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Improvement of tensile properties and toughness of an epoxy resin by nanozirconium-dioxide reinforcement

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Abstract Zirconium dioxide (ZrO_2) nanoparticles were systematically added as reinforcement to a diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin. A series of composites with varying amounts of nanoparticles was prepared and their morphology and mechanical properties were studied. The obtained nanocomposites were characterized by tensile tests, dynamic mechanical thermal analysis, and fracture toughness (K_{IC}) investigations; by standardized methods, to define the influence of the nanoparticle content on their mechanical and thermal properties. The morphological analysis of the composites shows that nanoparticles form small clusters, which are uniformly distributed into the matrix bulk. The tensile modulus (E) and the K_{IC} of the epoxy matrix increase at rising zirconia content. Improvements of more than 37% on modulus and 100% on K_{IC} were reached by the nanocomposite containing 10 vol.-% ZrO_2 with respect to the neat epoxy ($E_o = 3.1$ GPa, $K_{ICo} = 0.74$ $MPam^{0.5}$). The presence of nanoparticles produces also an increment on glass transition temperature (T_g). The epoxy resin added with 8 vol.-% ZrO_2 records a T_g approximately 8% higher than the unmodified matrix ($T_{go} = 100.3$ °C).

Introduction

Epoxy resins have been used extensively to manufacture composites, because they are able to withstand high mechanical and tribological loads, especially in engineering applications. They have usually been reinforced with numerous inorganic fillers such as fibers and particles of diverse nature. In traditional composites, the fillers possess dimensions in the range of micrometers. They have proved to be an effective way to improve the mechanical properties of polymeric materials. The resultant composites had enhanced stiffness and strength, and also superior toughness. However, the micro fillers may reduce other important properties, as the resistance against impact, and cause a negative effect on the processability of the final material [1].

The solution of this problem may be to use smaller fillers, with dimension reach the nanometer range. Advantages of small fillers are that they can be homogeneously distributed within the polymer by different techniques, and produce an efficient reinforcement effect with minimal loss of ductility and impact strength, improving the wear resistance and reducing residual stresses.

Recently, some nanoparticles as clay [2], silica [3, 4], alumina [5], and titanium dioxide [6] had been studied as fillers in epoxy resins. All of them have demonstrated their ability to enhance the mechanical behavior of epoxies, and in some cases to improve especially their toughness.

Zirconium dioxide possesses excellent properties like: high strength, high fracture toughness, excellent wear resistance, high hardness, and excellent chemical resistance [7, 8]. Hence, ZrO_2-nanoparticles appear as an attractive option to be used as reinforcement of polymers, in order to produce composites with enhanced performance.

In the present research epoxy resins containing different amounts of nano-ZrO_2 were prepared. The nanoparticles were dispersed into the epoxy matrix by mechanical shear forces. Mechanical and thermal properties of the obtained nanocomposites were investigated, in order to establish

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how the properties of the epoxy are modified due to the presence of nanoparticles.

Experimental

Materials

A DGEBA epoxy resin, modified with Hexadioldiglycidyl ether was used (Cetepox VP 823–30 R by Chemicals and Technologies for the Polymers GmbH, with equivalent weight 172.12 g/eq).

Nanoparticles of ZrO_2 with 12 nm average size and specific surface of 60 ± 15 m^2/g (VP Zirconium Dioxide PH by Degussa AG) were used as filler.

The epoxy systems were cured with a cyclic aliphatic polyamine (Cetepox VP 823–2 H by Chemicals and Technologies for Polymers GmbH, with equivalent weight of 50.7 g/eq.).

All the materials were used directly as received.

Compounding

The nanocomposites with different amounts of ZrO_2 were prepared in a torus mill (Dispermat AE 01–10 M, Getzmann GmbH), which contains mill and dissolver chambers. The mill chamber acts as a pearl-mill, breaking the particles agglomerates, meanwhile the dissolver produces intensive particle dispersion. The mill was operated at 3,500 rpm, 80 °C, and normal pressure, during 2 h; using pearls with 1.2–1.7 mm of diameter.

