FRACTURE BEHAVIOR OF EPOXY/NANOPARTICLE NANOCOMPOSITES AT LOW AND HIGH TEMPERATURE

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Abstract
In the present paper the fracture behaviour of an epoxy/silica nanoparticle nanocomposite system is analysed, discussing the results from CT fracture tests. It is found that nanomodification significantly enhances the fracture toughness of the epoxy resin at room temperature. Differently, at higher and lower temperatures the effect of nanoparticle loading is less evident.

1. Introduction

The possibility to obtain outstanding improvements of mechanical properties at low nanofiller contents has received significant interest in the use of nano-modified epoxy resins from the scientific community and, in particular, many authors focused their attention on the use of nanoparticles to improve the fracture toughness of polymer resins.
Among these, Chen et al. [1] investigated the mechanical properties of epoxy–nanocomposite resins filled with 12-nm spherical silica particles dispersed with minimal aggregation and obtained, for filler contents lower than 10%, substantial improvements of the tensile modulus and the fracture toughness. The silica nanoparticle size effect was studied experimentally by Liang and Pearson [2] and Dittanet et al. [3] who agree that the Young's modulus and the fracture toughness of epoxy resins can be significantly improved by nanomidification, the effect of particle size being almost negligible. In agreement with previous findings by Hsieh et al. [4], Dittanet et al. [3] noted the presence of debonding of silica nanoparticles, matrix void growth, and matrix shear banding on the surfaces of fractured specimens. Different from the above mentioned works, Zamanian et al. [5] showed that the mechanical properties of epoxy resins were largely improved by the addition of different nanosilica particles, the better improvements being obtained with the smaller nanoparticles. As far as the effect of testing temperatures is concerned, worthy of mention is the work by Kim et al. [6] who used a modified bisphenol-A epoxy adhesive nanoreinforced with carbon black and montmorillonite clay to perform tests from -150°C up to room temperature. Their results indicate that nanomodification enhances the fracture toughness at room temperature, but not at low temperatures. This result was thought of as due to the fact that at low temperatures the intermolecular forces between polymer networks of the epoxy are much dominant than the nanoreinforcement toughening effect. Zhang et al. [7] considered the effect of nanomodification of an epoxy resin at room temperature and at 80°C, using a DGEBF resin

loaded with nanosilica, and noted that the fracture toughness of the neat epoxy was reduced due to higher temperatures, but nanomodification managed to transform this reduction in an increase proportionately to the amount of nanofiller. Han and Cho [8] studied the fracture toughness of reinforced epoxy composites from room temperature up to 175°C. In particular they considered a byphenil epoxy resin reinforced with silica micro and nano particles and obtained the strain energy release rate from the elastic properties evaluated by means of DMA tests and the data from tests on SENB samples. Considering just the neat and nanomodified epoxies, they reported an increase in fracture toughness for both cases up to a certain temperature, followed by a drastic reduction and attributed this increase to an improved molecular mobility of network chains and the following yielding of the epoxy resin. Moreover, they highlighted how, at room temperature, the addition of nanosilica resulted in an increase of the G_{Ic}, while at higher temperatures it reduced the peak of G_{Ic} improvement shown by the neat epoxy.
In the present paper the fracture behaviour of an epoxy/silica nanoparticle nanocomposite system is analysed, discussing the results from CT tests carried out at room temperature (20°C) and at -20 °C and +40 °C. As far as results at room temperature are concerned, it is found that nanomodification significantly enhances the fracture toughness of the epoxy resin. Such ameliorations can be thought of as due to the energy absorption mechanisms taking place at the nanoscale, as evident from FEG analyses of fracture surfaces, revealing the presence in a large extent of particle debonding. The experimental results from CT tests are compared to the theoretical predictions based on a multiscale and multimechanism model recently developed by the present authors, showing a satisfactory agreement. Finally the attention is moved to the results from low and high temperature tests where a clear effect of nanomodification was not noted and further analyses need to be carried out to better understand this behaviour.

