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Preparation and characterization of epoxy resins filled with submicron spherical zirconia particles

Summary — Submicron spherical zirconia particles were synthesized and used as a reinforcement for epoxy resins. In fact, recent developments indicate that a significant improvement in the thermoset polymer performance may be obtained by using submicron inorganic filler. In this paper, different composites with weight fraction of the filler in the range 1—5 % were prepared and characterized in terms of mechanical properties. A numerical model suitable for the description of such materials was set up and employed to estimate the properties as functions of the reinforcement content.

Key words: epoxy resin, submicron spherical zirconia particles, nanocomposite, elastic modulus, modelling.

OTRZYMYWANIE I CHARAKTERYSTYKA ŻYWIC EPOKSYDOWYCH NAPEŁNIANYCH SUBMIKROSKOPOWYMI CZĄSTKAMI DITLENKU CYRKONU

Streszczenie — Zsyntetyzowano submikroskopowe cząstki ditlenku cyrkonu i scharakteryzowano je metodami analizy rentgenowskiej i elementarnej. Za pomocą transmisyjnego mikroskopu elektronowego (TEM) wykonano zdjęcia (rys. 1) i wyznaczono średnice, powierzchnię właściwą i gęstości (tabela 1) cząstek wytrąconych z roztworów o dwu różnych stężeniach wody (0,35 M i 0,6 M). Otrzymanymi cząstkami napełniano (1, 3 lub 5 % mas.) żywicę epoksydową a produkty badano metodą skaningowej mikroskopii elektronowej (SEM, rys. 2) oraz wyznaczano moduł sprężystości wzdłużnej (E , tabela 2). Opracowano i przetestowano modele pozwalające na przewidywanie wartości E badanych nanokompozytów w zależności od zawartości napełniacza (rys. 3, tabela 3).

Słowa kluczowe: żywica epoksydowa, submikroskopowe sferyczne cząstki ditlenku cyrkonu, nanokompozyt, moduł sprężystości wzdłużnej, modelowanie.

As advanced engineering materials, composites are used in many applications where excellent performances under hard working conditions are required. Such materials must provide unique mechanical and tribological properties combined with a low specific weight and a high resistance to degradation in order to ensure safety and economic efficiency [1]. In this way, the properties can be varied substantially through changes in the microstructure, morphology, volume fraction and mechanical properties of the reinforcing phase, and the nature of the interface between matrix and reinforcement.

Some of composite materials for technical applications may be represented by those with a thermosetting polymer matrix, *e.g.* an epoxy resin, which already gives some of the required properties. Good mechanical strength and hardness, as well as thermal and chemical resistance of the materials, in fact, favor their applications as engineering materials. However, because the polymer matrix must withstand high mechanical and

tribological loads, it is usually reinforced with fillers. These fillers can be chosen from the fibers (glass, carbon or aramid) or particles such as ceramic powders. Dimensions of the particles usually are in the range of 1—10 or even more micrometers. Epoxy matrix composites filled with inorganic particles have been extensively studied during the last two decades due to their increasing applications as coatings, electronic packagings and dental fillings [2, 3]. Use of nanometer-scale particles is nowadays attracting a great attention [4]. This new approach demonstrates the potential to change characteristics of thermosetting and thermoplastic polymers fundamentally, with the aim to improve their general performances [5, 6]. Nanoparticle filled polymers, the so-called polymeric nanocomposites, present, in fact, specific features, mainly due to their very high interfacial area, and the very short distance between the reinforcing particles. It was verified experimentally by several research groups that nanoparticles of metallic or inorganic type showed the ability to reinforce effectively thermoplastic and also thermosetting polymer matrices [7]. Specifically, the reinforcement improve the fracture toughness

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and impact strength which, however, depend strongly on the filler volume content [8, 9]. It has been shown that a considerable improvement of the mechanical and tribological properties can already be achieved at very low filler content, *i.e.* in the range of 1–5 vol. % [10–14]. A comparable improvement of these properties has not been observed using conventional fillers. Moreover, the low volume fractions of nanoparticles are potentially interesting for incorporation them into polymers by existing processing techniques, thus providing low production cost for commodity polymers and increased tailor-made options for advanced composites. However, the understanding of the role of these inorganic fillers in the micro- and nanometer scales is still very limited.

