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Fracture behaviour of epoxy nanocomposites modified with triblock copolymers and carbon nanotubes

T. Gómez-del Río [a,*], A. Salazar [a], R.A. Pearson [b], J. Rodríguez [a]

[a] DIMME, Grupo de Durabilidad e Integridad Mecánica de Materiales Estructurales, Universidad Rey Juan Carlos, Tulipán s/n, 28933 Móstoles, Madrid, Spain
[b] Center for Polymer Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015, USA

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ABSTRACT

The effect of the addition of a combination of rigid nanofillers and soft rubber nanoparticles on the fracture toughness of epoxy resins was studied. Carbon nanotubes (CNTs), as rigid nanofillers, and polystyrene-polybutadiene-poly(methyl metacrylate) (SBM) triblock copolymers, as rubber nanoparticles that self-assemble in the epoxy matrix, were used. Fracture tests according to ESIS TC4 protocol were performed on neat epoxy, epoxy reinforced with CNTs, epoxy nanostructured with SBM triblock copolymers and, finally, epoxy with CNTs and SBM triblock together. Finally, it was found that both fracture toughness and critical energy release rate increased significantly with the addition of rubber and rigid particles. The analysis of the fracture surfaces revealed the toughening micromechanisms.

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1. Introduction

Epoxy resins are thermosets with high thermal, chemical and mechanical resistance and good electrical properties. That is the reason of their use in high perfomance applications such as structural adhesives, composite materials or electronic encapsulation. However, their inherent brittleness and poor resistance to crack growth has limited their use in structural applications.

It is well known that the addition of reinforcement of rubber or rigid particles can improve the fracture toughness and energy at crack growth initiation of epoxy systems. Substantial differences in mechanical properties and toughening mechanisms have been reported for these different types of toughening agents [1–14].

Regarding rigid fillers [7–14], toughening mechanisms depend on the good or poor adhesion of the second phase to the matrix. If they are well bonded, they can stop the crack by pinning, branching, bridging and/or deflection leading to a reduced crack-driving force at the crack tip and consequently, to rougher fracture surfaces. On the other hand, weakly bonded rigid particles debond easily and the toughening mechanism is likely to be matrix shear yielding or plastic void growth, which dissipate more energy. Other type of second phase reinforcement is rubber particles. In this case more significant toughening can be achieved from soft rubbery particles by cavitation [1–6] to promote matrix shear yielding and further plastic deformation. Specifically, matrix shear banding and matrix dilation form a plastic zone ahead of the crack tip, which shields the crack tip from the applied crack driving force and blunts crack propagation [2,5]. Actual rubber particle cavitation contributes very little to the overall toughness directly but indirectly rubber particle cavitation enables matrix dilation and shear banding [4,5]. Huang and Kinloch [2,3] have proposed a toughening model that attempts to quantify the contributions of three distinct micromechanisms to the overall fracture toughness. In their model, rubber particle bridging gives the lowest contribution to the overall fracture toughness, falling more than 90% contribution of fracture energy enhancements at room temperature to matrix shear banding and matrix plastic dilation micromechanisms. Nevertheless, the addition of rubber particles results in a decrease in stiffness and strength, when compared to the epoxies toughened by the other two types of toughening agents.

One way to further enhance the fracture toughness of epoxies is to take advantage of different toughening mechanisms, i.e., soft particles and rigid fillers can be simultaneously mixed into epoxy resins to increase fracture toughness.

Typically, the fillers are of micron size. But, the size of the fillers is also expected to play a crucial role on the types of toughening mechanisms operating in filled epoxy-based composites. Previous studies indicate that silica nanoparticles improved properties of

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[*] Corresponding author. Tel.: +34 914887176.
E-mail address: mariateresa.gomez@urjc.es (T. Gómez-del Río).

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composites compared to microparticles. The toughening mechanisms are modified due to the increased interfacial area between the nanoparticle surface and polymer matrix [15,16]. In terms of toughening efficiency, silica nanoparticles were found to toughen epoxies by similar mechanisms to those promoted by rubber particles, i.e. matrix shear banding and void growth.

For example, hybrid epoxy composites formed by rubber particles and nanosize rigid particles have been shown to have a higher toughening effect, for example using nanosilica particles [17–19], even though not always a synergistic effect is observed. The toughening mechanisms in the ternary epoxy composite were evaluated, and it seems that the combination of rigid and soft particles induced higher plastic deformation around the crack tip, improving the fracture toughness in this material.

Previous papers showed that the addition of CNTs can improve significantly some mechanical, electrical and thermal properties of epoxy resin. However, the crack resistance of epoxy reinforced with CNTs is still very poor [20]. An interesting analysis by Blanco et al. [21] suggests that CNTs are not very effective toughening agents due to the high stresses involved in bridging and pullout mechanisms when such nanofillers are used. Such stresses often exceed the strength of CNTs.