2. Materials and sample preparation

A DGEBA-based epoxy resin from ELANTAS ITALIA was used (EC157 with W152LR hardener). A masterbatch of 40%wt of silica nanoparticles (average diameter of about 20nm) diluted in DGEBA epoxy resin from EVONIK (Nanopox F400) was used as nanoreinforcement with weight fractions 1, 3, 5 and 8%wt. Compact Tension (CT) specimens have been manufactured according to the following steps:

- As suggested by the supplier the masterbatch was heated for 15 minutes at 50°C to reduce its viscosity.
- The masterbatch was then added to the resin and shear mixing was carried out (3600 rpm for 5 minutes). The blend is then sonicated through a HIELSCHER UP 200S sonicator (amplitude 1 and duty cycle 1) for 15 minutes. Eventually the hardener is added and a further shear mixing at 350 rpm for 5 minutes is carried out.
- During the shear mixing process, a large amount of air is trapped into the blend thus requiring a careful degassing process, carried out inducing a very low pressure in the resin pot with a low-vacuum pump (30 minutes). The nanomodified resin was later slowly poured into silicone rubber moulds.
- All specimens have been cured at room temperature for 7 days, and post-cured in an oven at 90°C for 15h.

3. Testing

Fracture tests have been carried out on Compact Tension specimens (Figure 1) according to the ASTM D5045-99 suggestions [9].

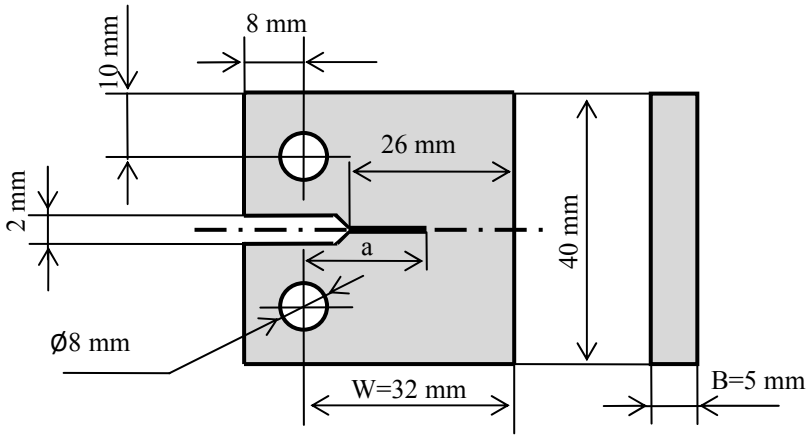

Figure 1. Geometries of the specimens used in testing neat and nanomodified resin.

A MTS858 servo-hydraulic machine equipped with a 2.5kN load cell has been used. Before testing, specimens have been pre-cracked by manual tapping and at least 3 values for each material have been obtained. Mode I fracture toughness has been computed by the following expression [9]:

$$K_{Ic} = \frac{P_{cr}}{B\,W^{0.5}} f\left(\frac{a}{W}\right) \tag{1}$$

where P_{cr} is the critical load, B, a and W are defined in Figure 1, while f(a/W) can be assessed as [10]:

$$f\left(\frac{a}{W}\right) = \frac{\left(2+\frac{a}{W}\right)\left[0.886+4.64\frac{a}{W}-13.32\left(\frac{a}{W}\right)^2+14.72\left(\frac{a}{W}\right)^3-5.6\left(\frac{a}{W}\right)^4\right]}{\left(1-\frac{a}{W}\right)^{1.5}} \tag{2}$$

4. Morphological analyses

The fracture surface of the nanomodified resins was analysed by using Field Emission Gun Scanning Electron Microscope (FEG-SEM, Quanta FEG 250 FEI) at an accelerating voltage of about 5 kV. Prior to SEM observation, the fracture surfaces were gold-sputtered for about 10 s.

