Preparation and Characterization of Organic/Inorganic Hybrid Epoxy Networks from Reactive Inorganic Precursors

Hynek Beneš,[1,2,3] Jocelyne Galy,[1,2] Jean-François Gérard,[1,2] Josef Pleštil,[3] Ludovic Valette[4]

[1]Université de Lyon, F-69361 Lyon, France
[2]CNRS, UMR 5223, Ingénierie des Matériaux Polymères, F-69621 Villeurbanne, France
[3]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic
[4]The Dow Chemical Company, Dow Epoxy R&D, 2301 N. Brazosport Blvd, Freeport, Texas 77541

ABSTRACT: Organic/inorganic hybrid networks were prepared by a novel solvent-free two-step synthesis method. In the first step, prehydrolyzed–condensed reactive inorganic precursors (clusters) were prepared by a sol–gel process from monomeric alkoxysilanes with amino and glycido groups. The second step comprised their addition into epoxy resin and amine hardener, followed by the reaction of all components giving the final hybrid cross-linked materials. Their structure was evaluated by small-angle X-ray scattering, transmission electron microscopy, scanning electron microscopy, and dynamic mechanical and thermal analysis. The morphology of the organic/inorganic hybrid structures formed from glycidoprecursor revealed spherical silica-rich domains forming agglomerates with diameter from 100 to 500 nm. The aminoprecursor led to large highly condensed and branched silicon-rich structures. The organic/inorganic hybrid networks obtained from this precursor consisted of mixed silicon–organic phases covalently interconnected via epoxy–amine bonds. Such hybrid networks showed significantly improved thermomechanical properties and better resistance against thermooxidation when compared with the neat epoxy–amine network. Thin films as well as bulk materials were successfully prepared by this process. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1000–1011, 2012

Key words: sol–gel; epoxy; silica; organic–inorganic materials; hybrid network

INTRODUCTION

Nanostructured materials combining organic and inorganic phases, denoted as hybrid organic–inorganic (O/I) nanomaterials, have recently received much attention in the field of polymer science research as well as in industrial applications. These materials can be designed to combine desirable properties of both phases: toughness of the organic phase and hardness and thermal stability of the inorganic phase, resulting in the overall improvement of the thermal and mechanical properties of materials.

Epoxy resins are broadly used for casting and encapsulation of electronic and electrical devices. To improve the thermal, mechanical, and electrical properties of the epoxy-based material, silica filler (microparticles or nanoparticles) is often added in these applications.[1–13] The incorporation of filler usually increases the viscosity of the formulations, leading to processing limitations. The homogeneous dispersion of the silica filler in the organic matrix may represent another challenge.

An alternative route to incorporate silica into the epoxy-based matrix is the sol–gel process involving hydrolysis and condensation of various types of alkoxysilanes.[14–16] By this process not only silica particles[17] but also silica networks[18] can be prepared. A particular interest of the sol–gel process is the opportunity to control the hybrid O/I nanostructure from the initial mixture of the organic precursors (mainly alkoxysilanes) to the inorganic network. Inorganic (silica) networks with various architectures can be formed.[19] However, a major problem associated with the sol–gel process is the use of solvent, which must be removed from the final network. Relatively high amounts of volatile byproducts such as water and alcohols from the hydrolysis and condensation of alkoxysilanes also have to be removed before the incorporation of the inorganic phase into the formulation. Residual volatile compounds cause significant problems during processing and are responsible for the formation of bubbles or cracks in the final product. As a consequence, only thin materials (membranes and protective coatings) have been developed, whereas bulk materials have hardly been exploited.

It seems to be a recurring challenge to develop a process for the preparation of hybrid O/I materials

via the sol–gel method without the addition of any solvent. This would make possible the preparation of bulk materials with improved thermomechanical properties. Phonthamachai et al.[20] prepared silica/epoxy nanocomposites by solvent-free one-pot synthesis, which comprised simultaneous sol–gel process of alkoxysilanes and a crosslinking of epoxy–amine matrix. Relatively high curing temperature (270°C) was necessary to obtain the homogeneous nanocomposites with oval-shaped silica nanoparticles. Slight improvement in mechanical properties was achieved for the prepared nanocomposites when compared with the corresponding neat epoxy material.

Recently, we have developed a solvent-free sol–gel process, which produced reactive inorganic precursors bearing glycido- or amino-functional groups prepared from monomeric alkoxysilanes.[21] This cost-effective procedure enabled the production of storage-stable precursors in which the majority of alkoxysilane groups were already condensed into Si—O—Si bonds. Such pre-reacted precursors had very low volatile content and were suitable for the conventional manufacturing processes of polymeric materials, for example, casting or encapsulation with epoxy-based formulations. Hybrid O/I materials prepared from these precursors were not only limited to thin films (coating) but were also available as thicker, bulk products. The incorporation of these reactive precursors into an epoxy–amine matrix proved that hybrid O/I materials with better thermomechanical properties than the neat epoxy–amine matrix can be obtained.

The goal of this study was to prepare and characterize O/I hybrid materials based on reactive inorganic precursors and epoxy–amine matrix [diglycidyl ether of bisphenol A and poly(oxypropylene)diamine (POPDA)]. The morphology of the hybrid materials as well as their thermomechanical properties were evaluated by means of small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), dynamic mechanical and thermal analysis (DMTA), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Preparation of reactive inorganic precursors

A detailed study of the preparation of the inorganic precursors has been recently described in a previous article.[21] Two types of inorganic precursors with (i) amino or (ii) glycido groups were prepared.

Preparation of reactive precursor with amino groups

The aminoprecursor was prepared from the mixture of 3-aminopropyltriethoxysilane (APS) and 3-aminopropylmethyldiethoxysilane (APMS) in a molar ratio APS/APMS = 3/1 mol Si—O bonds. The mixture of 150 g APS (97%; ABCR, Karlsruhe, Germany) and 64.8 g APMS (97%; ABCR, Karlsruhe, Germany) was purged with inert gas (nitrogen) saturated by water vapor. The water necessary for the hydrolysis and condensation reactions of alkoxygroups was introduced into a reactor in the gaseous state. The entire sol–gel process was performed under inert atmosphere, and the total amount of water introduced to the system was thoroughly controlled. The saturation of nitrogen with gaseous water took place at 25°C in a bubbler. The outgoing nitrogen contained 16 mg H_2O per dm^3. The reaction mixture was heated to 90°C, and the course of the hydrolysis and condensation reactions was controlled by measuring the viscosity of the reaction mixture. The first sample was collected when the viscosity reached 72 mPa s (measured at 25°C). From the ^{29}Si nuclear magnetic resonance (NMR) results, the conversion of alkoxysilane groups was 63%. The second sample was collected when the viscosity reached 559 mPa s (measured at 25°C). The conversion of alkoxysilane groups determined by ^{29}Si NMR was 85%. Both reactive precursors were stored under argon in a refrigerator before being used for the preparation of O/I hybrid materials.

Preparation of reactive precursor with glycido groups

The glycidoprecursor was prepared from the mixture of 3-glycidoxypropyltriethoxysilane (GPS) and tetraethoxysilane (TEOS) in a ratio of GPS/TEOS = 1/6 mol Si—O bonds. The mixture of 20.2 g TEOS (95%; Sigma-Aldrich, Steinheim, Germany), 6 g GPS (98%; Sigma-Aldrich, Steinheim, Germany), and 0.262 g dibutyltin dilaurate (Sigma-Aldrich, Steinheim, Germany) was allowed to react with water vapor for 70 min in the same reactor setup as described for the preparation of aminoprecursor. At the end of the reaction, the product was stored under argon in a refrigerator before being used for the preparation of O/I hybrid materials.