The stoichiometric amount of curing agent was added to the modified epoxy resins at 60 °C, mixing at 50 rpm, during 10 min. After that, the reactive mixture was filled into a pre-heated aluminum mold and cured at 60 °C for 2 h and at 80 °C for 8 h.

Characterization

Thin sections (approx. 100 nm) of the specimens were cryo-cut with a diamond knife at −120 °C to be investigated by Transmission Electron Microscopy (TEM), using a high-resolution microscope (LEO 912, Omega GmbH) with an accelerating voltage of 120 kV.

Tensile tests were performed on a universal testing machine (1474, Zwick Roell AG), according to the standard ISO 527, with a 10 kN load cell, 10 mm/min of crosshead speed. Molded specimens, type 5A, were used; in compliance with the same standard. Precision sensor-arm extensometers were used to measure the specimen strain during the test.

The viscoelastic response of the obtained materials as a function of temperature was studied by Dynamic Mechanical Thermal Analysis (Eplexor 150 N, Gabo Qualimiter). The test was carried out using rectangular specimens $50 \times 10 \times 4\ mm^3$ in tensile mode at a frequency of 10 Hz, in the temperature range from −100 to 150 °C and a heating rate of 1 °C/min.

Fracture toughness and fracture energy (G_{IC}) of the studied materials were determined according to the standard ISO 13586. The test was carried out on a universal testing machine (1445, Zwick Roell AG), using a 5 kN load cell and a constant cross-head speed of 1 mm/min. Compact tension (CT) specimens $50 \times 50 \times 10\ mm^3$ were machined from molded plates. The machined notch was sharpened by tapping on a razor blade, method that produces the smallest pre-crack tip radius and also low residual stresses around it [9].

The fractured surfaces of the samples were studied in a scanning electron microscope (JSM 5400, Jeol Ltd.). Prior to scanning electron microscopy (SEM) investigation, the surfaces were sputtered for 150 s with a Pt/Pd alloy (SCD-050 Balzers).

Results and discussion

Morphology

The obtained materials are opaque. The transparency, inherent to the epoxy resin, disappears once that nanozirconia is added.

TEM-analysis of representative samples was carried out in order to study the particle distribution of the nanozirconia in the obtained composites. Figure 1 shows the micrographs obtained from the epoxy resins modified with 3 vol.-% and 8 vol.-% of nano-ZrO_2. In both cases an adequate dispersion of particles is observed. However, the presence of small agglomerates is evident. The amount of clusters is obviously related to the filler fraction present in composites.

The clusters appear like three-dimensional arrangements, considering that the dark dots on the micrographs correspond to overlapped particles in depth direction, with an average size in range 20–100 nm. Nevertheless, their dimensions are enough to cause light scattering and form opaque materials. The number of single particles, whose dimensions correspond to the size specified by the supplier (12 nm), is reduced.

The shear forces, applied during the milling and dispersion processes, were not efficient enough to break the clusters. A detailed study of the mixing parameters must be done, in order to avoid the presence of agglomerates.

One of the most important aspects of the polymer nanocomposites is that they have a great interfacial area filler-matrix, as direct consequence of the large specific-

