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Improving Epoxy Adhesives with Zirconia Nanoparticles

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Abstract

Zirconia nanoparticles were synthesized by a sol-gel route and dispersed into an epoxy base for structural adhesives. Nanoparticles were used as-synthesized or after calcination. Moreover, the effect of silane functionalization was also investigated. According to preliminary tensile mechanical tests on bulk nanocomposite samples, calcined and untreated zirconia nanoparticles were selected for the preparation of adhesives with various filler contents.

The glass transition temperature increased up to a filler content of 1 vol% and then decreased, probably due to the concurrent and contrasting effects of chain blocking and reduction of the crosslinking degree. Also tensile modulus, stress at break and fracture toughness of bulk adhesives samples were positively affected by the presence of an optimal amount of zirconia nanoparticles.

Mechanical tests on single lap aluminium bonded joints indicated that zirconia nanoparticles led to relevant enhancements of the shear strength of the joints. In particular, the shear strength increased by about 60% for an optimal filler content of 1 vol%, and an adhesive failure mechanism was evidenced for all the tested specimens. Concurrently, a significant decrease of the equilibrium contact angle with water was observed for adhesives containing zirconia nanoparticles. It can therefore be concluded that the addition of zirconia nanoparticles can effectively improve epoxy adhesives, both by increasing their mechanical properties and by enhancing the interfacial wettability with an aluminium substrate.

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Keywords

Zirconia nanoparticles, epoxy, nanocomposites, adhesives, bonded joints, contact angle

1. Introduction

In the last few years, polymeric nanocomposites have attracted the interest of both academic and industrial researchers, and a huge number of scientific papers can be found on the thermo-mechanical properties of nanomodified thermoplastic and thermosetting matrices [1, 2]. From a general point of view, nanostructured ma-

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terials are expected to yield improvements over neat polymers in a wide range of properties, such as mechanical properties [3–7], dimensional stability and barrier properties [8], thermal degradation resistance [9, 10], etc. The major part of available literature on epoxy based nanocomposites is focused on the preparation and characterization of layered silicates (clays) filled systems [2, 3, 7, 8, 11-19]. Liu et al. [5] synthesized epoxy-clay nanocomposites through a solution dispersion technique and observed interesting enhancements of the fracture toughness, accompanied by a significant reduction in the water diffusivity and water uptake. Basara et al. [13] studied the effects of the clay content and typology on the structure and mechanical properties of epoxy-clay nanocomposites, concluding that the tensile modulus, the tensile strength and the impact strength were strongly improved by nanofiller addition. Zunjarrao et al. [19] analyzed the influence of processing parameters and particle volume fraction of epoxy/clay nanocomposites, prepared through high-speed shear dispersion and ultrasonic disruption techniques. Both the flexural modulus and the fracture toughness were observed to increase at low clay volume fractions. The addition of organo-modified clays has been also associated with an increase of the fibre-matrix adhesion in glass/epoxy composites [20].

A significant amount of scientific information is also available on the usage of metal oxides (mainly alumina and titanium oxide) in epoxy based particulate nanocomposites [6, 15, 21]. Jia *et al.* [15] studied the mechanical properties and tribological behavior of epoxy nanocomposites containing spherical silica nanoparticles, reporting remarkable improvements of the fracture toughness upon silica addition. Johnsen *et al.* [21] prepared epoxy resins containing silica nanoparticles synthesized through a sol–gel technique. Both the elastic modulus and toughness were increased by the introduction of nanosilica. Moreover, a theoretical model of plastic void growth was used to confirm that this mechanism was most likely to be responsible for the increased toughness of the nanofilled samples.

Relatively few works can be found on epoxy/zirconia nanocomposites [22, 23]. Zirconium dioxide possesses outstanding properties, such as high strength, high fracture toughness, excellent wear resistance, high hardness, and excellent chemical resistance [24, 25]. For these reasons, zirconia nanoparticles may represent an attractive option to be used as reinforcement of polymers, in order to prepare high mechanical performances composites. Bondioli *et al.* [22] synthesized submicron spherical zirconia particles to be used as reinforcement for epoxy resins, varying the filler weight fraction between 1 and 5%. A numerical model was also developed to estimate the tensile properties as functions of the reinforcement content. Medina *et al.* [23] added zirconium dioxide nanoparticles to a diglycidyl ether of bisphenol A based epoxy resin, conducting a morphological and mechanical characterization of the resulting composites. Both tensile modulus and fracture toughness of the epoxy matrix increased as the zirconia content was raised. The presence of nanoparticles produced also an increment of the glass transition temperature with respect to the pure resin.