Preparation of neat epoxy–amine network

The neat epoxy–amine network (no addition of inorganic precursors) was prepared by reacting an epoxy resin (oligomeric 2.2-bis[4-(2′,3′-epoxypropoxy)phenyl]-propane, commonly called DGEBA: diglycidylether of bisphenol A; D.E.R.™ 332, The Dow Chemical Company, West Drayton, Middlesex UB7, UK) with POPDA (JEFFAMINE™ D 230; Hunstman Holland, Rotterdam, The Netherlands). The equivalent weight per functional group (epoxy group in DGEBA and NH group in POPDA) was $E_E = 178$ g mol^{-1} and $E_{NH} = 59.5$ g mol^{-1}, respectively. DGEBA and POPDA were mixed together and homogenized with a disc-shaped mixer (15 min at 2400 rpm). The formulation was degassed under

vacuum at 40°C until no bubbles were visible. Then, it was poured into a preheated aluminum open mold, cured for 2 h at 80°C, and postcured for 12 h at 150°C.

Preparation of organic/inorganic hybrid material

The same raw materials were used for the preparation of the O/I hybrid materials. DGEBA and POPDA were mixed together and the prehydrolyzed–condensed inorganic precursors were added and homogenized with a disc-shaped mixer (15 min at 2400 rpm). The formulations were degassed under vacuum at 40°C until no bubbles were visible. Then, they were poured into a preheated aluminum open mold with different thicknesses—from about 1 mm (samples for dynamic mechanical analysis) up to about 6 mm (samples for fracture toughness measurement), cured for 1.5 h at 65°C followed by 2 h at 80°C and postcured for 12 h at 180°C. A stoichiometric amount of epoxy/NH groups (1/1 mol) was used in all cases. The amino or glycido groups from the inorganic precursors were taken into consideration for the calculation of the epoxy/amino molar ratio.

Small-angle X-ray scattering

SAXS experiments were performed using a pinhole camera (Molecular Metrology SAXS System, Molecular Metrology, Northampton, USA) attached to a microfocused X-ray beam generator (Osmic Micro-Max 002) operating at 45 kV and 0.66 mA (30 W). The camera was equipped with a multiwire, gas-filled area detector with an active area diameter of 20 cm (Gabriel design). Two experimental setups were used to cover the q range of 0.007–1.1 Å^{-1} [$q = (4\pi/\lambda) \sin \theta$, where λ is the wavelength and 2θ is the scattering angle]. The scattering intensities were put on absolute scale using a glassy carbon standard.

Transmission electron microscopy

The samples for TEM were cut as thin layers (60 nm) by means of ultramicrotome (Leica Microsystems, Germany) with a diamond knife. The thin layers were placed between copper grids and observed using a TEM Philips CM 120 (Philips, Japan) with an acceleration voltage of 80 kV.

Scanning electron microscopy

The samples were prepared by cutting the materials under liquid nitrogen. SEM photographs were obtained with an electron microscope Philips XL 20 (Philips, Japan), with an acceleration voltage of 15 kV.

Dynamic mechanical and thermal analysis

DMTA of the cured samples was carried out on Rheometrics Solid Analyzer (RSA II, Rheometrics, Piscataway, USA) operating in tensile mode under the following experimental conditions: sample dimension: about $40 \times 5 \times 1$ mm^3; frequency: 1 Hz; and heating rate 2 K min^{-1}. T_α (temperature of main transition) was determined by the maximum of tan δ peak. The rubbery modulus (E_r') was determined at the rubbery plateau. The typical precision of the measurements was $T_\alpha \pm 2°C$ and $E_r' \pm 5\%$.

Thermogravimetric analysis

TGA was performed on a TA Q500 TGA (TA Instruments, USA). The weight loss was measured under oxidizing atmosphere (air) in a platinum pan using a heating rate of 10 K min^{-1} up to a temperature of 800°C. The thermal stability of the materials and the amount of the inorganic phase were determined from the TGA data.

Tensile measurement

Tensile measurements leading to the determination of Young's modulus E at 25°C were performed with an Instron machine (sample dimension: $6 \times 12 \times 80$ mm^3; straight strain gages, speed: 0.2 mm min^{-1}). The typical precision of the measurements was $E \pm 5\%$.

Fracture toughness test

Fracture toughness K_{Ic} tests were carried out on pre-notched samples (by thin blade) with a MTS-2/M machine (sample dimension: $6 \times 12 \times 80$ mm^3; three-point bending test; speed: 10 mm min^{-1}). The typical precision of the measurements was $K_{Ic} \pm 5\%$.

Thermal aging (thermooxidative test)

Thermal aging (thermooxidative test) was performed at 150°C in a ventilated oven for 500 h. Thin films with two different thicknesses, 30 and 1000 μm, were prepared for the test. The evaluation consisted in the visual inspection of the film after aging (color), the measurement of transmittance at a wave length of 520 nm (Perkin Elmer, USA, UV–vis spectrophotometer Lambda 35), and the evaluation of the thermomechanical properties by DMTA.

RESULTS AND DISCUSSION

Structural characterization of organic/inorganic hybrid networks

The morphology of the prepared O/I hybrid materials was studied by means of SAXS and TEM

methods. The SAXS curves of O/I hybrid materials with different amounts of inorganic (silica) phase prepared from the inorganic reactive precursor with amino groups are given in Figure 1. The SAXS curves of the O/I hybrids with 2.5 and 5.2 wt % of inorganic phase (expressed as equivalent of SiO_2 content: equiv SiO_2) were very similar to each other. In the case of 10.2 wt % equiv SiO_2, a significant increase in intensity due to the higher amount of silica particles was observed. In all cases, the SAXS curves exhibited one maximum at $q = 4.5$, 4.4, and 4.1 nm^{-1} for the samples with 2.5, 5.2, and 10.2 wt % equiv SiO_2, respectively. Spirkova et al.[22] found very similar maximum ($q = 3.3$ nm^{-1}) on the SAXS curve of epoxy–amine (DGEBA/POPDA) hybrids with an inorganic phase prepared via sol–gel of GPS. This maximum was assigned to an ordered O/I two-phase structure. In the current study, the maximum at $q = 4.6$ nm^{-1} was observed on the SAXS curve of neat epoxy–amine network as well (see Fig. 1). This indicated a regular inner structure of the organic phase formed by the relatively short chains of DGEBA and POPDA. In comparison with the neat epoxy–amine network, the maxima of the SAXS curves of the O/I hybrids shifted to larger particles dimension. It could be caused not only by the formation of an ordered O/I two-phase structure but also by an increased scattering intensity in the middle SAXS region ($q \approx 1$ nm^{-1}) overlapping with the maximum of neat epoxy–amine matrix. Scattering intensity was shifted to higher levels with no peaks developing in the middle SAXS region of the O/I hybrid materials, which was caused by the local
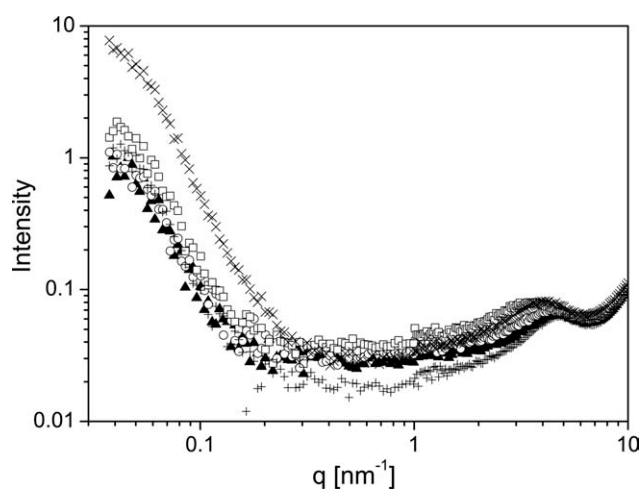
Figure 2 SAXS curves of neat epoxy–amine network (■) and organic/inorganic hybrid materials containing 10.2 wt % equiv SiO_2 prepared from reactive inorganic precursors with amino (x) and glycido (○) groups.

