIO nanoparticles.

3.2. X-ray diffraction
Fig. 2 illustrates the XRD for untreated and treated samples. The obtained diffraction patterns ascribed for the “rhombohedral phase” for “α-Fe₂O₃” according to ICDD ref. card 04-008-7623. The illustrated diffraction patterns demonstrate highly crystalline and pure “α-Fe₂O₃” specimens [12]. Also, the increase of the peaks heights confirms increasing the intensity of crystallization. The mean crystalline size of functionalized iron oxide nanoparticles was determined to be about 200 nm using Scherrer’s formula as illustrated in “Eq. (1)”.

\[
T = \frac{K \lambda}{\beta \cos \theta}
\]

“T” is the average crystalline size. “K” is a factor (0.89) for “dimensionless shape”. “θ” and “λ” are respectively the Bragg’s angle and wavelength. “β” is the value of peak width at half of maximum height after subtracting the line width in radians.

3.3. Transmission electron microscopy
Fig. 3(a and b) illistrates the TEM photos for epoxy-untreated/silane treated Fe₂O₃ nanoparticles (NPs), respectively. Images with low magnification in Fig. 3(a and b) give a general observation for the dispersion of untreated and treated Fe₂O₃ NPs within polymeric matrix. We can notice that SIO has more homogenous distribution with the lack of agglomerated structures with particle size ranged from 100 to 300 nm. However, IO particles suffer from the bad distribution through displaying greater agglomerated (collected) structures with higher average of particle size. In this case, the nanofillers can form agglomerated areas that resulted from incompatibility with matrix. This incompatible attaching may lead to weak bonds and large cavities at the matrix-nanofiller interface. The nanoparticles here cannot bear or transfer the external load.
3.4. **Dynamic light scattering**

The measured “particle size distribution” for IO and SIO nanofillers are given in Fig. 4(a and b), respectively. In Fig. 4(a), the average of particle size for IO particles is 843; this reveals the larger agglomerated area and bad dispersion. Actually, DLS deals with the collected or agglomerated structures as a single molecule and measures its whole size [13]. On the other hand, the SIO sample showed smaller particle size with average of 211 nm regarding fewer agglomerated structures and better
after nanoindentation test the stiffer surface tested [14,15]. The surface analysis of the influence of the applied load on the IO-epoxy and SIO-epoxy nanocomposites was studied using nanoindentation technique. Fig. 6 shows three dimensional representation maps for hardness variation in case of neat epoxy (a), epoxy-IO (b) and epoxy-SIO (C). The hardness, calculated from Eq. (2) following “ASTM E-2546”, for neat epoxy is 0.04 GPa as the least value. The observed difference in peaks height in Fig. 6(b) representing the variation in hardness values is due to agglomeration of IO in epoxy matrix. However, in Fig. 6(c), the values of surface hardness show a lower variation which approves that less agglomeration and more homogeneity have been occurred with SIO. Moreover, the improved hardness in treated Fe$_3$O$_4$ nanocomposites indicates that the applied stress is efficiently transferred from epoxy to the treated nanofiller through a stronger filler–matrix interface, the hardness in this case reached to maximum value at 0.075 GPa. Actually, the stronger filler–matrix interface the more enhanced composite that having an effective reinforcing material [16].

$$H = \frac{P}{A}; \quad A = f(h_c)$$ (2)

where “H” is hardness of the tested specimen, “P” is maximum load applied by the nanoindenter and “A” is the surface-contacted indentation area, which is a function of the indentation depth “hc” on the tested surface. A surface grid of 25 (5x5) indentations under 100 mN load with 10 mN/s loading rate is shown in Fig. 6(d). The modulus values (measured by nanoindentation) for blank epoxy, epoxy-IO and epoxy-SIO are displayed in Fig. 7. The modulus increased from 1.47 GPa for epoxy to 1.61 and 1.75 GPa for epoxy-IO and epoxy-SIO nanocomposites, respectively. The silane-treated nanocomposite achieved an improved modulus due to the stronger interfacial adhesion between treated nanoparticles and matrix than untreated filler. A similar observation was noticed from Fig. 8 at which the creep behavior is studied. Our results approved that inclusion of IO into epoxy led to improve the creep compliance through lowering the deformation depth from 10900 to 9020 nm for epoxy and IO-epoxy, respectively. Nevertheless, SIO nanoparticles affected creep behavior significantly by the decrease till 8100 nm. Lower indentation depth, higher hardness, more creep resistance and higher modulus reveal the enhanced properties after chemical treatment with silane.