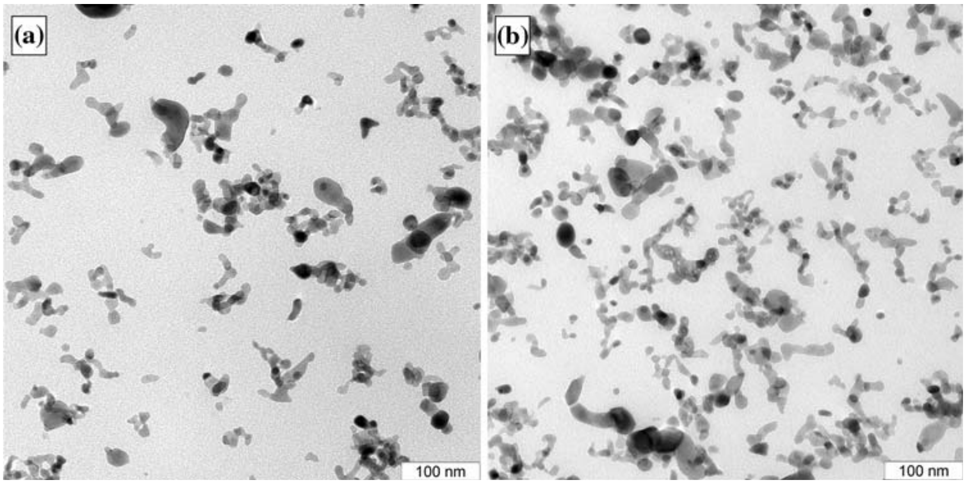

Fig. 1 TEM micrographs of the modified epoxy resins (**a**): 3 vol.-% and (**b**): 8 vol.-% ZrO_2

surface area of the nanoparticles, and the fact that the properties of the interface are quite different from the bulk polymer matrix, due to the inherent superficial phenomena. This information is particularly important because the physicochemical properties of a composite are determined in great measure by the size and properties of the interface between filler and matrix [10].

Tensile properties

Figure 2 summarizes the tensile properties of the studied materials. Figure 2a shows the characteristic stress–strain curves, from the tensile test, of the neat and modified epoxies. The tensile modulus of the epoxy matrix is increased by the addition of nanozirconia (Fig. 2a, b). It is possible to see an important increment on the elastic modulus even at low-particle content, between the neat epoxy and the modified ones (jump in graph 2b). The elastic modulus of the pure epoxy resin was found to be 3.1 GPa, while the modified epoxy containing 0.5 vol.-% ZrO_2 reaches a modulus 18% higher, up to 3.7 GPa. From this point on, the elastic modulus increases almost linearly, with the nanoparticle content. The elastic modulus of the epoxy matrix was increased by 37%, up to 4.35 GPa, once it was modified with 10 vol.-% ZrO_2

The modulus calculated from typical models such as Halpin–Tsai rule [11] and Lewis–Nielsen equations [12–14] are also plotted in Fig. 2b (dotted lines) as reference.

The Halpin–Tsai model predicts the composite modulus as a function of the modulus of the polymer matrix E_m, the modulus of the filler E_f, and a factor of reinforcement geometry shape form ζ, according to the expression:

$$\frac{E}{E_m} = \frac{1 + \varsigma \eta V_f}{1 - \eta V_f} \tag{1}$$

where V_f is the volume fraction of filler and η is a constant defined as:

$$\eta = \frac{\left(\frac{E_f}{E_m}\right) - 1}{\left(\frac{E_f}{E_m}\right) + \varsigma} \tag{2}$$

In the present work $E_f = 200$ GPa [8].

The factor ζ is defined from the reinforcement dimensions by the ratio w/t, where w is the particle length and t its thickness, but also depends on loading conditions. The limiting values of ζ are $\zeta = 0$ and $\zeta = \infty$. It is suggested

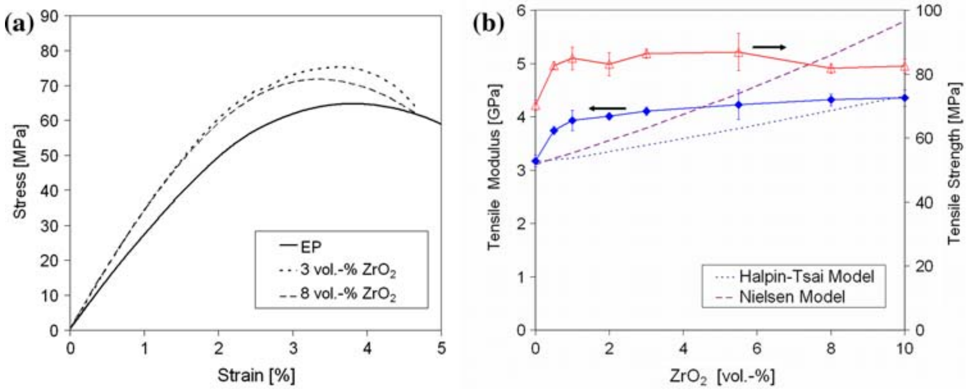

Fig. 2 Tensile properties as a function of nano-ZrO_2 volume content: (**a**) typical stress–strain curves (**b**) tensile modulus and tensile strength. Error bars correspond to 1 standard deviation

that $\zeta = 2\ w/t$, when filler particles are aligned to loading direction, and $\zeta = 2$, when particles are perpendicular to the loading direction.