From a general point of view, epoxy resins display excellent properties as adhesives. High-performance adhesives are needed for joining metals, composites, ceramics and plastics to themselves and to each other. They are utilized in a variety of applications in aerospace, automotive, electronic, domestic household, oil and other industries [26]. Quite recently, it was demonstrated that the addition of small quantities of inorganic nanoparticles to polymeric adhesives can improve the shear resistance of structural joints. Park and Lee [27] utilized nano-size carbon black particles in order to improve the tensile lap shear strength and durability of composite (glass/epoxy) adhesively bonded joints. The lap shear strength and the durability under thermal loadings was interestingly improved and attributed to the better thermal stability and lower thermal expansion coefficient of the carbon black reinforced adhesive. By solution polymerization, Patel et al. [28] synthesized nanocomposite adhesives based on acrylic polymers and silica or clay, in order to investigate the effect of these nanoparticles on the adhesion behavior of the hybrid adhesives against different substrates (aluminium, wood, polypropylene). Aluminium and wood joints displayed higher joint strength, because of the interaction of the adhesive with the hydroxyl groups present on the surface of these substrates. Xi et al. [29] analyzed the electrical conductivity and the shear strength of electroconductive adhesives, prepared from polyurethane resins filled with different kind of modified graphites. It was observed that the strength of the adhesive joints to aluminium increased up to a filler content of 20 wt%. Yu et al. [30] developed epoxy adhesives reinforced with carbon nanotubes (CNTs), to be utilized in aluminium joints. In particular, they reported that the addition of CNTs in concentrations up 1 wt% greatly improved the durability of epoxy-based adhesive joint in tests under water at 60°C.

Starting from these considerations, in the present study we focus our attention on the effect of zirconia nanoparticles on the mechanical behaviour and adhesive properties of an epoxy resin. Zirconia nanoparticles were synthesized by the sol–gel method in a commercial microwave-heated flow vertical tube reactor. In particular, the synthesis conditions which produced spherical nanopowders with narrow grain size distribution were selected on the basis of a previous study [31]. Moreover, the synthesized powders were *ex situ* functionalized to evaluate the effects of a coupling agent on the performances of the filled adhesive.

2. Experimental

2.1. Preparation and Characterization of Powders

Synthesis of zirconia nanoparticles was conducted in hydrothermal conditions starting from a 0.1 M solution of tetra-*n*-propylzirconate (TPZ, Aldrich) using a commercial microwave-heated flow vertical tube reactor (MLS ETHOS CFR Continuous Flow Reactor) in agreement with a procedure described elsewhere [31]. TPZ, caproic acid (CA, Aldrich) and ethanol (EtOH, Eurobase) were used as received without further purification. Synthesis of zirconia particles was performed by slow addition of an alcoholic solution containing CA (0.016 M) and TPZ (0.1 M), pre-

Codes adopted for zirconia nanoparticles		
Particle type	Thermal and/or surface treatment	
A	None	
AM	Surface modification with GPTMS	
В	Calcination at 600°C for 4 h	
BM	Calcination at 600°C for 4 h and surface modification with GPTMS	

 Table 1.

 Codes adopted for zirconia papoparticles

viously reacted for 30 min at room temperature, to a mixture of EtOH and water (50:1 molar ratio) directly to the inlet of the reactor. The flow rate was fixed at 50 ml/min as optimized to obtain spherical monomodal nanoparticles [31]. The water concentration was fixed to 0.6 M. After the synthesis reaction, the powder was filtered, washed and dried. Part of the obtained powder was calcined at 600°C for 4 h in order to improve its crystallinity. Both the as-obtained and the calcined powders were successively functionalized using 3-glycidoxypropyltrimethoxysilane (GPTMS, Aldrich) using the procedure reported elsewhere [32]. A list of all the synthesized particles is reported in Table 1.