In the present paper, zirconia spherical submicron particles were synthesized by the sol-gel process and used to prepare for the first time, to the best of the authors' knowledge, epoxy based composites. We focused on the effect of particle size on the mechanical properties of nanocomposites at low levels (1–5% by weight) of filler content. Two distinct uniform sizes of submicron spherical zirconia were used. The values of elastic modulus of the nanocomposites, depending on the particle size and size distribution, particles' content, and interfacial interactions between the particles and matrix resin, were evaluated. Moreover, the mechanical properties of the composites were studied and simulated by using a finite element code able to construct a numerical model from a microstructural image of the material.

EXPERIMENTAL

Materials

Tetra-*n*-propylzirconate (TPZ, Aldrich), capronic acid (CA, Aldrich), ethanol (EtOH, Eurobase), ammonium hydroxide (NH₄OH, Aldrich) were used as received without further purification.

For the composites preparation, commercial bisphenol A diglycidyl ether epoxy resin and aliphatic polyamine hardener were supplied by Conchem and used as received.

Particles and composites' preparation

Zirconia particles were prepared by sol-gel method. Precipitation of zirconia nanoparticles was done by slow addition of an alcoholic solution containing CA (0.016 M) and TPZ (0.1 M), previously reacted for 30 min at room temperature, to a mixture of EtOH and water (50:1 molar ratio). Particles' precipitation was carried out at temperature of 40 °C for 35 min under vigorous magnetic stirring. After complete evaporation of volatiles (12 h at 100 °C), particles showing different grain size distribution were obtained depending on the water concentration (0.35 M or 0.6 M, respectively) [15].

Different mixtures of inorganic particles and epoxy prepolymer (with a filler content of 1, 3 or 5 % by weight) were prepared by mechanical stirring at 26000 rpm. After degassing under dynamic vacuum, the hardener (200 phr) was added and the system was cast into cavities formed by a suitable silicon rubber mold blocked by two glass plates to produce the specimens 80 × 10 × 4 mm thick. The resins were cured for 2 h at 70 °C and postcured for 2 h at 120 °C.

Samples characterization

X-ray diffraction (XRD) data were collected by Philips 3710 diffractometer using Cu-K α radiation and a nickel monochromator, over the 2 θ range 10–80° at a scanning rate of 2 s for step and a step size of 0.02°.

To determine the residual carbon content in the zirconia particles, elemental analyses were carried out using Carlo Erba 1110 apparatus.

Particles morphology was examined by transmission electron microscopy, TEM (Jeol, JEM 2010). Specimens were prepared by dispersion of the obtained powders in distilled water and then placing a drop of suspension on a copper grid with a transparent polymer, followed by drying. To estimate the particle size distribution, image analysis was carried out on TEM micrographs by using Image Pro Plus 4.5.1 software equipped with the module Materials Pro. The specific surface area and density of the powders were determined by the B.E.T. method (Micromeritics, Gemini 2360) and by a picnometer (Micromeritics, Accupic 1330), respectively.

To evaluate the mechanical properties of the obtained composites, tensile tests were carried out using an Instron 4455 instrument, according to ASTM 3039/D 3039 M-95 standards. Moreover, fracture surfaces were gold-coated and examined by Scanning Electron Microscopy (SEM) using a Philips XL-40 instrument.

Modelling of the mechanical properties

In order to estimate the mechanical performance of nanocomposites as a function of a filler particle size and volume fraction, a numerical code called OOF (Object-Oriented Finite Element Analysis) [16, 17] was used to prepare microstructural models.