Figure 2. Analysis of the fracture surfaces of 5%wt nanomodified resins by using Field Emission Gun Scanning Electron Microscope.

High magnification FEG-SEM micrographs of the fracture surfaces of 5%wt nanomodified CT specimen are shown in Figures 2, where a very satisfactory degree of dispersion and distribution of the fillers within the material can be noted as well as a significant surface roughness. The mean diameter of the particles was found to be approximately 30 nm, in agreement with the data provided by the supplier (20-50 nm).
Moreover the presence of some voids around the nanoparticles can be observed, which might be thought of as due to nanoparticle debonding taking place during crack propagation.

5. Experimental results and discussion

5.1 Tests at room temperature

A summary of the experimental data from CT tests at room temperature, expressed in terms of K_{Ic} according to Eq. (1), is shown in Figure 3. It is evident that nanomodified specimens exhibit a fracture toughness higher than that of the pure resin with a monotonic amelioration of the K_{Ic}, up to a maximum value (for 8%wt of silica nanoparticles) of 1.26 MPam$^{0.5}$.

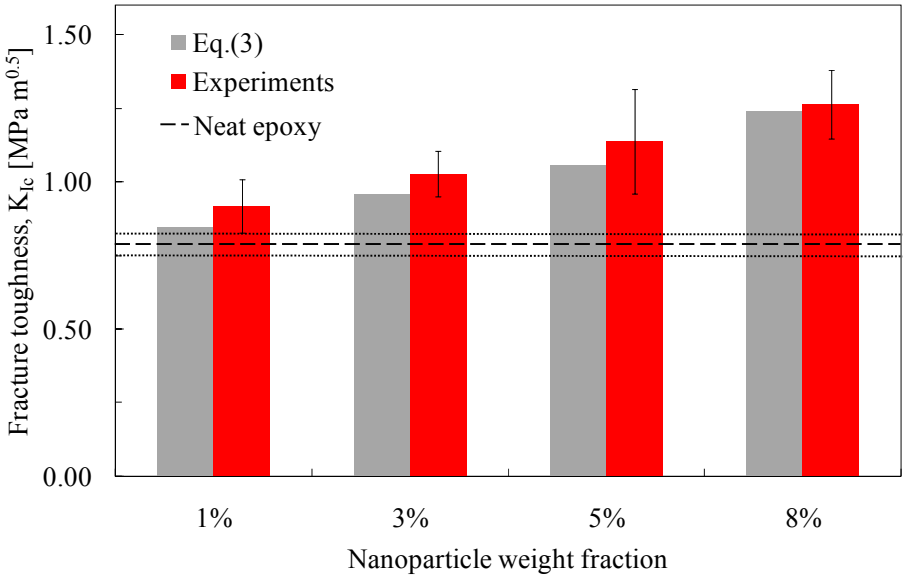

Figure 3. Results of mode I fracture tests on neat and nanomodified CT specimens. The scatter band of the values for neat epoxy is given by the dashed lines.

In Figure 3 the experimental values are also compared to the theoretical predictions based on the multiscale and multimechanism model recently proposed in Ref. [10], according to which:

$$K_{Ic} = K_{Ic,m}\sqrt{\frac{E_o}{E_m}\frac{1-\nu_m^2}{1-\nu_o^2}\times\frac{1}{1-f_{p0}\left(\psi_{db}+\psi_p+\psi_{SB}\right)}} \qquad (3)$$

where $K_{Ic,m}$ is the unloaded polymer toughness, f_{p0} is the filler volume fraction, E_o, ν_o and E_m, ν_m are the Elastic modulus and the Poisson' ratio of the nanocomposite and the matrix, respectively. Parameters ψ_i, instead, quantify the energy dissipation caused by each damaging mechanisms, namely, nanoparticle debonding (i=db), plastic yielding of nanovoids (i=p) and shear banding (i=SB) [10]. It is evident that the agreement is very satisfactory.