The synthesized zirconia nanoparticles were analyzed with a computer-assisted conventional Bragg–Brentano diffractometer (X'Pert Philips) using the Ni-filtered Cu K_{α} monochromatic radiation ($\lambda = 1.5418$ Å). The X-ray diffraction (XRD) patterns were collected at room temperature in a 2 θ range of 20–80°, with a scanning rate of 0.005°/s and a step size of 0.02°. In order to determine the residual carbon content in the zirconia particles, elemental analyses were carried out on a Carlo Erba EA 1110 apparatus (Carlo Erba, Italy). Sample morphology and microstructure were examined by transmission electron microscopy, TEM (JEM 2010, Jeol). For TEM analysis, specimens were prepared by dispersing as-obtained powders in distilled water and then placing a drop of suspension on a copper grid with a transparent polymer followed by drying. The average diameter Φ of the spherical particles was also estimated as follows [33]:

$$\Phi = \frac{6}{\text{SSA}\rho},\tag{1}$$

where the specific surface area (SSA) and density (ρ) of the powders were determined by the BET method [34] (Gemini 2360 apparatus, Micromeritics, Norcross, GA, USA) and by a helium picnometer (AccuPyc 1330 apparatus, Micromeritics, Norcross, GA, USA), respectively.

2.2. Preparation and Characterization of Bulk Adhesives

A bi-component epoxy resin commonly used for the preparation of structural adhesives was supplied by Elantas[®] Camattini (Collecchio, Italy). In particular, EC57 epoxy base (density and viscosity at 25°C of 1.15 g/cm³ and 1500 mPa s, respectively) and W635 amine hardener (density and viscosity at 25° C of 0.95 g/cm³ and 750 mPa s, respectively) were mixed at a weight ratio of 100:50.

Zirconia nanoparticles were added to the epoxy base and the mixture mechanically mixed for 10 min in a Dispermat[®] F1 mixer operating at 2000 rpm, and then degassed at ambient temperature. The hardener was then added and mechanically mixed for 5 min at 2000 rpm. Finally, the mixture was degassed again at ambient temperature and poured in the cavities of a silicone mould. A curing cycle of 15 h at 65°C was then conducted. According to this procedure, pure epoxy samples and nanocomposites filled with different zirconia nanoparticles at the same volume content (1 vol%) were prepared. After a preliminary mechanical characterization under quasi-static tensile conditions, calcined and not functionalized zirconia nanoparticles (type B) were selected for the preparation of nanocomposites filled at different loadings, from 0.5 vol% to 1.5 vol%. The samples were denoted indicating the matrix (Epoxy) and the kind of zirconia (A, AM, B, BM), followed by the filler content. As a title of example, the nanocomposite filled with 1 vol% of calcined and not functionalized zirconia nanoparticles was indicated as Epoxy-B-1.

Optical transparency was assessed using a Nikon Coolpix 4500 digital camera at a distance of 30 cm from the specimen.

The thermal properties of the samples were evaluated through differential scanning calorimetry (DSC) and dynamical mechanical thermal analysis (DMTA) tests. DSC tests were performed in a Mettler DSC30 apparatus. A thermal cycle, from 0°C to 220°C, at a heating rate of 10 K/min, under a nitrogen flow of 100 ml/min, was applied. DMTA tests were carried on by a MKII Polymer Laboratories machine. Rectangular samples, 25 mm long, 2 mm thick and 5 mm wide, were tested in tensile conditions, in a temperature range from 0 to 100°C, at a heating rate of 3 K/min. A sinusoidal strain, with an amplitude of 64 µm and a frequency of 1 Hz, was imposed. In this way, the temperature dependence of storage modulus (E') and of the loss factor $(\tan \delta)$ values were determined. The glass transition temperature (T_{σ}) of the samples was evaluated as the peak of tan δ curves. Quasi-static tensile properties were evaluated by using an Instron 4502 electromechanical tensile testing machine, at a crosshead speed of 1 mm/min. ISO-527 1BA dogbone specimens, with a gage length of 30 mm, a width of 5 mm and a thickness of 2 mm, were tested. The axial deformation was evaluated through an Instron 2620-601 extensometer, with a gage length of 12.5 mm. According to ISO 527 standard, the elastic modulus (E) was calculated as a secant value between the strain levels of 0.05%and of 0.25%. All tests were conducted at ambient temperature (23°C), and at least five specimens were tested for each sample. According to ASTM D 5045 standard, plane strain fracture toughness parameters K_{IC} and G_{IC} were evaluated on single edge notched bend (SENB) specimens (44 mm long, 10 mm wide and 4 mm thick) containing a sharp notch of about 5 mm depth. A cross-head speed of 10 mm/min was adopted in the three-point bending tests and at least five specimens were tested for each sample. In order to correlate the mechanical behaviour displayed by the tested samples with their fracture mechanism, fracture surfaces of SENB specimens were observed at various magnifications by a Zeiss Supra 40 Field Emission Scanning Electronic Microscope (FESEM), at an acceleration voltage of 12 kV and a pressure of 10^{-6} Torr.