fluctuations of scattering length density indicating a heterogeneous system without the presence of a homogeneous fraction of regular particles with dimension of about 0.5–5 nm. The importance of the first synthetic step (sol–gel) to the final morphology can be observed from the comparison of SAXS curves of O/I hybrids with 10.2 wt % equiv SiO_2 prepared from the prehydrolyzed–condensed aminoprecursors with conversion of alkoxysilane groups of 63 and 85%. At 63% conversion, the intensity in the middle SAXS region was shifted to higher level, indicating the presence of small particles. At 85% conversion, the scattering intensity was lowered in this region, and on the contrary, the SAXS intensity at lower q (≈ 0.1 nm^{-1}) was shifted to higher level, which indicated the connection of the small particles into larger objects.

The SAXS curves of two O/I hybrid materials with 10.2 wt % equiv SiO_2 prepared from inorganic precursors containing amino and glycido groups, respectively, are compared in Figure 2. The SAXS curve of the material based on glycidoprecursor exhibited a slower decrease of scattering intensity due to the higher amount of smaller particles with dimension of about 1–10 nm.

The TEM images of the O/I hybrid based on glycidoprecursor, as shown in Figure 3(B,C), confirmed that the material contained spherical silica-rich domains and some agglomerates (dark areas on the TEM images) with diameters ranging from 100 to 500 nm in size. These domains consisted of smaller silica particles (with diameter below 10 nm), which were also detected by SAXS. The interface between the silica-rich domains or the agglomerates and the epoxy–amine matrix was not sharp but diffused. It indicated that interconnections between the two phases existed. When comparing the amount of

Figure 1 SAXS curves of neat epoxy–amine (+) and organic/inorganic hybrid networks containing (i) 10.2 wt % equiv SiO_2 prepared from reactive inorganic precursor with amino groups having alkoxysilane conversion of 63% (□) or containing (ii) 2.5 (▲), 5.2 (○), and 10.2 (×) wt % equiv SiO_2 prepared from reactive inorganic precursor with amino groups having alkoxysilane conversion of 85%.
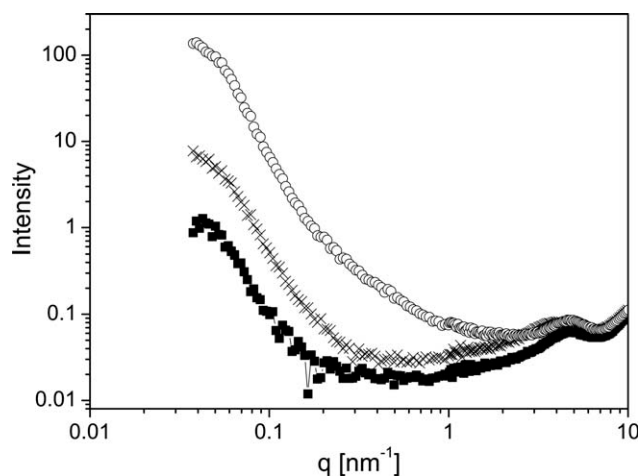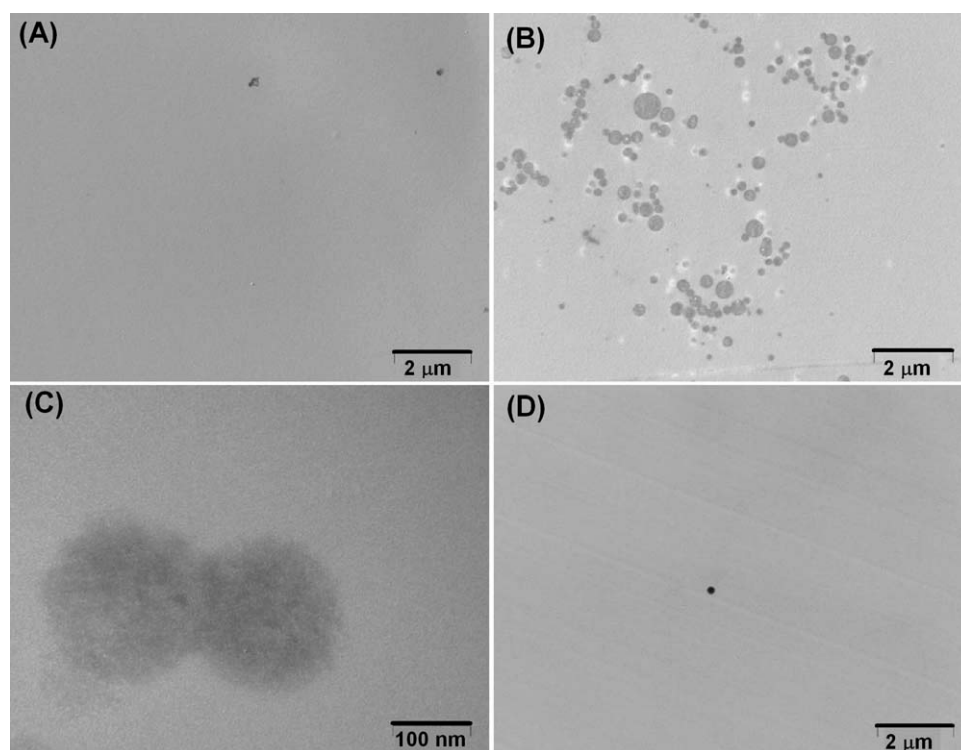
Figure 3 TEM images of neat epoxy–amine (A) and organic/inorganic hybrid materials with 10.2 wt % equiv SiO$_2$ prepared from reactive inorganic precursors with glycido (B and C) and amino (D) groups.

inorganic phase with the area of dark regions in the TEM images, it was concluded that the dispersed domains were formed by a mixture of epoxy–amine and silica phases. Because of the presence of agglomerates, with size ranging from hundreds of nanometers up to micrometers, the hybrid material was not transparent.

The morphology of the O/I hybrids with aminoprecursor showed a much less distinct contrast, which made it difficult to image by TEM [Fig. 3(D)]. In comparison with the TEM image of neat epoxy–amine matrix, it seemed that the size of the silica domains approached the resolution limits of the TEM technique. The same phenomenon was described by Bauer et al.[23] on a similar O/I network based on DGEBA and a mixture of POPDA with different molecular weights (JEFFAMINE^{TM} D 2000, D 400, and D 230), in which silica phase was prepared by simultaneous (*in situ*) polymerization of TEOS. The size of the silica domains was estimated to be 10 nm or less; however, the precise size determination was difficult because the interface was too diffuse. In the current study, the inorganic silicon-rich phase created from aminoprecursor was very well dispersed in and mixed with the epoxy–amine matrix.[24,25] Kaddami et al.[26] reported similar results for a system prepared with poly(2-hydroxyethyl methacrylate) and TEOS. The black dot (with dimension of about 200 nm) on the TEM image of the O/I hybrid with aminoprecursor [Fig. 3(D)] could be due

to a contaminant [similar ones were observed in the neat epoxy–amine matrix; see Fig. 3(A)] or possibly an aggregated silica domain.