### 3.5. Nanoindentation

The mechanical characteristics including indentation depth, hardness, modulus and creep for neat epoxy, epoxy-IO and epoxy-SIO composites were extracted from loading–unloading curve that shown in Fig. 5. The neat epoxy recorded the maximum indentation depth at 8510 nm. However, epoxy-IO and epoxy-SIO nanocomposites recorded lower depths at 7290 and 6780 nm, respectively, regarding a stiffer surface after filling process especially in case of epoxy-SIO nanocomposite that achieved the least depth. Actually, the smaller depth recorded dispersion, Fig. 4(b). This manner resulted from silane treatment that succeeded in dispersing and functionalizing the IO particles in addition to reduce the particle size and increase the surface area. The DLS measurements are matching with that obtained from TEM images through more dispersion, less agglomeration and smaller particle size achieved after treatment with silane coupling agent.

![Fig. 4 – Statistical particle size distribution by DLS for untreated (a) and treated (b) Fe$_3$O$_4$ NPs.](image)

![Fig. 5 – Load–depth curve for neat epoxy, epoxy-IO and epoxy-SIO nanocomposites.](image)

### 3.6. Dynamic mechanical analysis

DMA was employed to evaluate the effect of filling epoxy with IO and SIO on its dynamic response. The storage modulus “E’” curves for neat epoxy, epoxy-IO and epoxy-SIO are represented in Fig. 9(a); E’ was calculated from Eq. (3) following “ASTM D-4065”.

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta; \quad \sigma = \sigma_0 \sin(\omega t + \delta), \quad \varepsilon = \varepsilon_0 \sin(\omega t)$$ (3)

where “$\sigma$” is stress, “$\varepsilon$” is strain, “$\delta$” is phase lag, “$t$” is time and “$\omega$” is the frequency of DMA oscillation. According to the results, the value of $E'$ for epoxy increased with adding
Fig. 6 – Three dimensional representation maps of hardness variation; (a) for neat epoxy, (b) for epoxy-IO and (c) for epoxy-SIO. (d) A surface grid set for 25 indents on epoxy nanoparticle composite.

Fig. 7 – Modulus of neat epoxy, epoxy-IO and epoxy-SIO (measured by nanoindentation).

Fig. 8 – Creep behavior of neat epoxy, epoxy-IO and epoxy-SIO nanocomposites.
IO filler from 1.45 to 1.59 GPa, this resulted from the high storage modulus of these nanoparticles. Whereas addition of SIO nanoparticles exhibited much higher storage modulus at GPa, which further implied more reinforcing effect for silane-treated Fe₂O₃ nanoparticles. These values confirm the enhancement in mechanical characteristics for the treated nanocomposite that investigated by nanoindentation (Section 3.3). Furthermore, storage modulus measured here by DMA is matched with the modulus measured by nanoindentation for all specimens. This observation reflects the good dispersion of treated nanofiller into matrix that leading to uniform nanocomposite with the same properties at any point on its surface. It is concluded that silane modification of nanoparticles could reduce their domain size and improve the “dispersion state” and “interfacial adhesion” for all components by “physiochemical interaction”. From “tan δ” curves shown in Fig. 9(b), the main mechanical relaxation is improved and Tg of the nanocomposites increases linearly. Since the interfacial layers rising from the interaction between treated nanofiller and epoxy throughout the process of crosslinking can provide “segmental dynamics” dissimilar to neat matrix. The prepared SIO-epoxy nanocomposites show higher Tg (49 °C) than untreated or neat epoxy systems (44 °C). With good dispersion of SIO nanofiller into epoxy matrix, the “free space” between different molecules decreases resulting in lowering the “segmental mobility” [17]. Oppositely, filling epoxy with untreated IO did not enhance or affect Tg value due to bad dispersion in epoxy. The incorporation of treated Fe₂O₃ into epoxy matrix has increased the Tg value.

4. Conclusion

- The functionalization of Fe₂O₃ (IO) nanoparticles was successfully performed by using 3-aminopropyltriethoxysilane (APTES) as coupling agent to prepare SIO nanoparticles.
- The chemical structure of the crystalline SIO was confirmed by FTIR spectrum and XRD pattern.
- The reduction in particle size distribution for silane treated nanoparticles from ~800 to 200 nm was observed statistically by DLS technique.
- SIO nanoparticles were incorporated into epoxy matrix by 5% wt fraction and their distribution was clearly observed using TEM.
- The mechanical and thermal properties improved as investigated by nanoindentation and DMA techniques. Compared to neat epoxy, the incorporation of SIO nanoparticles into epoxy had been found to:
  - Increase the storage modulus from 1.45 to 1.71 GPa.
  - Improve the creep compliance from 10 900 to 8100 nm and reduce the indentation depth from 8510 to 6780 nm.
  - Enhance the Tg of the used epoxy from 44 to 49 °C.
  - Increase the hardness from 0.04 to 0.075 GPa.
- Enhancement of mechanical and physical properties for the modified APTES–Fe₂O₃–epoxy nanocomposites is due to good dispersion and less agglomeration of SIO in epoxy matrix resulting in stronger interfacial adhesion.

Conflict of interest

Compliance with Ethical Standards; the authors declare that they have no conflict of interest.

References


