Epoxy-Silica Nanocomposites: Preparation, Experimental Characterization, and Modeling

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ABSTRACT: Silica nanoparticles having different sizes were obtained by the sol-gel process and characterized. The prepared nanoparticles were subsequently used as reinforcing fillers to prepare epoxy-based composites with a silica content ranging from 1 to 5 wt %. SEM analysis and tensile tests carried out on the silica-epoxy nanocomposites indicated the absence of particle aggregation and a reinforcing effect in terms of increased elastic modulus. Mechanical properties were also modeled by using a finite element code able to construct a numerical model from a microstructural image of the material. A more reliable model was prepared by considering the presence of an interphase layer surrounding the particles with intermediate elastic properties between the epoxy and the inclusions and a characteristic size proportional to the particle radius. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2382–2386, 2005

Key words: epoxy resins; mechanical properties; modeling; nanocomposites; silica nanoparticles

INTRODUCTION

The development of new polymeric materials with improved strength, hardness, and heat resistance represents an important goal from both academic and industrial points of views. In this respect, organic polymers reinforced with nanosized inorganic fillers are very interesting materials, taking into account the dramatic increase in the interfacial area between fillers and matrix, which in turn can significantly improve the overall properties of the polymer.

Epoxy resins are widely used in industrial applications thanks to their high mechanical and adhesion characteristics and good solvent and chemical resistance, together with their curability in a wide range of temperatures without the emission of volatile byproducts.[1] The properties of epoxy based organic-inorganic composites can be finely tuned by an appropriate choice of the structures of both epoxy prepolymer and hardener and of type and amount of inorganic filler. Several approaches have been proposed[2] for the incorporation of inorganic structures into organic polymers on a nanoscale: formation of interpenetrating networks, incorporation of metals and metals complexes in polymers by coordination interactions, intercalation of 2D layered materials or 3D frameworks (zeolites, molecular sieves, etc.), and incorporation of inorganic particles and clusters.

As already said, the use of inorganic nanoparticles can be particularly interesting thanks to their easy applicability to the common processing techniques used for epoxy-based conventional composites. In fact, micrometer sized inorganic particles are currently widely used for the reinforcement of epoxy matrices to lower shrinkage on curing and thermal expansion coefficients, to improve thermal conductivity, and to meet mechanical requirements. The final properties of the composite material are affected by several factors, such as intrinsic characteristics of each component, the content, the shape and the dimension of fillers, and the nature of the interface.[3] Strong interfaces between matrix and filler are needed to achieve high performances, taking into account that the load applied on the composites is mainly transferred to the fillers via the interface. To enhance the properties, smaller size and a larger amount of fillers are required, and in this respect the use of submicron particles can lead to a significant improvement of the mechanical properties of the composite materials.

In the last decade, a lot of work has been carried out in the field of preparation of submicron inorganic particles,[4] leading to the possibility of preparing composites reinforced with nanofillers. Epoxy resin reinforced with silica particles having submicron dimensions represents one of the most studied systems. Already published results[5–7] evidenced that well-dispersed silica nanoparticles can effectively enhance the comprehensive properties of epoxy-based nano-

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TABLE I
Elemental Analysis of Silica Particles Obtained from Ethanol and Methanol (n.d.: not detected)

Particle	Nitrogen (wt %)	Carbon (wt %)	Hydrogen (wt %)
SiO$_2$ from ethanol	n.d.	0.80	1.39
SiO$_2$ from methanol	n.d.	0.76	1.44

composites, which are unique and different from any other current conventional microcomposite with typical filler amounts of less than 5 wt %.

However, to the best of the authors' knowledge, most studies generally focus on one aspect only, for example, either preparation and mechanical characterization of nanocomposites or, alternatively, modeling. The present study represents an attempt to couple experimental analysis with modeling of mechanical properties, thus interpreting experimental and simulated data in a synergic way.

On the basis of these considerations, in this study silica nanoparticles were prepared by the sol-gel process and fully characterized and were used to prepare epoxy-based nanocomposites. The mechanical properties of the nanocomposites were experimentally investigated and simulated by using a finite element code able to construct a numerical model from a microstructural image of the material.