The SEM images of fracture surfaces of the O/I hybrids with 10.2 wt % equiv SiO$_2$ derived from the glycidoprecursor and the aminoprecursor are compared in Figure 4. The SEM of the former clearly revealed a rough fracture surface with sharp semi-round cracks at the interface between the spherical silica-rich domains (size about 1 μm) and the surrounded epoxy–amine matrix. The SEM results correlated well with the TEM images. On the contrary, the SEM fracture image of the latter did not indicate any phase interface. This confirmed that the inorganic and organic phases were compatibilized through covalent connections (epoxy–amine bonds). Based on the SEM results, we could exclude the presence of larger silica particles, which were not detectable via the TEM technique either. The silica domains had to be present in the epoxy–amine matrix in a form which was different than in the case of the O/I hybrids derived from the glycidoprecursor. Both O/I hybrids contained the same amount of equivalents of SiO$_2$. The inorganic phase originating from the glycidoprecursor was prepared by the sol–gel process of the mixture of GPS and TEOS. The formed silica-rich domains had a spherical particle-like morphology. The silica structures formed from the aminoprecursor by the sol–gel of APMS/APS mixture had a more branched chain-like architecture.
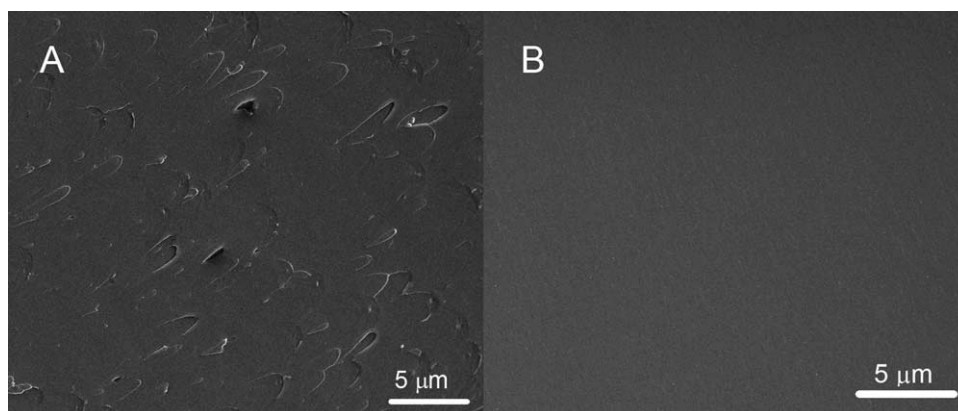
Figure 4 SEM images of organic/inorganic hybrid materials with 10.2 wt % equiv SiO_2 prepared from reactive inorganic precursors with glycido (A) and amino (B) groups.

It correlated well with the results of SAXS measurements performed on the dispersion of prehydrolyzed–condensed reactive inorganic precursors published in our previous work.[21] The SAXS results of the neat aminoprecursor dispersions indicated the presence of larger structures, which did not exhibit typical particle-like behavior and whose size was dependent on the concentration.

Thermomechanical properties of organic/inorganic hybrid networks

The DMTA curves of the O/I hybrids prepared from the reactive inorganic precursor with amino groups containing different amounts of inorganic phase are shown in Figure 5. The incorporation of silica into the organic epoxy–amine network increased the modulus in rubbery state (E_r') of the final O/I hybrid materials and shifted the main thermomechanical transition region to higher temperature. Higher silica content also caused a broadening of the main transition (α relaxation) when compared with the neat epoxy–amine network. The DMTA results supported the above conclusion on the morphology of the hybrid materials, with mixed epoxy–amine and silica-rich phases.

In the beginning of the crosslinking stage, the epoxy oligomer, the amine hardener, and the prehydrolyzed–condensed inorganic precursor coexisted in the reactive formulation. The inorganic precursor still contained about 15% of unreacted ethoxysilane groups. Therefore, a distribution of highly and slightly condensed silicone structures was present in the system. In our previous work, we found that around 9% of uncondensed ethoxysilane bonds came from the monomeric alkoxysilanes (APS and APMS) in the prehydrolyzed–condensed inorganic amino precursor.[21] During the final crosslinking stage, the polycondensation of the uncondensed ethoxysilane structures and simultaneously the step polymerization of the organic phase (epoxy–amine reaction) took

place. At the same time, the amino groups of the inorganic precursor reacted with the epoxy groups of DGEBA, leading to the creation of covalent bonds between the organic and inorganic phases. With increasing amount of inorganic precursor in the reactive system, the proportion of O/I interphase became larger. As a result, an interconnected network structure with higher crosslinking density and improved thermomechanical properties (higher T_α and E_r') was formed. The well-dispersed and more condensed structures from the aminoprecursor formed an inorganic silica network (SiO_X) having connections with the epoxy–amine network via covalent bonds. The aminoprecursor acted as a cohardener for the epoxy groups. The noncondensed alkoxysilanes that were also present in the aminoprecursor could conversely reduce the crosslinking density. If one molecule of aminoprecursor was not connected to another molecule of aminoprecursor (i.e., its functionality was less
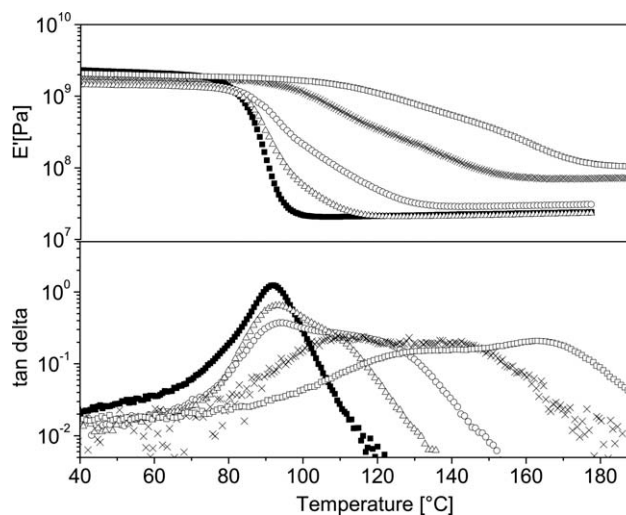

Figure 5 Dynamic mechanical spectra ($f = 1$ Hz) of neat epoxy–POPDA network (■) and organic/inorganic hybrid materials with 2.5 (Δ), 5.2 ($\bigcirc$), 10.2 (x), and 12.8 ($\square$) wt % equiv SiO_2 prepared from reactive inorganic precursor with amino groups.

TABLE I
Composition of the Neat Epoxy–POPDA Formulation (0 wt % equiv SiO$_2$) and Organic/Inorganic Hybrid Materials (2.5, 5.2, 10.2, and 12.8 wt % equiv SiO$_2$) Expressed as Molar Ratio of Primary Amino Groups (NH$_2$) from POPDA and Aminoprecursor and Their Influence on Rubbery Modulus (E_r', determined from DMTA, f = 1 Hz)

Equivalent of SiO$_2$ (wt %)	NH$_2$ (POPDA)/NH$_2$ (aminoprecursor) (mol %)	E_r' (MPa)
0	100/0	23.8
2.5	80/20	22.8
5.2	59/41	30.3
10.2	20/80	70.6
12.8	0/100	103.4

than or equal to two), only chain extension occurred instead of additional crosslinking. This was the case when reactive inorganic precursors with low content of highly condensed silica species were added. Therefore, the first step of the O/I hybrid synthesis (hydrolysis and condensation of alkoxysilanes) had to be performed for a sufficiently long time.[21] Before admixing of the aminoprecursor into reactive epoxy–amine system, ideally all alkoxysilane molecules should contain at least one condensed alkoxysilane bond. The condensed Si—O—Si bonds connecting several alkoxysilane molecules enabled the formation of high functional inorganic structures and additional crosslinking.

