

High- T_g , Heat Resistant Epoxy-Silica Hybrids with a Low Content of Silica Generated by Nonaqueous Sol-Gel Process

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ABSTRACT: The epoxy-silica hybrids showing high T_g and thermal stability are prepared by the non-aqueous sol-gel process initiated with borontrifluoride monoethylamine. Tetramethoxysilane (TMOS) is used as a precursor of silica and 3-glycidyoxypropyl trimethoxysilane as a coupling agent to strengthen the interphase interaction with an epoxy matrix. The basic factors governing the non-aqueous sol-gel process are studied in order to reveal the formation-structure-properties relationships and to optimize the hybrid composition as well as conditions of the nonaqueous synthesis. The formation of the hybrid, its structure, thermomechanical properties and thermal stability are followed by chemorheology experiments, NMR, DMA and TGA. The most efficient reinforcement of the epoxy network is achieved by the combination of both alkoxysilanes, showing synergy effects. The hybrids with a low content (~10 wt %) of the *in situ* generated silica exhibit dramatic increase in T_g and the high modulus, 335 MPa, up to the temperature 300°C. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40899.

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INTRODUCTION

Organic-inorganic nanocomposites have drawn a considerable attention in polymer science in last decades. Among the organic matrices the epoxy thermosets are most widely used due to excellent mechanical and thermal properties. Epoxy resin based organic-inorganic hybrid materials can be employed as tough, transparent and anti-scratch polymer films with good mechanical properties and thermal stability. As to the inorganic filler, silica tends to be the most suitable for epoxy resins. The epoxy-silica nanocomposites are often applied systems and their curing behavior, morphology, mechanical and thermal properties are well investigated.¹⁻⁴ Homogeneous dispersion of silica nanoparticles in an epoxy medium, however, brings about crucial synthetic problems. Therefore, silica generated *in situ* by a sol-gel technique has gained a reputation to be a convenient and cost-effective method.⁵ The sol-gel process is used for the preparation of epoxy-silica nanocomposites of good homogeneity and improved properties.⁶⁻¹³ Synthesis and properties of polymer-silica hybrids, prepared both from preformed silica and by the sol-gel process, have been recently reviewed by Zou et al.¹⁴

Epoxy-silica nanocomposites show high thermal stability and good mechanical properties at high temperatures, which is an important property for a high performance application, electronic packaging industry, coatings etc. Moreover, the coupling agents are often used to strengthen an interfacial interaction and enhance the properties.¹⁵⁻¹⁸ Wang et al.^{19,20} prepared heat resistant epoxy-silica hybrids based on diglycidyl ether of Bisphenol A (DGEBA)—diaminodiphenyl sulfone (DDS) epoxy matrix and silica nanoparticles. The great improvement of properties was achieved by using the coupling agent glycidyoxypropyl trimethoxysilane (GTMS). The glass transition temperatures T_g of the hybrids raised with GTMS amount up to 250°C and the modulus above glass transition maintained a very high value up to 300°C. At 30% silica content the hybrid T_g became indistinct. Moreover, the hybrid thermostability determined by TGA was improved. Also Ochi et al.^{7,21} reported a significant enhancement of thermomechanical properties of the DGEBA based epoxy network with silica formed by the sol-gel process from GTMS or tetramethoxysilane (TMOS). The epoxy-silica hybrids with GTMS exhibited a strong interphase interaction, increase in the modulus and disappearance of the

Table I. Designation and Compositions of the Hybrids

Designation	Content of TMOS/TEOS (%)	Fraction of GTMS, x	Theoretical equivalent of silica (%)
DGEBA-Laromin-TMOS(7), BF ₃ MEA	7	-	2.6
DGEBA-Laromin-TMOS(14), BF ₃ MEA	14	-	5.4
DGEBA-Laromin-TMOS(25), BF ₃ MEA	25	-	9.6
DGEBA-Laromin-TMOS(40), BF ₃ MEA	40	-	15.2
DGEBA-Laromin-TMOS(60), BF ₃ MEA	60	-	23.2
DGEBA-Laromin-GTMS(0.1), BF ₃ MEA	-	0.1	2.2
DGEBA-Laromin-GTMS(0.2), BF ₃ MEA	-	0.2	4.4
DGEBA-Laromin-GTMS(0.3), BF ₃ MEA	-	0.3	6.6
DGEBA-Laromin-TMOS(14)-GTMS(0.2), BF ₃ MEA	14	0.2	9.8
DGEBA-Laromin-TEOS(18), BF ₃ MEA	18	-	5.4

glass transition at a silica content ~10 wt %. It should be mentioned that the complete vanishing of a glass transition at such low filler content is exceptional.