EXPERIMENTAL

Materials

Tetraethoxysilane (TEOS, Aldrich), ethanol (EtOH, Eurobase), methanol (MeOH, Eurobase), and ammonium hydroxide (NH$_4$OH, Aldrich) were used as received without further purification. Commercial bisphenol A diglycidyl ether epoxy resin and aliphatic polyamine hardener were supplied by Conchem and used as received.

Preparation of silica particles

Precipitation of silica nanoparticles was obtained by rapid addition of an equimolar mixture of TEOS and alcohol (MeOH or EtOH) to an alcoholic solution of water and NH$_4$OH under vigorous magnetic stirring at a temperature of 40°C for 30 min. The correspondent concentrations of TEOS, water, and NH$_4$OH were 0.25M, 9.5M, and 0.9M, respectively. After complete evaporation of the volatiles (12 h at 100°C), particles with different granulometric size and distribution were obtained depending on the type of alcohol used, according to a procedure reported in literature.[8]

Preparation of nanocomposites

Different mixtures of silica particles and epoxy prepolymer (with a particle content of 1, 3, and 5% by weight) were prepared by mechanical stirring at 26,000 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 specimens having dimensions of 80 × 10 × 4 mm^3. The resins were cured for 2 h at 70°C and postcured for 2 h at 120°C.

Characterization of nanoparticles

X-ray diffraction (XRD) analysis was carried out on a Philips 3710 apparatus.

Elemental analysis was carried out on a Carlo Erba 1110 apparatus.

Transmission electron microscopy (TEM) analysis was carried out with a Jeol JEM 2010 microscope.

To quantitatively estimate the granulometric size and distribution, image analysis was carried out on TEM micrographs by using Image Pro Plus 4.5.1 software equipped with the module Materials Pro.

Surface area and density of the particles were determined by using a B.E.T. Micromeritics–Gemini 2360 instrument and a picnometer Micromeritics–Accupic 1330 instrument, respectively.

Thermogravimetry/differential thermal analysis (TG/DTA) was carried out on a Netzsch–STA 449C Jupiter instrument, and the results were used for the determination of the surface silanol concentration according to a procedure reported in literature.[9]

Characterization of composites

Fracture surfaces of specimens were gold-coated and examined by scanning electron microscopy (SEM) using a Philips XL-40 instrument.

Tensile tests were carried out by using an Instron 4455 instrument according to ASTM 3039/D 3039M-95 standards.

Modeling of the mechanical properties

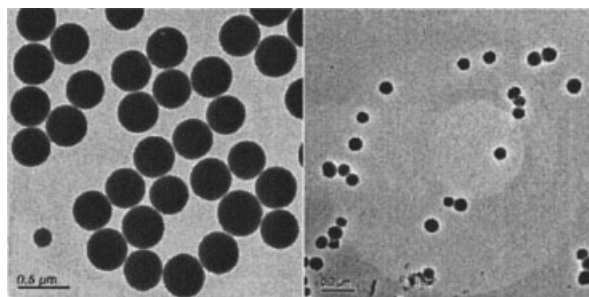To deepen knowledge regarding the mechanical behavior of the nanocomposites, a computational tool

Figure 1 TEM micrographs of silica particles obtained from ethanol (left) and from methanol (right).

TABLE II
Characterization of Silica Particles

Type of particle	Average diameter (nm)	Specific surface area (m^2/g)	Density (g/cm^3)	Silanol groups (mmol/g)
SiO_2 from ethanol	330 ± 80	16.05	1.9505	16.92
SiO_2 from methanol	75 ± 25	76.99	1.9453	4.63

called OOF[10] was used to prepare reliable microstructure-based numerical models.

In fact, OOF is a numerical code able to transform digitized images, such as SEM micrographs, into finite element meshes. The properties of the constituent phases are inserted as input data and attributed properly to the corresponding part of the image. Thus, microstructural relevant features, such as nanoparticle size, shape, weight fraction, and spatial arrangement, can be easily incorporated into the model. Such code has been extensively used to assess microstructure-properties relationships in traditional particulate composites and heterogeneous materials,[11,12] and recently it has been exploited for other nanocomposite systems.[13]

In this work, different microstructures, corresponding to 1, 3, and 5% by weight of particles both from ethanol and from methanol, were analyzed, building up the corresponding numerical grids. In this way, the effect of particle dimension and amount on the overall elastic properties was estimated for each nanocomposite typology.