In the studied case, the filler geometry was assumed as ellipsoidal, $w/t = 2$, due to the aspect displayed by single zirconia particles in Fig. 1. Additionally, it is clear that the particles have random orientation into the polymer matrix. Hence, the shape factor used to predict the composite modulus was $\zeta = 3$, which corresponds to the average between both, parallel and perpendicular, particle orientations.

The Lewis–Nielsen model predicts the composite modulus from the expression:

$$\frac{E}{E_m} = \frac{1 + (k_E - 1)\beta V_f}{1 - \beta\mu V_f} \tag{3}$$

where k_E is the generalized Einstein coefficient (or intrinsic viscosity), β is a constant defined as

$$\beta = \frac{\left(\frac{E_f}{E_m}\right) - 1}{\left(\frac{E_f}{E_m}\right) + (k_E - 1)} \tag{4}$$

and μ is a function of the $V_{\max}$, maximum volume fraction of particles and can be calculated from

$$\mu = 1 + \frac{(1 - V_f)}{V_{\max}}\left[V_{\max}V_f + (1 - V_{\max})(1 - V_f)\right] \tag{5}$$

The maximum volume fraction was also defined by Nielsen, specifically for different particles shapes and packing [13]. In the present work $V_{\max} = 0.37$, corresponding to random close packing agglomerates; and $k_E = 5.86$, corresponding to the Einstein coefficient for agglomerates of particles in random packing (6.76), reduced by a factor 0.867. This last because the Einstein coefficient is reduced when Poisson's ratio (v) is lower than 0.5. For epoxy resins $v = 0.35$ [13].

It is observed that the experimental values have poor agreement with the theoretical approximations. The Halpin–Tsai model underestimates the nanocomposites modulus, especially at low-particle content. This deviation is justified on the basis that geometrical factors defined by this model assume specific geometry and orientation of all the involved particles, which is not the real case. Additionally the model does not consider the special role that plays the particle-matrix interface on the mechanical properties of the nanocomposites; as mentioned in section "Morphology" [10, 15].

On the other hand, the theoretical approximation by the Lewis–Nielsen model presents opposed deviations, along the studied filler content interval. At low-particle content, it underestimates the tensile modulus of the composites, but at high-filler content, the modulus is over estimated. The Lewis–Nielsen curve was determined considering random closed agglomerated spherical particles; assuming that there are no single particles present and that the clusters have same dimensions; which is not the real case. On this basis, the controversial result can be explained, taking on account that at lower filler content, the presence of single particles increases the real maximum volume fraction and of course the filler-matrix interface, which results in moduli higher than theoretical calculated; meanwhile at high filler concentration the presence of large agglomerates, reduces the real maximum volume fraction and therefore the experimental modulus is lower than the theoretically estimated.

The tensile strength of the neat epoxy was increased by the addition of nanoparticles. The nanocomposites record tensile strengths improved by around 20%, but the composites containing 8 and 10 vol.-% zirconia, which record tensile strengths hardly 15% higher than the neat epoxy.

The increment in strength is attributed to the fact that the ZrO_2 has a much higher strength than the epoxy matrix and also to the good bonding between filler and matrix (see next paragraph), which permits the right stress distribution into both composite phases. The reduction of strength at high filler content is due to the presence of the higher quantity of clusters. The agglomerates tend to reduce the strength, because even if they may be strong enough to increase the modulus, they constitute weak points, which break fairly easily when stress is applied.