Recently, carbon nanotubes have been introduced, as rigid fillers, to rubber toughened epoxies with considerable improvements in fracture toughness [20–22]. It is interesting to note that the toughening mechanisms in these hybrid nanocomposites are not yet clearly understood. Factors such as waviness of the nanotubes can be relevant [23].

The objective of this work was to study the effect of adding both rubber nanoparticles and CNTs on the quasi-static fracture toughness of epoxy resin systems. The fracture surfaces were observed using Scanning Electron Microcopy (SEM) in order to compare them with the microstructure of the nanocomposite. The morphology, dispersion and size of the particles added were previously analyzed by the authors. This comparison was useful in order to find out the toughening mechanisms involved in the fracture process. Analytical models involving different toughening mechanisms were used to predict the fracture energy at crack growth initiation.

2. Experimental

2.1. Materials

A diglycidylether of bisphenol A (DGEBA-DER 331 epoxy resin from the Dow Chemical, Co.) cured with piperidine as curing agent at a concentration of 5 parts per hundred parts resin (phr) was used [25]. The effect of rubber and rigid reinforcements was analyzed. As rubber reinforcement, styrene/butadiene/methacrylate (SBM) triblock copolymer (Nanostrength™ E21, Arkema) was added to the epoxy matrix using 5 phr. The triblock copolymer self-assembled providing nanosize toughening phases. As rigid particles, CNTs concentrate (Nanosolve™) was diluted with neat epoxy resin to produce epoxies with 0.25 phr concentration. For all the materials, the final mixture was thermally cured at 160 °C for 6 h.

The morphology and structure of the epoxy systems were previously studied by means of field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy [24]. It showed the SBM self assemble in the epoxy matrix in spherical phases with diameter in the nanometer scale. Therefore, the curing procedures used produced SBM modified epoxy, nanocomposite CNT/epoxy and hybrid nanocomposite with uniform dispersions.

An average diameter of 60 ± 12 nm was measured using the TEM micrographs. The average diameter of the soft phase was a bit longer in the ternary nanocomposite (epoxy + SBM + CNTs), 88 ± 20 nm, but the morphology of the hybrid composites is quite similar to the SBM modified epoxy.

2.2. Materials characterization

The nanocomposites' density was obtained by the immersion method, both in water and ethanol. Assuming there were no voids, the rule of mixtures was used in order to obtain the density of both SBM block copolymer and CNTs reinforcements.

$$\rho_c = \frac{1}{\left(\frac{M_m}{\rho_m}\right) + \left(\frac{M_r}{\rho_r}\right)} \tag{1}$$

where ρ_i is the density and M_i is the mass fraction of the composite (c), reinforcement (r) and the matrix (m). The value calculated for the carbon nanotubes was compared with theoretical values used previously (1.71 g/cm^3 [23]). With all these data, the volume percent of reinforcement was calculated from the known weight percent.

$$V_r = \frac{M_r}{M_r + (1 - M_r)\frac{\rho_r}{\rho_m}} \tag{2}$$

Dynamic mechanical analysis (DMA) was performed with a TA INSTRUMENT, model Q800, in single cantilever mode at a frequency of 0.1, 1 and 10 Hz and temperature range from −150 °C to 180 °C and a heating rate of 2 °C/min. Differential scanning calorimetry (DSC) was performed on a METTLER-TOLEDO equipment, model DSC822. During the measurements, the samples were heated and cooled in three different stages. First, the samples, of approximately 10 mg, were heated from room temperature (20 °C) up to 200 °C, then, a cooling stage to −50 °C and finally a second heating stage to 200 °C. All the temperature changes were at a rate of 10 °C/min. The storage modulus, loss tangent, tan δ, and α and β relaxation peaks associated with the glass transition temperature of the epoxy resin and the composites were measured.

Fracture energy (G_{IC}) and fracture toughness (K_{IC}) were determined using a single-edge notch bend (SENB) specimen with dimensions 6 × 12 × 52.8 mm. The tests were performed at a rate of 10 mm/min. The average value and the standard deviations of at least five samples for each material were calculated. The specimens had an initial crack terminating in a V-notch with 0.2 mm in root radius. The procedure for sharpening consists of tapping with a razor blade frozen at liquid nitrogen temperature, located at the root of the V-notch following the guidelines described by ESIS TC4 protocol [25]. The total initial crack depth, a_0, to width ratio after sharpening for the bulk specimens utilized for fracture characterization was of 0.5.

For these materials based on epoxy resin, the linear elastic fracture mechanics assumptions are met and fracture toughness, K_{IC}, can be calculated:

$$K_{IC} = f\frac{P}{BW^{1/2}} \tag{3}$$

where P is the maximum load, B is the thickness, W is the width of the specimen and f is a geometrical factor that can be computed using the expression:

$$f = 6\alpha^{1/2}\frac{\left[1.99 - \alpha(1-\alpha)\left(2.15 - 3.93\alpha + 2.7\alpha^2\right)\right]}{(1+2\alpha)(1-\alpha)^{3/2}} \tag{4}$$

for SENB specimens and being $\alpha = a_o/W$ with a_0, the initial crack length.

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