EPOXY/TITANATE MODIFIED NANOSILICA COMPOSITES: MORPHOLOGY, MECHANICAL PROPERTIES AND FRACTURE TOUGHNESS

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ABSTRACT

In this paper, the effect of modified nanosilica as a reinforcement agent on the performance of epoxy resin using tetrabutyl titanate (TBuT) hardener were investigated. Morphology of the epoxy/modified silica composites was determined by Scanning Electron Microscopy (SEM) method. Impact strength and flexural strength of the composites were measured by Charpy impact test and three-point bending test mode methods, respectively. Fracture toughness and fracture energy were calculated according to pre-cracked, single edge notched method with specimens in three-point bending geometry and suitable equations. The mechanical properties and fracture toughness of composites were significantly enhanced with loading nanosilica content to 5 wt.%. 

Keywords: epoxy, modified nanosilica, nanocomposite, tetrabutyl titanate (TBuT) hardener, fracture toughness.

1. INTRODUCTION

Composite materials based on polymers and nanosized additives can provide engineering applications by some advantages of nanosized additives such as high stiffness, strength, wear resistance, and fracture toughness [1-2]. Thanks to high mechanical performance and high adhesive strength, epoxy resins have been commonly applied in aerospace, construction, structural adhesive and so on. However, cured epoxy systems have one main drawback: considerable brittleness, which shows poor fracture toughness and poor resistance to crack initiation and propagation, so limited their application in fields requiring high fracture strength [3-6]. Among nanosized additives, nanosilica particles can be mainly used in paints, plastic, sealants, adhesives and many other fields. Dettanet et al. [7] showed the size of nanosilica has affected significantly on mechanical properties of epoxy composite containing 2.5 wt.% nanosilica, in which, the particle size of nanosilica is bigger, the tensile strength of the epoxy
composite is decreased more. In a publication of Brunner et al. [8], the fracture toughness of epoxy/7.2 wt.% nanosilica systems reached to 160 J.m\(^{-2}\) and increased 23% in comparison with the neat epoxy resin. Liu et al. [9] demonstrated that the fracture toughness of epoxy nanocomposite can be improved as combining nanosilica with rubber nanoparticles in the epoxy system. The SEM image results revealed toughness mechanism in nanocomposite due to debonding and pull-out of nanosilica and particles matrix deformation. Liang and Pearson [2] also investigated the toughness mechanism of nanosilica epoxy system with different particles size of nanosilica (20 nm and 80 nm in diameter).

However, the effect of nanosilica particles modified by KR-12 titanate coupling agent on mechanical properties and fracture toughness of epoxy/silica composite has been limited. Therefore, in this study, the effect of nanosilica modified by KR-12 titanate coupling agent on the mechanical properties and fracture toughness of the epoxy/modified silica composites as well as morphology of the composites after flexural and fracture failure was focused. In particular, fracture energy of the composites was also calculated and presented.

2. EXPERIMENTS

2.1. Materials

Bis-phenol A epoxy resin (DGEBA type YD-128) with an epoxy equivalent weight of 188 g/mol was purchased from Dow Chemical Company; KR-12 tetrabutyl titanate (TBuT 99.0 %, C\(_{16}\)H\(_{35}\)O\(_4\)Ti, MW 340.32 g/mol) as a hardener was supplied by Sigma Aldrich. Nanosilica K-200 (Korea) purchased from DC Chemical Co. Ltd, average particles size of 20 – 30 nm, specific surface area of 200 m\(^2\)/g was used for preparation of epoxy/modified silica (m-silica) nanocomposites. Acetone (AR grade, China 99.5 %) was used as purchased without any treatment or purification.