The SEM fractograms from the tensile specimens (Fig. 3) reflect the different failure mechanisms of pure and modified

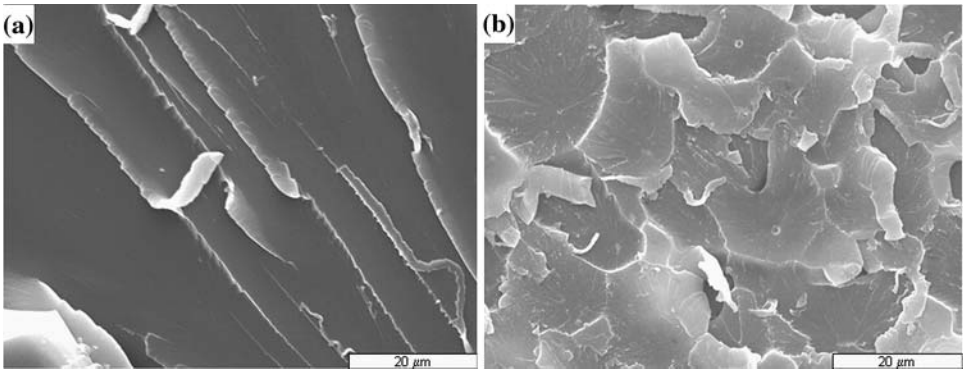

Fig. 3 Fracture surfaces from tensile testing (**a**) neat epoxy resin (EP), (**b**) EP + 3 vol.-% ZrO_2

epoxy matrices. The neat epoxy shows a fracture surface with large smooth zones, which are typical of brittle failure. The fracture surface of the nanocomposites appears as a rough surface characterized by the presence of small craters, in whose center, particle or cluster debonding marks are assumed. Under load, the nanoparticles and agglomerates act as stress concentrators [10, 16]. When the load is high enough, the particles are debonded forming little craters that grow radially until they meet another particle. The rough fracture surfaces of the nanocomposites tensile specimens confirm the good adhesion particle-polymer [13].

The amount of craters (debonded particles) depends directly on the particle content. However, the failure surface is dominated by this mechanism even at low-particle content. This fact explains the significant difference recorded between the tensile modulus of the neat and modified epoxy resins.

The recorded debonding of particles is lower than the observed in other epoxy nanocomposites and also in epoxy resins modified with microfillers. This supports the hypothesis of a strong particle-matrix interface [10].

Dynamic mechanical thermal analysis

The DMTA results are summarized in Fig. 4. The complex modulus of the epoxy resin increases, as expected, with the nanoziconia content (Fig. 4a). The stiffening effect of nanoparticles on the matrix is evident, and remains almost in the same proportion, along all the studied temperature range; inclusive at temperatures higher than T_g. This result can be associated also with a good bonding particle-matrix [5].

The addition of zirconia causes a gradual increase of the epoxy T_g, from 100 °C of the neat epoxy, up to 108 °C of the epoxy containing 8 vol.-% ZrO_2. This increment can be explained by the adsorption of polymer onto the particle surface, which reduces the polymer-net mobility and modifies the conformation of chain segments [5, 13].

The damping of the epoxy resin records no important change in the glassy stage (-100 to 35 °C) due to the addition of nanofiller, Fig. 4b. It indicates that both, storage and loss modulus, increase almost in the same proportion, along this temperature range. On one hand the nanoparticles induce a higher stiffness on the epoxy resin, and by the other hand they induce new mechanisms of energy dissipation, as filler/filler and filler/matrix friction, which were suggested as main reason for damping in composites systems [13, 17].

In the elastic zone (35–100 °C), the damping of nanocomposites is lower than the damping of neat epoxy. In this stage the macromolecules start to move. The particles hinder the movement of the polymer chains resulting in lower-energy dissipation.

In the rubbery stage (100–150 °C), the damping of nanocomposites is higher than for the pure epoxy. Nanoparticles maintain their reinforcement effect on the matrix. However, all polymer chains are in movement and the internal friction becomes more representative.

Fracture toughness

Fracture toughness of nano-modified epoxy resins increases with particle content (Fig. 5). The addition of 0.5 vol.-% of nano-ZrO_2, results in an approximately 26% enhanced K_{IC} up to 0.93 $MPam^{0.5}$. While the nanocomposite with 10 vol.-% ZrO_2 shows a $K_{IC} = 1.53$ $MPam^{0.5}$, more than twice as high as the neat epoxy ($K_{ICo} = 0.74$ $MPam^{0.5}$).