Wettability of adhesives and aluminium substrates were evaluated by water contact angle measurements. At this scope, 3 µl volume drops of MilliQ grade water were deposited on cured epoxy samples, previously washed in an ultrasonic bath. Pictures of the drops were acquired through a digital camera positioned on a static contact angle analyzer. The acquired pictures were then analyzed with Image J 1.34S software, and the contact angle calculations were performed by applying the spherical approximation of the drop. The measurement on the sessile drop as deposited from the syringe returned an advancing contact angle. An equilibrium contact angle was measured by a vibrational method (vibration-induced equilibrium contact angle, VIECA) [35, 36]. According to this method, the supply of vibrational mechanical energy to the drop induces the relaxation of the meniscus to an equilibrium shape, independently of its initial state (advancing or receding). Equilibrium contact angles were measured after the sample holder vibrated for 10 s at a frequency of 200 Hz with a controlled amplitude. Only when the volume of the water droplet was steady, so that a negligible absorption occurred, was the equilibrium contact angle measured. At least five measurements were performed for each experimental condition. The same procedure was also applied to evaluate wateraluminium contact angle. In this case, the metallic substrate was washed in acetone, ground down and washed again.

2.3. Preparation and Characterization of Single-Lap Bonded Joints

In order to evaluate the adhesive properties of the epoxy nanocomposites, metallic single-lap joints were realized. A 6082 aluminium alloy, possessing high corrosion resistance and good weldability, was utilized as a substrate. The experimental apparatus for the preparation of the joint is depicted in Fig. 1(a). First of all, metallic substrates were washed in acetone and ground with abrasive paper, in order to reach a mean roughness of about 1 μ m. The substrates were washed again in acetone and arranged on silicone moulds. Thin copper wires, having a diameter of 0.5 mm, were placed in the overlap area, in order to control the thickness of the joints, while the overlap area was 25.4 mm × 12.7 mm. The epoxy adhesive was then carefully poured on the overlapping area. After the deposition of the upper aluminium sheet, a weight (1 kg) was applied to exert a constant pressure. The joints were then cured with the same cycle utilized for the bulk adhesives (15 h at 65°C). In this way single lap metallic joints with pure epoxy and nanofilled adhesives, with a zirconia content between 0.5 and 1.5 vol%, were realized.

Single-lap joints were mechanically tested under quasi-static conditions by using an Instron 4502 electromechanical tensile testing machine. According to ASTM D 1002 standard, a cross-head speed of 1.3 mm/min was adopted. All tests were



Figure 1. Aluminium–epoxy single lap joints. (a) Preparation stage, (b) stress distribution in the adhesive during the quasi-static tensile tests, (c) image of a failed specimen.

conducted at ambient temperature (23°C), and at least five specimens were tested for each sample. A simplified version of the Volkersen model was utilized for the analysis of the mechanical behaviour of the joints [37]. As reported in Fig. 1(b), a single lap joint with perfectly rigid adherends and with an adhesive behaving like a linear elastic solid was hypothesized. Under these assumptions a pure shear stress (τ), constant over the whole overlapping region, is generated in the adhesive [38]. The maximum shear stress (τ_{max}) acting on the joints is therefore computed as:

$$\tau_{\rm max} = \frac{F_{\rm max}}{bl},\tag{2}$$

where F_{max} is the maximum load registered during the tensile tests, b and l are respectively the width and the length of the overlapping area of the joint.