2.2. Preparation of epoxy/modified silica composites

Surface of silica nanoparticles was treated by KR-12 titanate coupling agent according to Ref. [6]. To prepare epoxy/modified nanosilica (m-nanosilica) composites, a series of various m-nanosilica content dispersed in acetone was mixed with epoxy resin (EP) on a mechanical stirring device at a speed of 1500 rpm for 30 minutes and ultrasonic treatment at a speed of 20000 rpm for 1 hour at room temperature. Then, the mixture was heated under a vacuum oven at 65 °C for 5 hours to remove acetone solvent. Afterwards, the TBuT hardener was added into above mixture (the weight mixing ratio of the epoxy and the hardener is 100:15). The mixture with hardener was continuously stirred and ultrasonicated until obtaining a uniform mixture. Next, the mixture was degassed by vacuum-pumping for 1 hour at room temperature. Finally, the mixture was poured into a polytetrafluoroethylene used mold. The samples were cured in an oven at 120°C for 3 hours.

2.3. Characterization and measurements

2.3.1. Mechanical properties

Charpy impact strength of the epoxy/modified nanosilica (m- nanosilica) composites was measured by a Charpy impact strength tester (Tinius Olsen, USA) in accordance with the
standard ISO 179. The dimension of samples was 80 mm (length) × 10 mm (width) × 5.0 mm (thickness).

Flexural strength of the epoxy/m- nanosilica composites was determined in accordance with the standard ISO 178: 2010 using three-point bending test mode at room temperature on a INSTRON 5582-100KN Machine (USA) and loaded cell capacity of 100 kN. The span distance of the three-point bending test was 32 mm and the crosshead had a speed of 5 mm/min. The dimension of samples was 40 mm (length) × 10 mm (width) × 2 mm (thickness). The values of the flexural strength were obtained by measuring five times and then averaging.

2.3.2. Microscopic analysis

Scanning electron microscopic (SEM) analysis of the epoxy/m- nanosilica composites was done to evaluate the nanosilica dispersion and toughness mechanism in epoxy matrix. The samples were cut into 60 nm ultrathin sections at room temperature by a diamond knife using a Leica Ultracut S microtome, then put on 200 mesh copper grids and examined using JEM1010 instrument (JEOL, Japan) at an accelerating voltage 80 kV.

2.3.3 Fracture toughness and fracture energy

Fracture toughness of the epoxy/m- nanosilica composites was conducted using a LLoyd 500 N (England) material testing instrument, following the ASTM standard D5045 as shown in Figure 1. The plane strain fracture toughness (KIC) was measured using pre-cracked, single edge notched, specimens in three-point bending geometry. A pre-crack was made by lightly tapping a fresh razor blade between adjoining plates, with samples dimension of 120 mm (length) × 12.0 mm (width) × 6.0 mm (thickness). For each composite, 5 specimens were evaluated at a rate of 1 mm/min. The fracture toughness of sample was calculated using the following (1) and (2) equations. Where P0 - maximum load, B- width of the specimen; a- crack length; W- height of the specimen; x = a/W.

\[
K_{IC} = \left( \frac{P_0}{BW^{3/2}} \right) f(x) 
\]

\[
f(x) = 6x^{1/2} \left[ 1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2) \right]
\]

\[
(1 + 2x)(1-x)^{1/2}
\]

Figure 1. Fracture toughness test specimen models, 0.45 ≤ a/W ≤ 0.55.

The fracture energy (GIC) of sample was calculated from \( K_{IC} \) and E, using the relationship:

\[
G_{IC} = K_{IC}^2 \left( 1 - \mu^2 \right) / E
\]

where E is the modulus of elasticity of sample was obtained from tensile test, \( \mu \) is the Poisson’s ration.
\[ \mu = \frac{\varepsilon_{\text{trans}}}{\varepsilon_{\text{axial}}} \]  

where \( \varepsilon_{\text{trans}} \) is transverse strain; \( \varepsilon_{\text{axial}} \) is axial strain.