The G_{IC} of studied epoxies varies with same tendency, but slightly higher proportion than the K_{IC} (Fig. 5). The G_{IC} of the pure epoxy ($G_{ICo} = 0.15$ kJ/m^2) is enhanced up to 0.2 kJ/m^2 due to the addition of 0.5 vol.-% of nano-ZrO_2 that means an increment around 35%. When the epoxy is modified with 10 vol.-% ZrO_2 its G_{IC} triples to 0.47 kJ/m^2.

The increase in the toughness, as a result of the nanoparticle addition, can be explained analyzing the SEM pictures of the fracture surfaces of pure and modified epoxy resins (Fig. 6). The neat epoxy shows a smooth fracture surface, which is typical of brittle thermosetting materials.

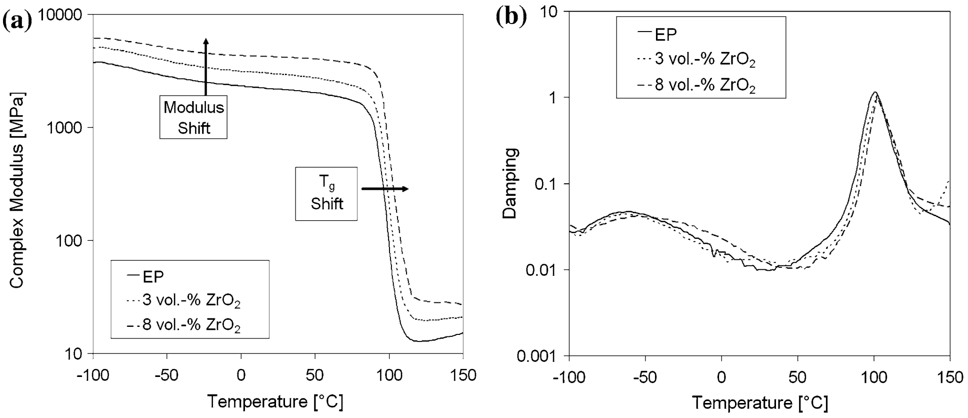

Fig. 4 Dynamic mechanical properties (**a**) complex modulus (**b**) damping

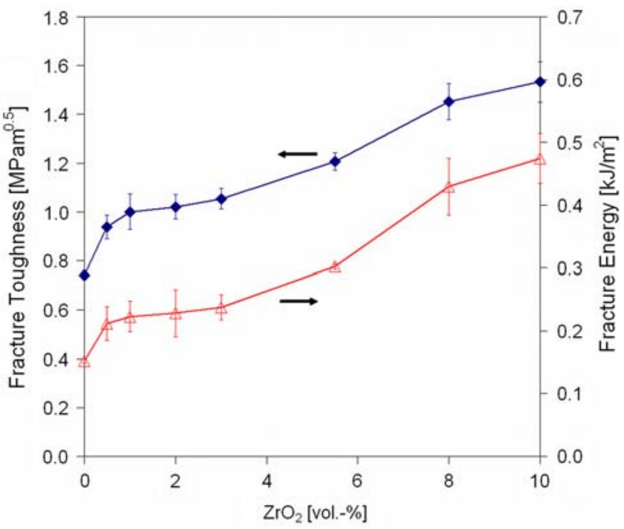

Fig. 5 Fracture toughness and fracture energy as a function of nano-ZrO_2 volume content. Error bars correspond to 1 standard deviation

It presents almost straight fracture lines, with no other fracture marks.

The nanomodified epoxy, containing 5.5 vol.-% zirconium oxide, shows a textured surface with similar fracture features, but also with a variety of small paths, which reveal the existence of alternative fracture mechanisms attributed to the presence of particles [16, 18].

Many researches have shown that brittle polymers may be toughened by addition of rigid particles. The toughening effect of the particles has been explained in terms of specific fracture mechanisms, being the most recognized the crack pinning, crack deflection, and plastic deformation [18–20].