3. Results and Discussion

3.1. Characterization of the Powders

The elemental analysis carried out on zirconia A particles (Table 2) showed a significantly high carbon and hydrogen content (7.4 and 3.5%, respectively) that can be attributed to an incomplete sol–gel reaction of the zirconia precursor TPZ. The calcination step (sample B) eliminated all the residual organic elements in the powders, while the functionalization (samples AM and BM) slightly increased the carbon content.

XRD patterns of synthesized zirconia powders are reported in Fig. 2, which clearly shows that the as-obtained powders (curve a) were amorphous while, after

 Table 2.

 Physical properties and elemental analysis of the synthesized powders

Particle type	C%	H%	BET specific surface area (m ² /g)	Average diameter by BET (nm)	Average diameter by TEM (nm)	Density (g/cm ³)
A	7.38	3.52	115	18	50	2.842 ± 0.004
AM	12.22	2.95	46	49	50	2.664 ± 0.002
В	0.53	0.00	12	109	15	4.581 ± 0.005
BM	1.01	0.00	9	129	20	5.157 ± 0.007



Figure 2. XRD patterns of type A (a) and type B (b) zirconia powders (M: monoclinic; T: tetragonal).

the calcination step (curve b), the powders were crystallized and composed mainly of tetragonal zirconia, showing the monoclinic zirconia peaks with very low intensity. This behaviour is in agreement with the observed increase of the density values (Table 2) induced by the thermal treatment.

TEM observations revealed that A powders were characterized by spherical aggregates with an average dimension of 50–60 nm (Fig. 3(a)) tightly connected to one another. TEM micrograph of AM particles (Fig. 3(b)) indicates the presence



Figure 3. TEM micrographs of (a) type A, (b) type AM, (d) type B and (e) type BM particles. (c) EDS spectra of type AM particles.

of an external thin layer with respect to the as-prepared A particles. This consideration was qualitatively supported by the EDS analysis, which revealed the presence of silicon and thus the effectiveness of the surface modification treatment with GPTMS (Fig. 3(c)). TEM images of calcined powders (samples B and BM, Fig. 3(d) and 3(e)) show that the average particle size was slightly decreased even if a hard agglomeration was observed. The significant decrease of SSA of type A nanoparticles after surface treatment with GPTMS was presumably due to a partial pore closing. A minor decrease of SSA values was also evident comparing B and BM powders.

The mean diameters of powders determined from SSA data were completely in disagreement with those directly determined by TEM. For A particles a possible explanation could be the presence of a porous structure that implies an underestimation of the particle size determined by BET method. On the other hand, the very low SSA data observed for B and BM particles could be due to their partial agglomeration.

3.2. Characterization of Bulk Adhesives

At a preliminary stage, a selection of the nanofiller was conducted on the basis of quasi-static tensile tests on bulk specimens. Representative stress–strain curves of pure epoxy and of 1 vol% filled nanocomposites are reported in Fig. 4, while the most important parameters, such as the Young's modulus E, tensile strength σ_b and strain at break ε_b , are summarized in Table 3. The introduction of nanozirconia in these systems led to an enhancement of the elastic modulus of the epoxy resin. The increase of the stiffness due to the presence of inorganic nanofillers is well documented in the scientific literature [13, 14, 39, 40], and it is generally ascribed to a physical chain blocking mechanism provided by nanoparticles on the polymer



Figure 4. Representative stress–strain curves of quasi-static tensile tests on epoxy–zirconia nanocomposites ($\Phi = 1$ vol%).

macromolecules. It is important to underline that the improvement was more effective when calcined and non-functionalized nanoparticles (type B) were utilized (+27% with respect to the pure matrix), while only marginal improvements were obtained for non-calcined nanoparticles. Stress at break of nanocomposites filled with calcined and non-functionalized zirconia was 15% higher than that of the neat resin, while for the other composites σ_b was practically equal to that of the epoxy resin. The introduction of zirconia led also to a slight enhancement of the strain at break, regardless of the filler type. Therefore, an interesting stiffening effect, accompanied by a slight improvement of the tensile properties at break could be detected for nanofilled samples. With regard to the role played by the nanofiller type on the quasi-static tensile behaviour of the samples, it can be noticed from Table 2 that calcined nanoparticles (B, BM) were denser and smaller than the untreated ones (A, AM). Therefore, it is reasonable to assume that the presence of stiffer particles with lower dimensions may more intensely affect the mechanical behaviour of the epoxy resin. As previously observed for polyethylene-titania [41] and cyclolefin/polyhedral oligomeric silsesquioxanes nanocomposites [42], it is possible that also in this case the surface modification of the nanoparticles led to the formation of an organic interphase, presumably softer than the epoxy matrix, with detrimental effects on the elastic properties of the material. This is probably the reason why type B zirconia filled nanocomposites showed the best mechanical performances.