The final hybrid network was crosslinked via epoxy–amine bonds with two amino hardeners: POPDA and the aminoprecursor. The relationship between the composition of the O/I hybrid materials expressed as the ratio of primary amino groups originating from POPDA or the aminoprecursor and their rubbery modulus (E_r') is given in Table I. The influence of the ratio of POPDA versus aminoprecursor on the thermomechanical properties of the final O/I hybrid materials was evident. The addition of 2.5 wt % equiv SiO$_2$ did not influence the rubbery modulus (E_r') of the O/I hybrid material (Table I), whereas a minor broadening of the main transition was observed (Fig. 5). The material exhibited a single tan δ peak at 93°C, close to the neat epoxy–POPDA matrix (92°C) and a small shoulder at about 110°C. The network structure was mainly formed by DGEBA–POPDA bonds. The inorganic silica phase formed a minor part of the network, in which only around 20 mol % of epoxy groups were bonded to the aminoprecursor. The increase in the amount of the inorganic part to 5.2 wt % equiv SiO$_2$ significantly increased E_r'. The silica-based network was more interconnected to the DGEBA–POPDA organic network via the NH$_2$ groups of the aminoprecursor (41 mol %). Tan δ showed a broad maximum at 94°C and a large, high-amplitude shoulder at around 120°C. The addition of 10.2 wt % equiv SiO$_2$ in the

O/I hybrids led to a large increase of E_r' (about 200% increase when compared with the neat epoxy–POPDA matrix) and a significant shift of the main thermomechanical transition to higher temperature. Two broad peaks were observed on tan δ curve at 109 and 143°C. These two maxima indicated a shift of the network structure when compared with the networks containing lower amounts of aminoprecursor. The inorganic silica from the aminoprecursor was highly chemically interconnected to the DGEBA–POPDA matrix. The highest amount of silica was limited to 12.8 wt % equiv SiO$_2$ due to the stoichiometry of amino and epoxy groups. This formulation did not contain POPDA, and therefore, all epoxy–amino bonds originated from DGEBA–aminoprecursor. A completely new network was formed that exhibited an inorganic-like rigid network character. The material was extremely hard but brittle.

The DMTA curves of the O/I hybrid materials with 10.2 wt % equiv SiO$_2$ prepared from the reactive inorganic precursors with amino and glycido groups are compared in Figure 6. The silica domains from the glycidoprecursor increased the overall crosslinking density of the network, significantly increasing E_r'. The main thermomechanical transition was shifted to higher temperature (T_α = 109°C), with a slight broadening of the tan δ peak when compared with the neat epoxy–POPDA network. The inorganic structure formed by the sol–gel process of GPS/TEOS mixture had particle-like character, as proved by SEM, TEM, and SAXS techniques. Therefore, it had a similar effect on thermomechanical behavior to commonly used silica fillers.[27]
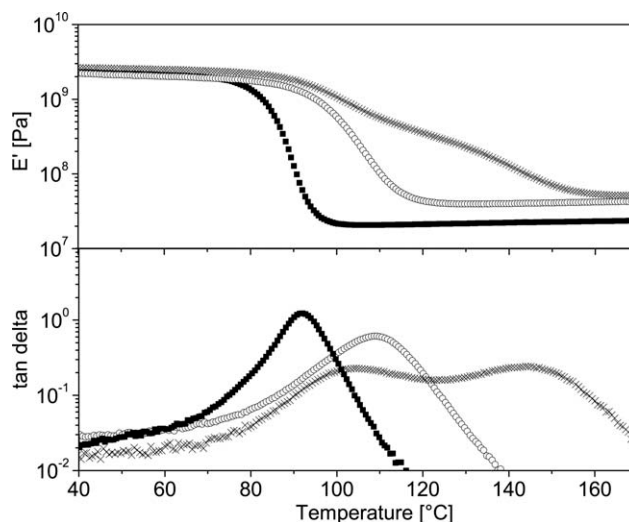

Figure 6 Dynamic mechanical spectra (f = 1 Hz) of neat epoxy–POPDA network (■) and organic/inorganic hybrid materials with 10.2 wt % equiv SiO$_2$ prepared from reactive inorganic precursors with glycido (○) and amino (x) groups.
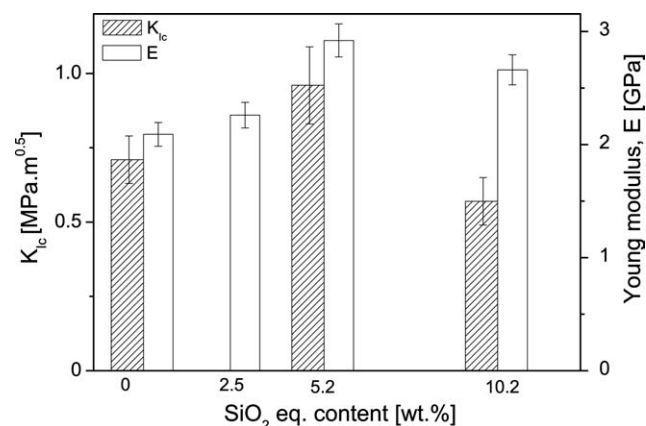
Figure 7 Fracture toughness (K_{Ic}) and Young's modulus (E) of neat epoxy–POPDA network (0 wt % equiv SiO$_2$) and organic/inorganic hybrid materials prepared from reactive inorganic precursor with amino groups containing 2.5, 5.2, and 10.2 wt % equiv SiO$_2$.

Tensile measurements and fracture toughness of organic/inorganic hybrid networks

It is known from the literature that the incorporation of silica structures into an epoxy-based matrix can lead to improved thermomechanical properties such as increased Young's modulus (E) and higher T_α.[25,27,28] Very often, the incorporation of hard domains of silica into an epoxy-based matrix leads to the formation of "inorganic-like" material, in which the main thermomechanical transition almost disappears due to little conformation changes. Such a material tends to be very hard, thermally stable with high E, and very brittle with limited toughness.[29–31]

We performed tensile measurements and fracture toughness tests on the O/I hybrid materials based on the aminoprecursor to determine E and K_{Ic}, respectively. The results of the tests given in Figure 7 showed that the incorporation of the reactive inorganic precursor with amino groups into the epoxy–POPDA formulation could improve the balance of thermomechanical properties. The silica phase significantly increased the Young's modulus when compared with the neat epoxy–POPDA matrix. The O/I hybrid material containing 5.2 wt % equiv SiO$_2$ exhibited an unusual combination of higher modulus (E and E'_r) and toughness (K_{Ic}) with respect to the neat epoxy–POPDA matrix. It meant that a stiffer yet tougher material was obtained with a slight shift of the thermomechanical transition toward higher temperature. The higher content of inorganic phase (10.2 wt % equiv SiO$_2$) led to the production of a O/I hybrid material with significantly increased modulus and T_α while maintaining an acceptable fracture toughness. The fracture toughness was similar to the neat epoxy–POPDA matrix, but slightly lower than in the case of the O/I hybrid with 5.2 wt % equiv SiO$_2$.