Crack pinning and crack deflection, according with the theories proposed by Lange [21] and Faber–Evans [22, 23], respectively, are processes that involve rigid particles as obstacles to the crack propagation. The propagating crack is blocked by a rigid particle and forced to change its direction; process that requires higher driving force and implies also higher-energy absorption. Deflection means that the crack is forced to move out of its initial propagation plane, by tilting or twisting. Meanwhile, pinning takes place when the crack front is forced to bow between the filler particles. Both mechanisms assume that the filler particles are larger than the crack opening displacement (COD).

The COD can be calculated from the expression [24]

$$\delta_c = \frac{K_{IC}^2}{E\sigma_y}\left(1 - \nu^2\right) = \frac{G_{IC}}{\sigma_y} \tag{6}$$

where σ_y is the yield stress of the matrix.

Crack deflection and pinning have been identified in epoxy resins filled with micro particles [25, 26], but in nanocomposites their occurrence has been widely questioned. However, some authors have considered the presence of these mechanisms, based on specific fractographic evidences [10, 18].

In the present work, the COD falls in the range 2.1–5.7 µm, for the neat epoxy and the nanocomposite containing 10 vol.-% ZrO_2 respectively, values that are much greater than the particle size. Hence, the existence of crack deflection and pinning is uncertain.

Higher magnification scanning electron micrographs, of nanocomposites fracture surfaces, Fig. 7, show characteristic paths, (i.e., tails, bifurcation) associated with crack pinning and deflection. Nevertheless, it is little probable that these mechanisms be the main responsible of the enhanced toughness of modified epoxies.

Epoxy resins, as thermosetting polymers in general, are highly resistant to plastic deformation. However, when they are modified with a second phase, the filler particles can induce shear yielding in the matrix by promoting a change in stress state. This may result from the formation of voids, cavities and debonding effects in the process zone at the crack tip state [18].

The fracture surfaces of nanocomposites (Fig. 7) show the presence of circular voids with average size 30 nm, which may be originated by debonding of particles or clusters. However, the incidence of these processes is so low, that they cannot be considered the principal cause of the toughness increment [27]. This fact supports also the

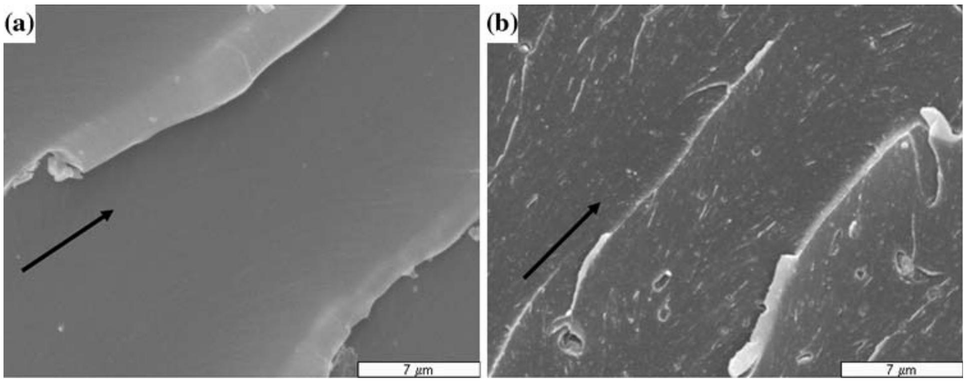

Fig. 6 Low magnification SEM images of CT specimens fracture surfaces (**a**) EP, (**b**) EP + 5.5 vol.-% ZrO_2