Therefore, this kind of nanoparticle was selected for the preparation of composites at different filler contents (from 0.5 to 1.5 vol%). In Fig. 5, photographs of the pure epoxy and of the nanofilled samples for the evaluation of the transparency are reported. It is evident that the addition of zirconia nanoparticles in these systems led to a progressive loss of transparency. The samples appeared haze even at low filler contents. This is an indirect indication of the fact that an inhomogeneous dispersion of the nanoparticles was reached during the shear mixing procedure, and some agglomerates with micrometric dimensions were probably present in the composites. The nanofiller agglomeration was even more evident for highly filled composites (1.5 vol%), in which the original transparency was completely compromised.

Sample	E (GPa)	$\sigma_{\rm b}~({\rm MPa})$	ε_{b} (%)
Ероху	1.95 ± 0.10	34.2 ± 1.9	2.5 ± 0.4
Epoxy-A-1	1.96 ± 0.07	30.1 ± 5.6	2.5 ± 0.9
Epoxy-AM-1	2.15 ± 0.28	33.0 ± 1.3	3.2 ± 0.4
Epoxy-B-1	2.49 ± 0.13	39.4 ± 2.6	2.9 ± 0.7
Epoxy-BM-1	2.19 ± 0.09	33.1 ± 5.4	2.6 ± 1.0

Tensile mechanical properties of epoxy–zirconia bulk adhesives ($\Phi = 1 \text{ vol}\%$;

E: Young's modulus; $\sigma_{\rm b}$: tensile strength; $\varepsilon_{\rm b}$: strain at break)

Table 3.

883



Figure 5. Optical transparency of Epoxy-B-x nanocomposites (x = 0.5, 1, 1.5 vol%).



Figure 6. Thermo-mechanical properties of Epoxy-B-*x* nanocomposites (x = 0.5, 1, 1.5 vol%). (a) DSC thermograms, (b) storage modulus (E'), (c) loss tangent ($\tan \delta$), (d) glass transition temperature (T_g).

DSC thermograms of pure matrix and nanofilled samples are reported in Fig. 6(a), while storage modulus (E') and loss tangent $(\tan \delta)$ values evaluated by DMTA tests are represented in Fig. 6(b) and 6(c), respectively. Moreover, glass tran-

Table 4.

Tensile mechanical properties of Epoxy-B-*x* bulk adhesives (x = 0.5-1.5 vol%; *E*: Young's modulus; σ_b : tensile strength; ε_b : strain at break)

Sample	E (GPa)	$\sigma_{\rm b}~({\rm MPa})$	ε_{b} (%)
Epoxy Epoxy-B-0.5 Epoxy-B-1	$\begin{array}{c} 1.95 \pm 0.10 \\ 1.70 \pm 0.15 \\ 2.49 \pm 0.13 \end{array}$	34.2 ± 1.9 37.8 ± 3.3 39.4 ± 2.6	2.5 ± 0.4 3.6 ± 0.5 2.9 ± 0.7
Epoxy-B-1.5	1.71 ± 0.12	36.5 ± 0.9	3.7 ± 0.3

sition temperature (T_g) trends obtained from DSC and DMTA tests are compared in Fig. 6(d). It is evident that there is a non-monotonic T_g trend with the zirconia content. The maximum T_g increment occurred at a filler content of 1 vol%, in agreement with the observations of Dean et al. on the chemorheological behaviour of epoxy-layered silicate nanocomposites [14]. For higher filler contents, the glass transition temperature started to decrease. As previously reported for polyurethaneclay nanocomposites [43], it is possible that even in this case the occurrence of two concurrent and opposite phenomena was responsible for the observed T_g trend. In fact, as the filler content increased, the chain blocking (stiffening) effect was likely to increase and, at the same time, polymer-filler chemical interactions and the increase of the viscosity of the system hindered the cross-linking process of the matrix, with a consequent reduction of its T_{g} . Furthermore, it can be noticed that glass transition values evaluated from $\tan \delta$ peak in DMTA tests were systematically higher than that obtained from DSC tests. As widely reported in the scientific literature [44], this discrepancy can be attributed to the differences in the sensed variable and testing conditions between the two techniques.