OOF is a computational tool able to convert digitized micrographs, *e.g.* SEM images, into finite element meshes. Thus, microstructural features, such as nanoparticles' size, shape and volume fraction, can be incorporated into the model. In particular, different microstructures, corresponding to 1, 3 and 5 % by weight of particles of both granulometries, were considered for the epoxy-zirconia nanocomposite and the corresponding numerical grids were constructed. Performing virtual test on such meshes, it was possible to assess the effect of particles' content and dimensions on the composite mechanical properties. In order to obtain a reliable estima-

tion, 5 different microstructures for each composite class were considered and average values of elastic modulus were calculated. Moreover, it should be noted that such microstructures were accurately selected to be a significant portion of the material under examination.

RESULTS AND DISCUSSION

Characterization of zirconia nanoparticles

XRD analysis of zirconia powders showed the completely amorphous nature of the obtained particles, independently on the raw materials concentrations. The elemental analysis of zirconia particles showed a significantly high carbon content (10.8 and 7.2 % for zirconia obtained with water concentration of 0.35 M and 0.6 M, respectively) and a hydrogen content ranging from 2.8 to 4.4 %. These residues can be attributed to an incomplete sol-gel reaction of the zirconia precursor TPZ.

TEM micrographs revealed the spherical shape and narrow grain size distribution of zirconia particles (Fig. 1a and b). Particles of greater sizes were obtained by water concentration decreasing, according to the results

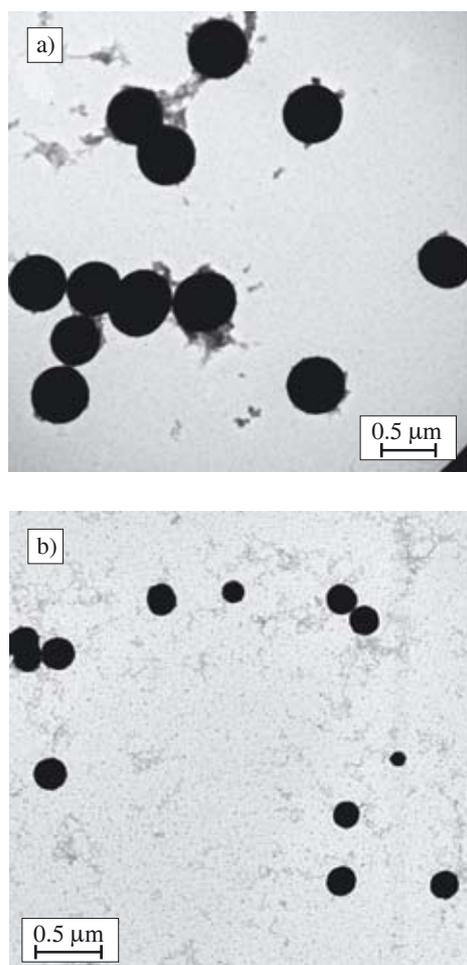


Fig. 1. TEM micrographs of zirconia particles obtained using solution with water concentration: a) 0.35 M, b) 0.6 M

reported already in the literature [18, 19]. Average particles' diameters, determined by TEM images elaboration, specific surface area and density of the powders are reported in Table 1.

Table 1. Average diameter, specific surface area and density of the powders obtained

Sample	Average diameter, nm	Specific surface area, m ² /g	Density g/cm ³
ZrO ₂ ([H ₂ O] = 0.35 M)	550 ± 60	9.5	2.80
ZrO ₂ ([H ₂ O] = 0.6 M)	220 ± 40	103.0	2.34

Characterization of epoxy based nanocomposites

SEM analyses of the fracture surfaces of composites containing 1, 3 and 5 wt. % of nanofillers were carried out in order to qualitatively evaluate the particle-matrix interface and evidence the eventual presence of filler particles' aggregations. In all cases a good adhesion between zirconia particles and epoxy matrix was shown as evidenced by the absence of voids around the particles. It can be seen for example in Fig. 2 for nanocomposites prepared with smaller and larger zirconia particles, respectively (similar micrographs were obtained also for the other systems). It is evident that the presence of residual alkyl chains in the zirconia particles (as evidenced by the previously discussed elemental analysis results) was enough to ensure a good particle-matrix interface.