A number of toughening mechanisms of epoxy–silica nanocomposites were proposed in the literature.[32–35] Generally, the effect of the toughening mechanism depends on (i) size, morphology and volume fraction of reinforcement, (ii) interfacial bond, (iii) properties of the matrix (e.g., crosslinking density) and reinforcement, and (iv) phase transformations. In our case of the O/I hybrids with aminoprecursor, the exact toughening mechanism was difficult to evaluate due to complex structure (broad distribution of shape and size) of the inorganic phase. Moreover, with increasing amount of the inorganic phase, the matrix morphology was changing substantially. At low concentrations of the aminoprecursor (2.5 and 5.2 wt % equiv SiO$_2$), the inorganic phase was dispersed in the form of branched silica–silicone structures in the organic matrix (DGEBA–POPDA). Very good compatibility between the organic and the inorganic phases was provided via covalent and hydrogen bonding of aminoprecursor with DGEBA–POPDA matrix. The covalent linkage between the aminoprecursor and DGEBA began to be dominant at higher amounts of the inorganic phase, for example, in the case of 10.2 wt % equiv SiO$_2$, which resulted in the formation of new matrix consisting uniquely of a mixed O/I phase (see later). Only minor presence of "flexible" POPDA chains (see Table I) probably caused that the resulting network had lower ability to absorb energy due to reduced network expansion, which caused lowering of the fracture toughness of this hybrid.[36]

TGA of organic/inorganic hybrid networks

TGA in air demonstrated that the hybrid materials exhibited an improved thermal stability at the beginning of the thermal degradation ($T = 300–350°C$). The thermal decomposition temperature measured at 10% weight loss (T_{d10}) increased with increasing amount of inorganic phase in the O/I hybrid material, from 356°C for the neat epoxy–amine network up to 381°C for 12.8 wt % equiv SiO$_2$ content (Table II). The final amount of solid residues after complete thermal degradation in air (pyrolysis) correlated well with the theoretical silica content. The theoretical content of silica was slightly higher than the experimental results (about 15% deviation). The theoretical calculation was derived from an ideal case, assuming that all Si—OC$_2$H$_5$ bonds condensed to the —Si—O— network structure. In reality, the silica network contained defects. As discussed above, a certain amount of unreacted Si—OC$_2$H$_5$ bonds was still present in the aminoprecursor before the final crosslinking stage. The presence of silanol groups (Si—OH) in the material could not be excluded either. These uncondensed structures could form volatile silicon compounds during final crosslinking

Thermal Decomposition Temperature Measured at 10% Weight Loss (T_{d10}), Calculated (Theoretical) Amount of SiO_X Content, and Weight Percentage of Solid Residues After TGA Measurement (in Air) of Neat Epoxy–Amine (0 wt % equiv SiO_2) and Organic/Inorganic Hybrid Materials Containing 2.5, 5.2, 10.2, and 12.8 wt % equiv SiO_2

Equivalent of SiO_2 (wt %)	T_{d10} (°C)	Calculated (theoretical) amount of SiO_X (wt %)	Solid residues from TGA (wt %)
0	356	0	0
2.5	365	2.1	1.6
5.2	368	4.3	3.3
10.2	372	8.4	7.4
12.8	381	10.6	9.0

stage and thus reduce the experimental determination of silica content. A small amount of residual ethanol (about 1–2 mol %) could also be present in the aminoprecursor as byproduct of the sol–gel process, which would add to the overall weight loss during curing.

Thermooxidation of organic/inorganic hybrid networks

The neat epoxy–amine network based on DGEBA–POPDA did not exhibit good resistance against oxidation. The results of the aging tests showed that the addition of the inorganic precursor with amino groups could improve the thermooxidative resistance of the material (Table III). The discoloration of the O/I hybrid materials was significantly reduced in comparison with the neat epoxy–amine network. The transmittance at 520 nm of the neat epoxy–amine material was already reduced to 0% after 250 h
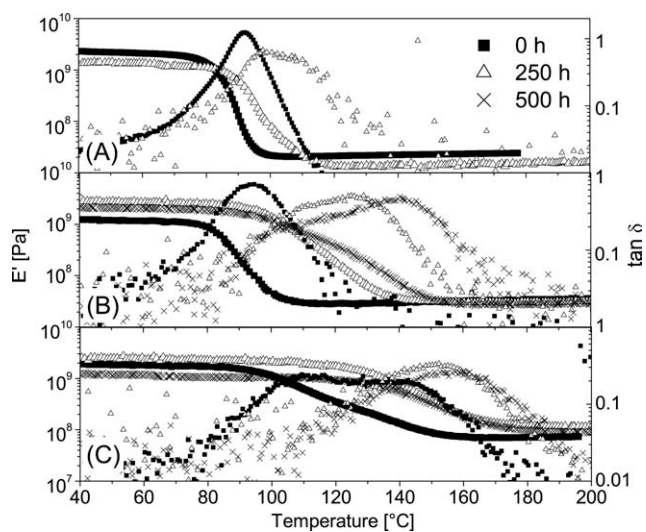

Figure 8 Dynamic mechanical spectra ($f = 1$ Hz) of (A) neat epoxy–amine and organic/inorganic hybrid materials prepared from inorganic precursor with amino groups containing (B) 5.2 and (C) 10.2 wt % equiv SiO_2 thermally aged at 150°C in air for 0 (■), 250 (Δ), and 500 h (x).

of exposure, whereas the O/I hybrid material with 5.2 wt % equiv SiO_2 still had a transmittance of more than 30% even after 500 h. The dynamic mechanical spectra of the samples before aging and after 250 and 500 h of exposure are given in Figure 8. The DMTA spectrum of the neat epoxy–amine network after 250 h of aging showed a slight increase of T_α but a significant reduction of E_r', indicating an overall degradation of the material. After 500 h of exposure, the neat epoxy–amine material was so brittle that DMTA measurement could not be done. The presence of the inorganic aminoprecursor prevented the network decomposition. Surprisingly, the thermomechanical properties (evaluated by DMTA) of the O/I hybrid materials during the aging were

TABLE III
Results of Thermal Aging (Thermooxidative Test) of Neat Epoxy–Amine (0 wt % equiv SiO_2) and Organic/Inorganic Hybrid Materials Prepared from Inorganic Precursor with Amino Groups Containing 2.5, 5.2, 10.2, and 12.8 wt % equiv SiO_2

	Equivalent of SiO_2 (wt %)				
	0	2.5	5.2	10.2	12.8
0 h at 150°C					
Visual appearance	Clear, transparent	Clear, transparent	Clear, transparent	Clear, transparent	Clear, transparent
Transmittance at 520 nm (%)	70	70	67	68	70
250 h at 150°C					
Visual appearance	Black	Brown	Light brown	Light brown	Light brown
Transmittance at 520 nm (%)	0	0	37	28	23
500 h at 150°C					
Visual appearance	Black	Black	Light brown	Light brown	Light brown
Transmittance at 520 nm (%)	0	0	34	22	17