In Table 4 the most important results from quasi-static tensile tests on pure epoxy and nanofilled samples are reported. Elastic modulus slightly increased until a filler concentration of 1 vol% was reached, and then started to decrease for higher zirconia concentrations, probably because of agglomeration phenomena. Interestingly, the introduction of zirconia nanoparticles led to an improvement of the tensile strength with respect to the neat resin. Stress at break values for the nanocomposites showed a maximum at $\Phi = 1$ vol%, and then slightly decreased. Even in this case it is possible that the presence of a fraction of zirconia agglomerates with micrometric dimension acted as crack nucleation sites, with detrimental effects on the tensile properties at break, accordingly to the existing scientific literature on nanofilled epoxy systems [3, 11, 18].

More relevant improvements due to zirconia nanoparticles were observed when fracture toughness tests were conducted. K_{IC} and G_{IC} values of pure epoxy and of the relative nanofilled samples are summarized in Fig. 7(a) and 7(b), respectively. An increase of K_{IC} of about 33% with respect to the neat resin could be observed for the 0.5 vol% filled nanocomposite, before reaching a plateau value for higher zirconia loadings. Even higher enhancements could be detected if G_{IC}



Figure 7. Fracture toughness of Epoxy-B-*x* nanocomposites (x = 0.5, 1, 1.5 vol%): (a) K_{IC} values, (b) G_{IC} values.

values are considered. Comparable increments of the fracture toughness have been reported already in the scientific literature on epoxy–clay nanocomposites [5, 15]. It could be hypothesized that, when a notch is already present on the sample, the presence of zirconia nanoparticles could render the crack propagation path more tortuous, with a positive contribution to the fracture toughness of the material. The best performances were obtained for a filler content of 0.5 vol%; for higher zirconia concentration the presence of aggregates with micrometric dimensions counterbalanced the reinforcing effect provided by the nanoparticles.

ESEM images of fracture surfaces of pure epoxy and relative nanocomposites are reported in Fig. 8. The morphology of the fracture surfaces was affected by the addition of zirconia nanoparticles. In fact, while the pure epoxy sample was relatively smooth, nanofilled samples displayed more corrugated surfaces. Moreover, the surface corrugation appeared to be more and more pronounced as the filler content increased. The corrugation of the fracture surface due to the presence of clay nanoplatelets has been widely reported in the scientific literature [5, 11, 16], and the creation of a higher amount of fracture surface could be correlated to the enhancement of the fracture toughness detected for nanofilled samples.

3.3. Characterization of Single-Lap Bonded Joints

Representative force–displacement curves obtained by quasi-static tensile test on pure epoxy and nanofilled single-lap joints are reported in Fig. 9, while maximum shear stress values are summarized in Table 5. The introduction of nanozirconia in these systems led to a significant enhancement of the shear resistance of the joints. As an example, the maximum shear stress sustained by 1 vol% filled nanocomposite joint was 60% higher than the shear resistance of the unfilled joints. For higher filler contents, the shear strength started to decrease. Even in this case, one can hypothesize that the presence of agglomerates had detrimental effects on the mechanical behaviour of the joints. It is also possible that the increase of the adhesive viscosity at elevated filler contents produced a non-optimal distribution of the adhesive in



Figure 8. ESEM micrographs of fracture surface of Epoxy-B-*x* nanocomposites. (a) Epoxy, (b) Epoxy-B-0.5, (c) Epoxy-B-1, (d) Epoxy-B-1.5.

the overlapping region. Also, the difficulties of the degassing process experienced for 1.5 vol% nanocomposites, due to the high viscosity of the resin, should be considered. The increase of the shear strength of epoxy joints due to the presence of nanoparticles is in agreement with the conclusions reported by Park and Lee [27] on carbon black reinforced adhesive systems and by Patel *et al.* [28] on nanomodified acrylic adhesives. Furthermore, the existence of an optimum filler content was already detected by Xi *et al.* [29] on graphite nanocomposite adhesives and by Yu *et al.* [30] on carbon nanotubes reinforced epoxy adhesive joints.