3. RESULT AND DISCUSSION

3.1. Mechanical properties

Mechanical strength of epoxy/m-nanosilica composites was evaluated by impact strength and flexural strength which can reflect the toughness of a material indirectly. Figure 2 shows impact strength and flexural strength of epoxy/m-nanosilica composites loading different m-nanosilica content. As can be seen in Figure 2a, the impact strength of epoxy/m-nanosilica composites was significantly increased with increasing m-nanosilica content and reached a maximum value (36.95 kJ.m\(^{-2}\)) at 5.0 wt. % m-nanosilica. The impact strength of epoxy/m-nanosilica composites was decreased with rising m-nanosilica content over 5.0 wt. %. Similarly, the flexural strength of epoxy/m-nanosilica composites reached a maximum value 116.6 MPa at 5.0 wt. % m-nanosilica (Figure 2b). The maximum values of impact strength, flexural strength of epoxy/m-nanosilica composites was obtained at 5.0 wt. % m-nanosilica and higher than those of neat epoxy resin (87.47 % and 31.45 %, respectively).

![Figure 2. Impact strength and flexural strength of epoxy/m-nanosilica composites loading different m-nanosilica content.](image)

The improved mechanical strength of epoxy/m-nanosilica composites loading 1-5 wt. % m-nanosilica could be explained by good dispersion of m-nanosilica in epoxy resin matrix. On the one hand, thanks to the good interfacial bonding between m-nanosilica and epoxy matrix, the extender force for debonding interfacial between m-nanosilica and epoxy matrix can be dissipated during the fracture process of composites. m-Nanosilica particles could promote the generation of shear yielding of the composites. Thus, the combination of interfacial debonding with shear yielding during the fracture process of composite consumed a large amount of energy, leading to enhancement remarkable of tensile strength of the composites [10]. However, as using m-nanosilica content higher than 5.0 wt. %, the impact strength and flexural strength of the composites were decreased. This is due to the nanosilica particles having a tendency to clumsy
together and form agglomerates in epoxy matrix. The presence of these agglomerates reduces the surface to volume ratio of additives and they constitute weak point, which breaks easily when stress is applied, therefore, the mechanical strength of composites is lower.

3.2. Morphology

Figure 3 displays SEM images of fracture surface of neat epoxy and epoxy/m-nanosilica composites loading 3 wt. % and 5 wt. % m-nanosilica after flexural failure. It is clear that the roughness of fracture surface of the epoxy/m-nanosilica composites was increased with rising m-nanosilica content. Observably, the total fracture surface area of nanocomposites was larger than that of neat epoxy, corresponding to dissipating a higher energy during the fracture process. This result helps to explained for greater impact and flexural resistance of the composites as above discussed.

![Figure 3. Fracture surface after flexural failure of neat epoxy (a) epoxy/3 wt. % m-modified nanosilica (b) and epoxy/5 wt. % m-modified nanosilica composites (c).](image)

3.3. Fracture toughness and fracture energy

Fracture toughness is a measure for the ability of a material to resist the growth of pre-existing cracks or flaws. Figure 4 and Table 1 perform the fracture toughness ($K_{IC}$), fracture energy ($G_{IC}$), modulus of elasticity ($E$), and Poisson’s ratio ($\mu$) of neat epoxy and epoxy/m-nanosilica composites loading different m-nanosilica content.

![Figure 4. Fracture toughness ($K_{IC}$), fracture energy ($G_{IC}$) of neat epoxy (a) and epoxy/m-nanosilica composites loading different m-nanosilica content.](image)
In case of neat epoxy, the determined fracture toughness value was 1.06 MPa.m$^{1/2}$, which correlates well with published literature for epoxy materials [2]. The addition of m-silica nanoparticles into the epoxy matrix causes an increase in fracture toughness ($K_{IC}$) of the composites and a maximum value of 1.73 MPa.m$^{1/2}$ at 5.0 wt.% m-nanosilica, which corresponds to a 91.51% increase in fracture toughness, compared with that of neat epoxy. At higher nanosilica content, the enhancement in $K_{IC}$ epoxy/m-nanosilica was diminished and at 7 wt. % m-nanosilica, the $K_{IC}$ of composite was reduced to 1.45 MPa.m$^{1/2}$. This can be also explained by agglomeration of m-silica nanoparticles, the appearance of agglomerates in epoxy matrix reduced the effective volume fraction of m-silica nanoparticles and net surface area. Therefore, the $K_{IC}$ of epoxy/m-nanosilica composite was reduced [11-12].