The sol-gel process consisting of hydrolytic polycondensation of alkoxy silane precursors provides significant benefits in synthesis of hybrids, however, also some shortcomings. The process requires solvents to be used because of incompatibility of alkoxy silanes with water and an epoxy system. The solvent and water evaporation during polymerization results in sample shrinkage and a removal of residual volatiles from the reaction mixture could lead to formation of bubbles or cracks in the final product. These problems can be eliminated by application of the solvent-free non-aqueous sol-gel procedure. Lee and Ma²² synthesized the nanosilica from tetraethoxysilane (TEOS) by nonaqueous sol-gel process in the epoxy matrix DGEBA-DDS catalyzed with borontrifluoride monoethylamine (BF₃MEA). Recently we have used the Lee's approach to prepare the epoxy-silica hybrids by the nonaqueous sol-gel process and investigated the basic conditions of the nonaqueous procedure.²³ The silica was generated *in situ* from the most common alkoxy silane precursor, TEOS, by using BF₃MEA as an initiator. The initiation mechanism of the non-aqueous process was proposed to involve protolysis of TEOS with BF₃MEA and/or OH groups which are present in the epoxy resin. The sol-gel reactions are relatively slow under nonaqueous conditions thus making possible to control the silica structure evolution and to prevent a phase separation that often occurs during the fast classical "aqueous" sol-gel process. As a result, homogeneous transparent hybrids were prepared. Moreover, GTMS was applied to further improve system homogeneity by interphase grafting. These epoxy-silica hybrids exhibited an enhancement of thermomechanical properties. Nevertheless, a limitation of the nonaqueous sol-gel process exists due to a low TEOS reactivity under nonaqueous conditions leading to an incomplete curing and formation of undercured silica/siloxane domains in the hybrids. This fact resulted in poor mechanical properties in the systems prepared without the coupling agent.

The aim of this article consists in the non-aqueous synthesis of the epoxy-silica hybrids with greatly enhanced thermomechanical

properties and thermal stability by overcoming the problems related to an incomplete curing. Instead of TEOS, the more reactive tetramethoxysilane (TMOS) precursor of silica was used, while a structure evolution was still under control so that well homogeneous transparent systems were produced. In addition, an investigation of the factors governing the nonaqueous sol-gel process was performed in order to reveal the formation-structure-properties relationships. These results facilitated optimization of the hybrid synthesis. The coupling agent GTMS was used to strengthen an interphase interaction by covalent bonding with an epoxy matrix. The epoxy network DGEBA-cycloaliphatic diamine (Laromin) was employed as a matrix for synthesis of transparent high-*T_g* epoxy-silica hybrids showing a high thermal stability.