5.2 Tests at low and high temperature

Fracture tests have been carried out on a servo-hydraulic machine equipped with a 2.5kN load cell at 10mm/min, according to the ASTM D5045-99 suggestions.
-20°C and +40°C has been chosen as reference temperatures to be imposed to specimens by means of a dedicated temperature control equipment. The temperature of specimens has been controlled by means of a thermocouple inserted in a hole drilled on the specimens, which were kept at testing temperature for 2 minute before performing the test.
Results are shown in Figure 4.

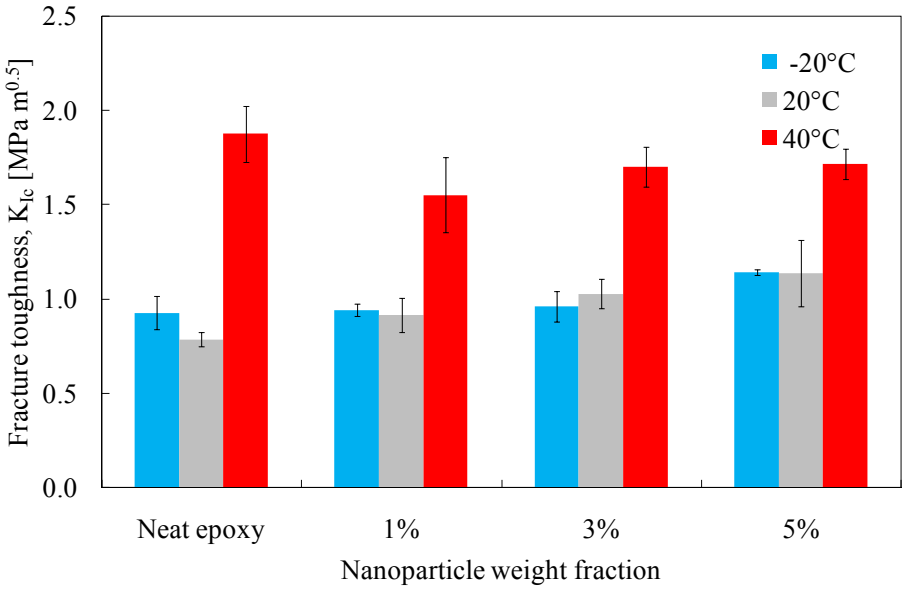

Figure 4. Results of mode I fracture tests on neat and nanomodified CT specimens at different testing temperatures.

In agreement with previous findings in Ref. [7], it is evident that the reduction of the testing temperature below the Room Temperature (RT) increases the fracture toughness of the neat epoxy resin, while the benefits induced by the nanomodification are progressively hampered.
Moreover, increasing the testing temperature (with respect to RT) a considerably increase in the neat epoxy fracture toughness is evident, in agreement with [8,9]. At the same time it is evident from Figure 4 that in this last mentioned case, the fracture toughness of nanomodified specimens almost equates that of the neat resin, with no evident effect of nanomodification.
Further analyses will be carried out by the present authors to better understand this behaviour.

6. Conclusions

In the present paper the fracture behaviour of an epoxy/silica nanoparticle nanocomposite system has been analysed, discussing the results from CT fracture tests. It is found that nanomodification significantly enhances the fracture toughness of the epoxy resin at room temperature. Such ameliorations can be thought of as due to the energy absorption mechanisms taking place at the nanoscale, as made it evident from FEG analyses of fracture surfaces, which revealed the presence in a large extent of particle debonding. The room temperature experimental results have been compared to the theoretical predictions based on a multiscale and multimechanisms model recently developed by the present authors, showing a satisfactory agreement.

Finally the attention has been moved to the results from low and high temperature tests where no clear effect of nanomodification was noted. Further analyses need to be carried out to better understand this behaviour.

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