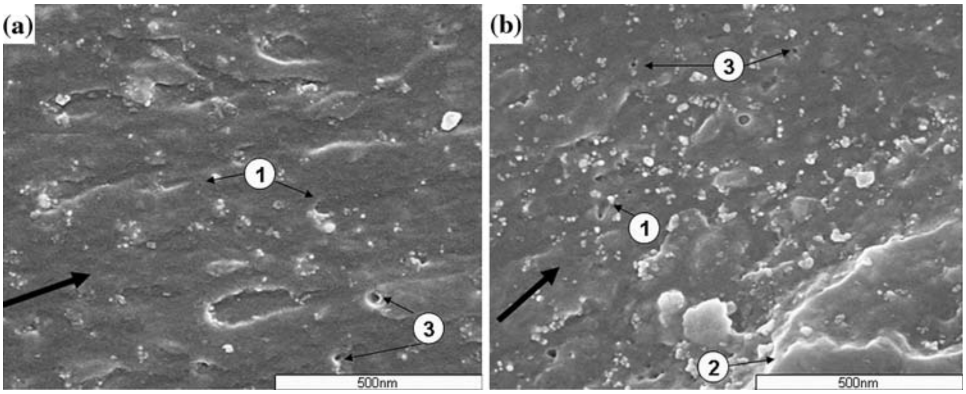

Fig. 7 High magnification SEM images of CT specimens fracture surfaces (**a**) EP + 2 vol.-% ZrO_2, (**b**) EP + 5.5 vol.-% ZrO_2. Features indicate 1. Tails, 2. Crack bifurcation, 3. Voids

hypothesis that obtained nanocomposites have a good particle-matrix bonding.

Recently, the particular behavior of the nanocomposites has been described from the existence of an interfacial layer particle-matrix, formed by immobilized polymer chains adsorbed by the particles surface; which has physicochemical properties quite distinct from those of the bulk polymer matrix. As is logical, at higher filler content, closer interparticle distance, and once that the interparticle distance reduces to a critical value, the interfacial layers may overlap, creating a tri-dimensional network that affects greatly the material properties [10, 28].

The existence of the interfacial layer can be confirmed using techniques as viscometry and thermal analysis. In this last it is expected that the immobilization of the polymer chains increases the T_g. Hence, in the present work, the results reported in section "Dynamic mechanical thermal analysis", together with the deviation between theoretical and experimental results reported in section "Tensile properties", suggest the presence of a strong interfacial layer filler-matrix, which may constitutes also the most important toughening mechanism induced by nanozirconia in the epoxy matrix [27].

Additional research must be done, in order to quantify, as possible, the contribution of each fracture mechanism to the overall toughening effect induced by the nanozirconia on the epoxy matrix.

Conclusions

Epoxy-ZrO_2 nanocomposites with good particle distribution were obtained by mechanical mixing and dispersing technologies. The presence of small agglomerates (size lower than 100 nm) is evident in all modified matrices. A detailed study of the mixing parameters must be done in order to avoid them.

The tensile modulus of the epoxy matrix is improved at rising nanozirconia content. The change of the tensile modulus as function of the filler content does not follow a lineal tendency. It is possible to increase the modulus of the neat epoxy up to 37%, adding 10 vol.-% ZrO_2. The tensile strength of the neat epoxy is also increased by the addition of nanoparticles.

The complex modulus of the epoxy matrix increases with the nanoziconia content. The stiffening effect of nanoparticles is evident along the temperature range from −100 to 150 °C, and remains almost in the same proportion inclusive at temperatures above T_g. The addition of nanoparticles increases also the T_g of the epoxy matrix, due to the particles interact with the polymer matrix and reduce the net mobility.

The ZrO_2 nanoparticles increase the K_{IC} and G_{IC} of the epoxy matrix. The K_{IC} of the epoxy matrix is duplicated, and its G_{IC} is increased by more than 200%, once that 10 vol.-% ZrO_2 is added.

The modification with the rigid nanoparticles induces specific fracture mechanisms in the epoxy matrix, which means greater energy absorption previous to failure. Observation of the fracture surfaces by SEM showed that the added nanoparticles induce crack pinning, crack deflection, and voids formation. The combined results, obtained from the mechanical and thermal tests, indicate also the existence of an immobilized polymer layer around the filler particles; which may play the principal role on the enhanced toughness recorded by zirconia-epoxy nanocomposites.

The contribution of each fracture mechanism to the overall toughening effect induced by the nanozirconia on the epoxy matrix has to be quantified.

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