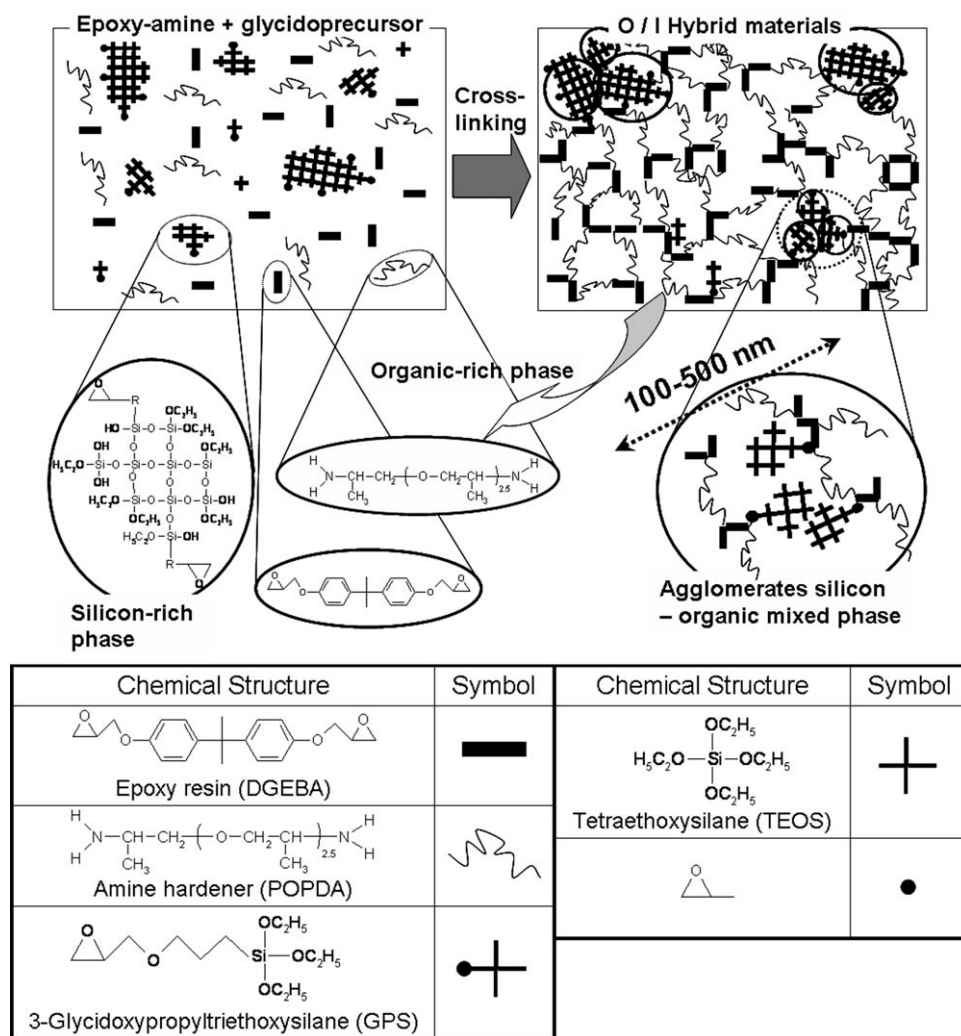Test conditions: 150°C in air; aging time = 0, 250, and 500 h.

Figure 9 Schematic morphology of the organic/inorganic hybrid material based on inorganic precursor with glycido groups (GPS/TEOS = 1/6 mol Si—O bonds) and epoxy–amine (DGEBA–POPDA) matrix.

even further improved. The O/I hybrid materials with 5.2 and 10.2 wt % equiv SiO$_2$ exhibited a significant shift of the main thermomechanical transition to higher temperature during the first 250 h of the thermooxidation test. No significant increase of E'_r was observed, indicating that the maximum epoxy–amine conversion was already achieved after 12 h of postcuring at 180°C. The silica part of the hybrid network could still contain partially condensed alkoxysilane structures. Uncondensed Si—OC$_2$H$_5$ and silanol (Si—OH) groups could be present within the silica network. During the additional thermal treatment, they could condense to Si—O—Si bonds. The conformational changes of the inorganic network would not cause a significant increase of the overall crosslinking density and E'_r of the O/I material, but could significantly shift T_α to higher temperature due to the improved structure of the rigid thermally stable silica network. This phenomenon was consistent with the above discussed concept of interconnected mixed

structure of the O/I hybrids based on the aminoprecursor. During thermal aging, a more homogeneous interconnected organic–inorganic structure was created in the O/I hybrid material with 10.2 wt % equiv SiO$_2$ as indicated by the DMTA spectra of tan δ curves. The two peaks observed on tan δ before aging turned into a single broad peak with a maximum shifted to higher temperature.

Proposed structure of organic/inorganic hybrid networks

Based on the analysis of the SAXS, TEM, SEM, and DMTA results, two schematic morphological structures for the O/I hybrid networks based on the glycidoprecursor and the aminoprecursor were proposed. In the case of the O/I hybrid network with the glycidoprecursor based on GPS and TEOS, the material contained spherical silica-rich domains and some agglomerates with diameters from 100 to 500 nm.
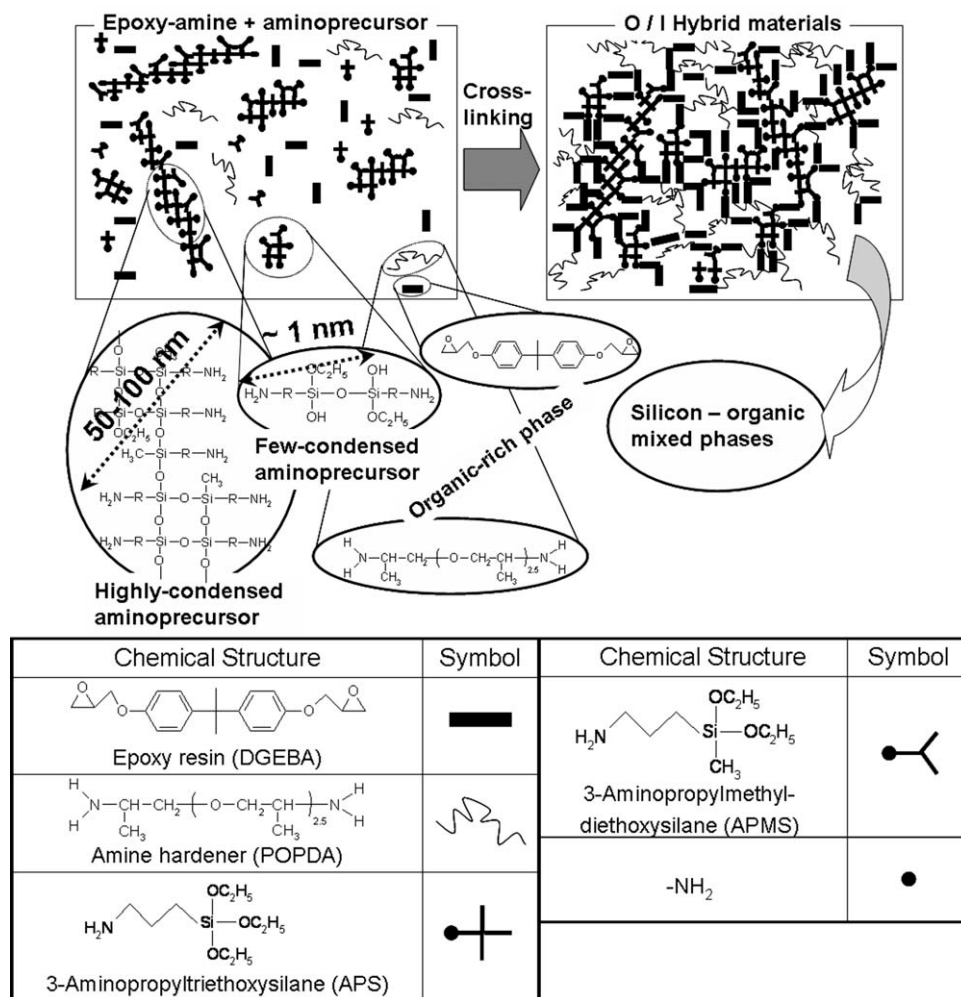
Figure 10 Schematic morphology of the organic/inorganic hybrid material based on inorganic precursor with amino groups (APS/APMS = 3/1 mol Si—O bonds) and epoxy–amine (DGEBA–POPDA) matrix.