RESULTS AND DISCUSSION

Characterization of silica nanoparticles

XRD diffractograms (here not reported) of silica particles showed only the presence of a wide band, indicating the completely amorphous nature of both types of particles.

Elemental analysis results are reported in Table I, which evidences a low carbon content (less than 1%), a hydrogen content of about 1.4%, and the complete absence of nitrogen. The residual presence of carbon and hydrogen can be attributed to an incomplete sol-gel reaction of the silica precursor TEOS, which contains organic groups. The higher hydrogen residual content can also be correlated to the presence of silanol groups on the surface of the particles.

TEM micrographs revealed that silica particles were characterized by a spherical shape and a homogeneous size (Fig. 1), and the image analysis showed a monomodal distribution. Particle size, specific surface area, density, and silanol group content are reported in Table II.

According to the results already reported in literature,[14] greater particle sizes were obtained by increasing the number of carbon atoms of the alcohol used for the preparation of the silica.

Characterization of epoxy-based nanocomposites

SEM analysis was carried out on the fracture surface of composites containing 1, 3, and 5 wt % of nanofillers to qualitatively evaluate the particle-matrix interface and evidence the eventual presence of particle aggregations.

In all cases, a good adhesion between silica particles and epoxy matrix was shown, as evidenced by the absence of voids around the particle (see, for example, Fig. 2 for nanocomposites prepared with silica from ethanol; similar micrographs were obtained also for the systems containing silica from methanol). It can be supposed that the presence of silanol groups on the surface of the silica particles (see data reported in Table II) was enough to ensure a good particle-matrix interaction.
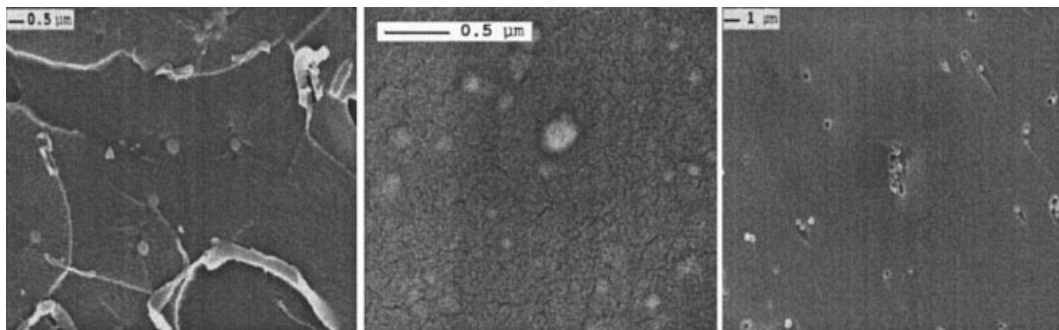

Figure 2 SEM micrographs of fracture surface of epoxy resins reinforced with silica particles from ethanol 1 wt % (left), 3 wt % (middle), and 5 wt % (right).

TABLE III
Experimental and Modeled Elastic Modulus of Epoxy/Silica Nanocomposites

Composite	SiO$_2$ content (wt %)	E (GPa) experimental	Standard deviation (experimental) (GPa)	E (GPa) two-phase model
Unfilled epoxy	—	2.000	0.100	2.000
Epoxy/SiO$_2$ from ethanol	1	2.135	0.149	2.018
	3	2.272	0.181	2.062
	5	2.370	0.123	2.099
Epoxy/SiO$_2$ from methanol	1	2.428	0.065	2.019
	3	2.506	0.147	2.061
	5	2.537	0.202	2.104

The state of dispersion was well satisfying for particle concentration of 1 wt % and 3 wt %. Partial aggregation of particles was shown only in the case of particle content of 5 wt %, for which the conventional mechanical mixing technique was not able to completely break up the agglomerates for reaching a homogeneous dispersion state of the nanoparticles.[15] In this case, a preventive surface treatment of the particle could be useful to obtain complete deagglomeration.

The mechanical properties (elastic moduli experimentally determined and modeled) for the nanocomposites are summarized in Table III.