The state of dispersion was satisfying for particle concentration of 1 and 3 wt. %. Partial aggregation of parti-

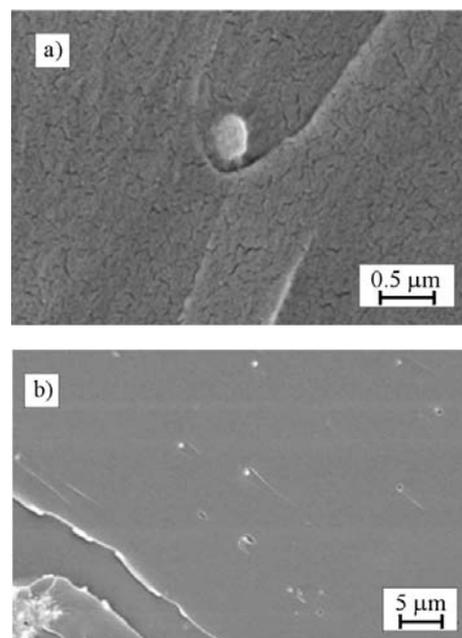


Fig. 2. SEM micrographs of fracture surfaces of epoxy resins reinforced with: a) smaller zirconia particles, 1 wt. %, b) larger zirconia particles, 3 wt. %

cles was shown only in the case of particles' content of 5 wt. %. At this concentration the conventional mechanical mixing technique was not able to break up the agglomerates for reaching a homogeneous dispersion state of nanoparticles [20]. In this case a pre-treatment of the particle surface could be useful to obtain complete deagglomeration.

The mechanical properties (tensile tests) of the nanocomposites are summarized in Table 2.

Table 2. Elastic modulus of nanocomposites

Composite	Filler content wt. %	Elastic modulus GPa	Standard deviation GPa
Unfilled epoxy resin	—	2.000	0.100
Epoxy resin / ZrO ₂ ([H ₂ O] = 0.35 M)	1	2.018	0.117
	3	2.175	0.256
	5	2.345	0.074
Epoxy resin ZrO ₂ ([H ₂ O] = 0.6 M)	1	2.008	0.078
	3	2.205	0.139
	5	2.645	0.200

For each composite class, 5 samples were tested and average values and standard deviation of the elastic modulus were calculated.

As expected, a systematic increase in elastic modulus was obtained by increasing the filler content. It is worth to note that the higher improvements were obtained in the cases of smaller dimensions of particles, *i.e.* for composites containing zirconia particles obtained with a water concentration of 0.6 M (average diameter of 220 nm). This result is in agreement with literature data [21].

Modelling of nanocomposites' mechanical properties

Elastic moduli were estimated for each composite class, namely 1, 3 and 5 wt. % both for the smaller and larger zirconia particles, basing on the knowledge of composite components. The numerical results, as illustrated in Table 3 for larger zirconia particles, were lower especially for higher filler content than those experimentally obtained. Analytical equations commonly em-

Table 3. Comparison of elastic moduli (E) of the composites (larger zirconia particles) obtained by numerical predictions and from analytical equations with experimental data

Filler content wt. %	E , GPa		
	experimental	numerical modelling	analytical equations
1	2.018	2.017	2.019
3	2.175	2.053	2.058
5	2.345	2.087	2.099

ployed for the composites [22] were used to get an additional estimation of the elastic properties. It is worth to note that such results are close to the numerical ones. This means that both analytical equation and numerical modelling consisting in traditional approaches for composites are not suitable for the investigation of the present materials. In fact, it is reported in literature that an interphase polymeric layer may form near the inorganic surface. Such interphase shows properties which are remarkably different from those of a filler and matrix [21]. Indeed, macroscopic properties of nanocomposite are affected by this phenomenon. Thus the effect of the interphase should be undoubtedly considered in order to obtain a reliable estimation of composite performance. A previous study, dealing with polycaprolactone reinforced with silica nanoparticles [23], pointed out the need of inclusion of an interphase layer into the numerical model.