An analysis of the failure mechanism of the joints is surely important to elucidate the effective contribution of the introduction of zirconia nanoparticles on the mechanical performances of the joints. A representative image of a failed joint



Figure 9. Representative force–displacement curves from quasi-static tensile tests on Epoxy-B-x nanocomposite joints.

Shear strength 0.5–1.5 vol%)	of Epoxy-B- x single	lap joints ($x =$
Sample	$\tau_{\rm max}$ (MPa)	$\Delta \tau_{\max}$ (%)

 7.7 ± 0.8

 10.0 ± 1.5

 12.3 ± 1.4

 8.0 ± 1.0

30

60

4

Table 5.

Epoxy

Epoxy-B-0.5

Epoxy-B-1.5

Epoxy-B-1

is shown in Fig. 1(c). Considering that for all the tested joints the adhesive remained on one of the substrates, it is possible to conclude that the behaviour of the joints was governed by a delamination mechanism. In these conditions it can be hypothesized that the reinforcing effect obtained through the introduction of zirconia nanoparticles in metallic joints was due to the formation of a stronger adhesive– substrate interface.

To support this hypothesis, epoxy-water contact angle measurements were conducted. Representative images of a water droplet on pure epoxy, on the 0.5 vol% filled sample, and on the aluminium substrate are reported in Fig. 10. As expected, the vibration produced a systematic decrease of the contact angle towards equilibrium values that are compared in Fig. 11. It is worthwhile to observe that the presence of zirconia nanoparticles led to a noticeable decrease of the equilibrium contact angle values. In fact, for pure epoxy sample an equilibrium contact angle of 82.1° was evaluated, while for Epoxy-B-0.5 nanocomposites a mean contact angle of 71.5° was determined. This means that water contact angle values



Figure 10. Epoxy–water contact angles images. (a, b, c) Static conditions, (d, e, f) equilibrium (vibrated) conditions. (a, d) Epoxy, (b, e) Epoxy-B-0.5, (c, f) aluminium substrate.



Figure 11. Epoxy–water equilibrium contact angles for Epoxy-B-x nanocomposites and aluminium substrate.

of the nanofilled sample are closer to that displayed by the aluminium substrate (59.4°) . For higher zirconia concentrations, the vibrated contact angle was slightly increased. Similar conclusions were reported by Prolongo *et al.* [45], who found a significant lowering of the contact angle between uncured carbon nanofiber filled epoxy adhesives and carbon fiber/epoxy substrates. The authors attributed this result to the nano-scale size of the nanofiber and the higher chemical compatibility between the carbon fiber/epoxy composite and the nanoreinforced epoxy adhesive. The subsequent increase of contact angle for relatively high filler contents was associated with the worsening of the dispersion degree of the nanofiller, possibly forming agglomerates of carbon nanofibers. Therefore, it can be concluded that the introduction of zirconia nanoparticles led to a better interfacial wettability and chemical compatibility between the adhesive and the substrate, with a positive contribution to the shear resistance of the joints.

4. Conclusions

The mechanical performances of an epoxy-based adhesive have been improved by the addition of zirconia nanoparticles. In particular, four kinds of nanofillers, different for the thermal treatment and for the surface properties, were synthesized through a sol–gel technique and added to epoxy resins at a filler volume content of 1 vol%. The preliminary mechanical testing revealed that calcined and nonfunctionalized zirconia filled samples showed the highest tensile modulus and the best properties at break. For this reason this nanofiller was utilized for the preparation and the characterization of epoxy–zirconia nanocomposites at different filler contents.

Quasi-static tensile tests on single lap aluminium joints evidenced that the introduction of nanozirconia in epoxy adhesives led to remarkable enhancements of the shear resistance of the joints. An improved wettability was attributed to the presence of zirconia nanoparticles, as evidenced from equilibrium water contact angle. The enhancement of the shear resistance of the joints provided by zirconia nanoparticles was therefore attributed due to a better interfacial wettability and chemical compatibility between the adhesive and the metallic substrate.

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890

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