As expected, a systematic increase of the elastic modulus experimentally determined by tensile tests was obtained by increasing the filler content. It is worth noting that the higher improvements were obtained in the cases of particles with smaller dimensions, that is, for composites containing silica particles prepared from methanol (average diameter of 75 nm).

Modeling of nanocomposite mechanical properties

Finite element meshes, prepared for each nanocomposite typology (1, 3, and 5 wt % of particles, both from ethanol and from methanol), were loaded in uniaxial tension; the composite elastic moduli were calculated from stress-strain curves. The results are plotted in Table III as well, as a function of the particulate content. As can be observed from the Table, the elastic modulus increases with higher amount of reinforcement, but the values predicted by the computational model are considerably lower.

It is worth noting that analytical equations, such as the Halpin–Tsai rule[16] or the Lewis–Nielsen equation,[17] give estimates that are in good agreement with the numerical results, and thus differ from the experimental ones. This means that analytical and numerical approaches commonly used for particulate composite are not suitable when a nanometric phase is involved.

In fact, the formation in nanocomposites of an interphase layer between the polymeric matrix and the inorganic reinforcement has often been reported in literature; such a region has properties that significantly differ from those of the matrix.[18] Since a uniform dispersion of nano-sized particles is able to produce ultra-large interfacial area per volume, it is straightforward that this enormous interfacial region can remarkably affect the composite global performance.

Thus, in this work, more refined models were prepared, taking into account the interphase between the matrix and the particles as a third constituent phase. It was assumed that such an interphase had properties in between the polymeric matrix and the inorganic filler. As regards the dimension of the interphase, it was hypothesized that its extension was proportional to the particle size, as previously reported in literature;[19] in particular, it was set equal to half of the average diameter.

With such characteristics, nanocomposites with fillers both from ethanol and from methanol were modeled, and the respective elastic moduli were evaluated with the same procedure described above. The results are plotted in Figure 3.

As can be seen from the graph, the numerical results are in good agreement with the experimental ones, especially if the error bars are taken into account. Thus, this demonstrates that such a model is able to reproduce the experimentally observed behavior. Therefore, the so-constructed model can be considered a reliable tool for the prediction of elastic properties of epoxy-silica nanocomposites.

However, future developments of the present work should aim at the experimental characterization of the nanocomposite interphase to support the hypotheses of the present work. In particular, the characteristic size and stiffness should be determined. This could be achieved by means of AFM techniques[20] or nanoindentation equipments.[21]

CONCLUSIONS

Epoxy nanocomposites reinforced with nanometric silica particles having two different granulometries were prepared. Such nanocomposites were experi-
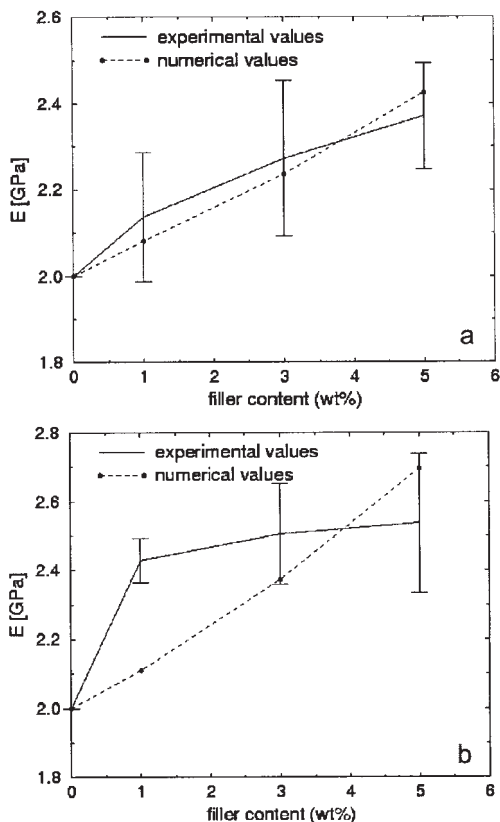
Figure 3 Elastic modulus as a function of filler content (three-phase model): (a) particles from methanol, (b) particles from ethanol.

mentally characterized by means of microscopy and tensile testing.

A numerical model was set to simulate the mechanical behavior of such materials. A three-phase model, which accounted also for the matrix-filler interphase, was adequate to describe the investigated composites.

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