Many recent studies focused on the effect of the interphase between the matrix and the inclusions. Zhong *et al.* [24] calculated the composite properties by assuming

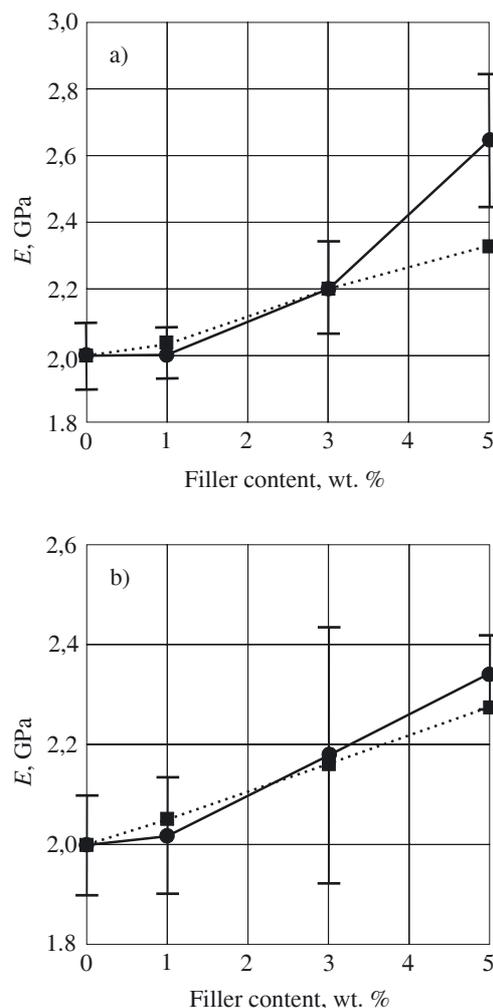


Fig. 3. Comparison of numerical values (interphase model, squares) of elastic moduli (E) with experimental data (circles) for: a) smaller zirconia particles, b) larger zirconia particles

the interphase properties linearly varying from those of the matrix to those of the reinforcement. Yang *et al.* [25] developed a thermodynamic model of interphase formation and properties' prediction. Tsui *et al.* [26] studied the effect of interphase characteristics on the composite behavior, by using a finite element method (FEM) and found that the interphase played a major role. On the other hand, other authors [27] demonstrated the feasibility of the application of FEM approach to nanocomposite systems.

Therefore, in this work, a third phase, namely the interphase, was introduced in the microstructure-based model. In particular, it was assumed that such interphase has the average properties between the matrix and the particles, in accordance with previous studies [24], and a dimension equal to half of diameter of the zirconia inclusions. With such a hypothesis, the elastic moduli were calculated as functions of a filler amounts. Figures 3a and 3b report the obtained results for the smaller and the larger particles, respectively. Such results show a good agreement with the experimental values, thus confirm the reliability of the numerical model: in fact the numerical predictions are mostly within the error bars of experimental measurements. Therefore, the numerical model, constructed as described above, can be considered as an useful tool for the prediction of composites' elastic properties, since such prediction is in good agreement with available experimental data.

Future development of the present work should include experimental determination of the interphase properties and dimensions, in order to validate the assumptions of the model. In particular, such characteristics could be determined *via* nanoindentation [28] or AFM [29].

CONCLUSIONS

Epoxy nanocomposites reinforced with zirconia particles were prepared and experimentally characterized. Moreover, a numerical model was set to simulate the mechanical behavior of such materials. Future research will include a more accurate estimation of the nanocomposite interphase, in particular the use of a nanoindentation equipment for the determination of the interphase elastic characteristics.

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