They consisted in smaller silica domains (<10 nm) with a diffused interphase with the epoxy–amine matrix. The silica domains were covalently connected via epoxy–amine bonds between GPS and POPDA. The structure is schematically shown in Figure 9.

The prehydrolyzed–condensed aminoprecursor based on APS and APMS contained a majority of large highly condensed silicon-rich structures and some lightly or noncondensed species of APS and APMS, which acted as "diluents." The silica structures had a branched chain-like architecture. The condensed silicon structures were well dispersed into the epoxy–amine formulation during the crosslinking of O/I hybrid network and formed strong covalent connections with the epoxy–amine network. The resulting O/I hybrid network consisted in an interconnected network of mixed silicon and organic phases (Fig. 10).

CONCLUSIONS

Reactive inorganic precursors with amino and glycido groups prepared according to a newly developed

solvent-free synthesis method were incorporated into O/I hybrid crosslinked materials based on a epoxy–amine organic matrix. The structures of the prepared O/I hybrids were studied by various techniques and morphological models of the formed hybrid networks were proposed. Depending on the type of reactive inorganic precursor, two different O/I hybrid structures can be obtained. The O/I hybrid network obtained with the glycidoprecursor contained spherical silica-rich domains and some agglomerates with diameters from 100 to 500 nm. The final material was not transparent, and the thermomechanical properties were only marginally improved. The reactive aminoprecursor produced large highly condensed and branched silicon-rich structures, which were well dispersed in and covalently bonded to the epoxy–amine matrix. Their final O/I hybrid networks were transparent. The thermomechanical properties and the resistance against thermooxidation were significantly enhanced.

It was concluded that the reactive inorganic precursor with amino groups based on APS and APMS

were promising for the preparation of O/I hybrid crosslinked materials. These materials could eventually replace or complement conventional epoxy-based formulations for electrical insulation or electronical encapsulation. The new two-stage synthesis method overcame the problem of the conventional sol–gel processes (evolution of volatile byproducts and solvents). It enabled the preparation of thick, bulk materials. Because of the incorporation of silica structures into the epoxy–amine matrix, the O/I hybrid networks exhibited higher modulus, the main thermomechanical transition shifted toward higher temperature, and improved thermooxidative stability.

References

1. Lee, A.; Lichtenhan, J. D. J Appl Polym Sci 1999, 73, 1993.
2. Chen, J. P.; Ahmad, Z.; Wang, S. H.; Mark, J. E.; Arnold, F. E. In Hybrid Organic-Inorganic Composites; Mark, J. E.; Lee, C. Y.-C.; Bianconi, P. A., Eds.; ACS Symposium Series 585; American Chemical Society: Washington, DC, 1995, p 297.
3. Lan, T.; Pinnavaia, T. J. Chem Mater 1994, 6, 2216.
4. Wang, Z.; Massam, J.; Pinnavaia, T. J. In Polymer–Clay Nanocomposites; Pinnavaia, T. J.; Beall, G. W., Eds.; Wiley: New York, 2001, p 127.
5. Liu, Y. L.; Hsu, C. Y.; Wei, W. L.; Jeng, R. J. Polymer 2003, 44, 5159.
6. Liu, Y. L.; Wei, W. L.; Hsu, K. Y.; Ho, W. H. Thermochim Acta 2004, 412, 139.
7. Preghenella, M.; Pegoretti, A.; Migliaresi, C. Polymer 2005, 46, 12065.
8. Kwon, S. C.; Adachi, T.; Araki, W.; Yamaji, A. Acta Mater 2006, 54, 3369.
9. Zhang, H.; Zhang, Z.; Friedrich, K.; Eger, C. Acta Mater 2006, 54, 1833.
10. Han, J. T.; Cho, K. Macromol Mater Eng 2005, 290, 1184.
11. Yuan, J.; Zhou, S.; Gu, G.; Wu, L. J Mater Sci 2005, 40, 3927.
12. Han, J. T.; Cho, K. J Mater Sci 2006, 41, 4239.
13. Roy, M.; Nelson, J. K.; MacCrone, R. K.; Schadler, L. S.; Reed, C. W.; Keefe, R. IEEE Trans Dielectr Electr Insul 2005, 12, 629.
14. Nazir, T.; Afzal, A.; Siddiqi, H. M.; Ahmad, Z.; Dumon, M. Prog Org Coat 2010, 69, 100.
15. Davis, S. R.; Brough, A. R.; Atkinson, A. J Non-Cryst Solids 2003, 315, 197.
16. Matejka, L.; Dukh, O.; Kolarik, J. Polymer 2000, 41, 1449.
17. Brinker, J. C.; Scherer, G. W. Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing; Academic Press: New York, 1990.
18. Mascia, L.; Prezzi, L.; Haworth, B. J Mater Sci 2006, 41, 1145.
19. Kickelbick, G. Prog Polym Sci 2003, 28, 83.
20. Phonthamachai, N.; Chia, H.; Li, X.; Wang, F.; Tjiu, W. W.; He, C. Polymer 2010, 51, 5377.
21. Benes, H.; Galy, J.; Gerard, J. F.; Plestil, J.; Valette, L. J Sol–Gel Sci Technol 2011, 59, 598.
22. Spirkova, M.; Brus, J.; Hlavata, D.; Kamisova, H.; Matejka, L.; Strachota, A. J Appl Polym Sci 2004, 92, 937.
23. Bauer, B. J.; Liu, D. W.; Jackson, C. L.; Barnes, J. D. Polym Adv Technol 1996, 7, 333.
24. Hajji, P.; David, L.; Gerard, J. F.; Pascault, J. P.; Vigier, G. J Polym Sci Part B: Polym Phys 1999, 37, 3172.
25. Landry, C. J. T.; Coltrain, B. K.; Landry, M. R.; Fitzgerald, J. J.; Long, V. K. Macromolecules 1993, 26, 3702.
26. Kaddami, H. PhD Thesis, INSA, Lyon, France, 1999.
27. Bugnicourt, E.; Galy, J.; Gerard, J. F.; Barthel, H. Polymer 2007, 48, 1596.
28. Fitzgerald, J. J.; Landry, C. J. T.; Pochan, J. M. Macromolecules 1992, 25, 3715.
29. Landry, C. H. J. T.; Coltrain, B. K. J Macromol Sci Pure Appl Chem 1994, 31, 1965.
30. Goda, H.; Higashino, T. U.S. Pat.6525160 (2003).
31. Takahashi, A.; Sastu, Y.; Nagai, A.; Umino, M.; Nakamura, Y. IEEE Trans Electron Packag Manuf 2005, 28, 163.
32. Ma, J.; Mo, M. S.; Du, X. S.; Rosso, P.; Friedrich, K.; Kuan, H. C. Polymer 2008, 49, 3510.
33. Rosso, P.; Ye, L.; Friedrich, K.; Sprenger, S. J Appl Polym Sci 2006, 100, 1849.
34. Zhang, H.; Tang, L. C.; Zhang, Z.; Friedrich, K.; Sprenger, S. Polymer 2008, 49, 3816.
35. Liang, Y. L.; Pearson, R. A. Polymer 2009, 50, 4895.
36. Walter, H.; Bierogel, C.; Grellmann, W.; Fedtke, M.; Michel, B. In Deformation and Fracture Behaviour of Polymers, Grellmann, W.; Seidler, S., Eds., Springer: Berlin, 2001, p 519.