Table 1. Fracture toughness ($K_{IC}$), fracture energy ($G_{IC}$), modulus of elasticity (E), and Poisson’s ratio ($\mu$) of neat epoxy and epoxy/m-nanosilica composites.

| Sample  | Modified nanosilica content, wt. % | $E_{\text{tensile}}, \text{GPa}$ | $K_{IC}$ (MPa.m$^{1/2}$) | $\mu$ | $G_{IC}$ (kJ/m$^2$) |
|---------|------------------------------------|-------------------------------|----------------------|------|-------------------|
| EP-N0   | 0                                  | 3.45                          | 0.97                 | 0.330| 0.243             |
| EP-N1   | 1                                  | 3.75                          | 1.27                 | 0.358| 0.375             |
| EP-N3   | 3                                  | 3.82                          | 1.55                 | 0.363| 0.546             |
| EP-N5   | 5                                  | 3.93                          | 1.73                 | 0.365| 0.66              |
| EP-N7   | 7                                  | 3.66                          | 1.45                 | 0.383| 0.47              |

The relationship between elastic modulus (E) and fracture toughness ($K_{IC}$) of the composites is reflected in the equation: $G_{IC} = K_{IC}^2 [(1 - \mu^2)]/E$, where $\mu$ is the Poisson’s ratio, E value is obtained from the tensile test. The fracture energy ($G_{IC}$) quantifies the energy required to propagate the crack in the material. Figure 4b indicated the $G_{IC}$ of neat epoxy was 243 J/m$^2$, which typically shows relatively low values of the $G_{IC}$ for brittle polymers [2]. The incorporation of m-silica nanoparticles into the epoxy caused a significant increase in the composite’s $G_{IC}$ up to 660 J/m$^2$ at 5.0 wt.% m-nanosilica, corresponding to 171.6% increase in fracture energy. This improved critical energy release rate for the epoxy/m-nanosilica composites is comparable to that of tough polymers [2]. These results expressed the potency of m-silica nanoparticles in toughening of the epoxy resin.

Figure 5. SEM micrographs fracture surface of neat epoxy (a), epoxy/3 wt.% m-nanosilica (b), and epoxy/5 wt.% nanosilica composites (c) after fracture toughness test.
Figure 5 demonstrates SEM images of fracture surface of neat epoxy and epoxy/m-nanosilica composites loading 3 and 5 wt.% m-nanosilica. The Figure 5a indicated that the fracture surface of neat epoxy sample was relatively smooth, which is typical of a brittle homogenous thermosetting polymer.

As shown in Figures 5b-c, the roughness of fracture surface of composites was increased with increasing m-nanosilica content, which is typical of a tough polymer. This result may confirm that during the destruction of the composite using investigated m-nanosilica content, the crack propagation of the composite is more difficult and consumes more energy. Nano additive as m-nanosilica can transfer stress effectively and prevent the cracks propagation in the cured epoxy resin [13-14].

4. CONCLUSION

The effect of modified nanosilica content on mechanical strength, fracture toughness, morphology of epoxy/modified silica composites loading modified silica different content were investigated. The epoxy/m-nanosilica composites had maximum values of impact strength, flexural strength, fracture toughness and fracture energy at 5.0 wt. % nanosilica. The significant increase in toughness and fracture energy of composites was shown that epoxy resin to change from brittle polymer to tough polymer.

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