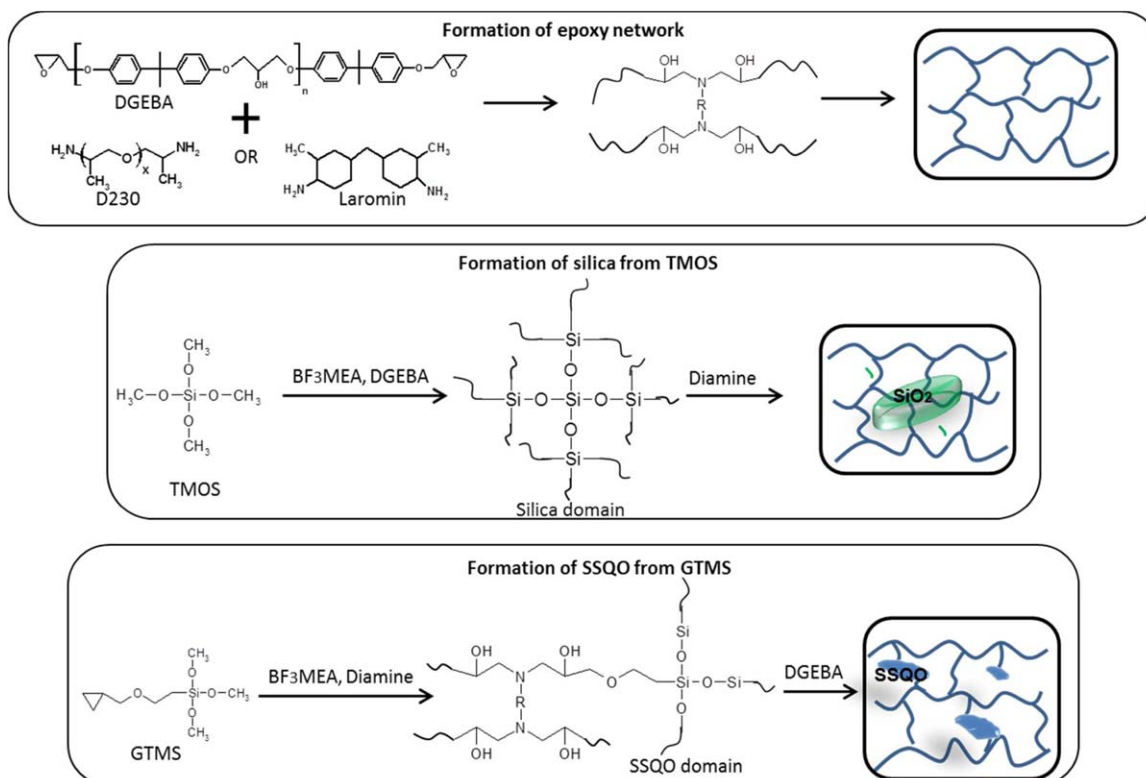
EXPERIMENTAL

Materials

The diglycidyl ether of Bisphenol A (DGEBA) based resin, Epilox A 19-03 (Aldrich) with the equivalent weight of the epoxy groups $E_E = 187 \text{ g mol}^{-1}$ epoxy groups was used. The following amines were applied as curing agents; 3,3'-dimethyl-4,4'-diaminocyclohexylmethane (Laromin[®] C 260) was received from BASF and poly(oxypropylene)diamine—Jeffamine[®] D230 ($M \sim 230$) (Aldrich). Inorganic components: tetramethoxysilane (TMOS) and 3-glycidyloxypropyl trimethoxysilane (GTMS) were purchased from Fluka. Borontrifluoride monoethylamine (BF₃MEA) was obtained from the Aldrich. All chemicals were used without a further purification.

Synthesis of the Hybrid

The epoxy-amine networks were prepared at a stoichiometric ratio of functional groups ($C_{\text{epoxy}}:C_{\text{NH}} = 1 : 1$) and the hybrids were synthesized by the modified two step Lee's synthesis procedure.²² (i) 2 wt % of BF₃MEA with respect to TMOS was mixed with the epoxy resin for 30 min at 70°C. After that, the specified amount of TMOS, e.g., 14 wt % (with respect to DGEBA) was added to the epoxy-BF₃MEA mixture and speedily mixed for 1 h. All the systems were mixed under weak inert conditions. (ii) Stoichiometric equivalent weight of amine was added to the prereacted mixture of TMOS in the epoxy resin and mixed for 20 min.



Scheme 1. Formation of the epoxy-silica hybrid with *in situ* formed silica/silsesquioxane (SSQO) domains. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The hybrids modified with the coupling agent GTMS were prepared by substituting a fraction of DGEBA by GTMS while keeping the epoxy groups concentration constant and the total ratio of epoxy and NH functionalities stoichiometric. The content of GTMS (x) in the nanocomposite synthesis was characterized by fraction of epoxy groups of DGEBA replaced by the coupling agent GTMS: $x = [\text{epoxy (GTMS)}] / [\text{epoxy (DGEBA)} + \text{epoxy (GTMS)}]$ and was varying from 0.1 up to 0.3.

The following curing regime of the sample in inert atmosphere or in the mold was applied: 90°C for 2 h; 130°C for 16 h and the postcuring for 5 h at 190°C in case of D230 and 5 h at 210°C for Laromin. In the special case of the reaction under the air atmosphere the sample was prereacted in the air at 25°C for 2 h.

The hybrids designation indicates the type of epoxy network, content of alkoxy silanes used and alternatively presence of the initiator BF₃MEA during synthesis, e.g. DGEBA-Laromin-TEOS(14)-GTMS(0.1), BF₃MEA shown in Table I.

The schematic structural description of the epoxy network and nanocomposites formation is shown in Scheme 1.

METHODS

Nuclear Magnetic Resonance Spectroscopy (NMR)

Solid-state ²⁹Si CP/MAS NMR experiments were measured at 11.7 T using a Bruker Avance 500 WB/US NMR spectrometer with double-resonance 4-mm and 7-mm probeheads, respectively. To compensate for frictional heating of the

spinning samples, all NMR experiments were measured under active cooling. The sample temperature was maintained at 308 K. The ²⁹Si CP/MAS NMR spectra were acquired at 99.325 MHz; spinning frequency was $\omega r/2\pi = 5$ kHz; the number of scans was 2048; spin lock 4 ms and recycle delay was 3 s. The spectra were referenced to M8Q8 (−109.8 ppm). During detection, a high-power dipolar decoupling (TPPI) was used to eliminate strong heteronuclear dipolar coupling.

The condensation conversion α_{Si} was determined as $\alpha_{Si} = \sum i Q_i / 4$. Q_i is the mole fraction of the Q_i structure units with i siloxane bonds Si—O—Si attached to the central silicon. The relative amount of the structural units was obtained from the deconvolution of the ²⁹Si CP/MAS NMR spectra. The assignment of the NMR bands is as follows: Q_0 from −80.6 to −84.7 ppm, Q_1 from −84.9 to −87.28 ppm, Q_2 from −89.7 to −91.6 ppm, Q_3 from −100.0 to −101.5 ppm, Q_4 from −105.9 to −110.0 ppm.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of the nanocomposites were tested using the ARES G2 apparatus (TA Instruments). An oscillatory shear deformation at the constant frequency of 1 Hz and at the heating rate of 3°C min^{−1} was applied.

ARES G2 rheometer was used also for the chemorheology experiments to follow molecular structure evolution and gelation during polymerization. Oscillatory shear deformation in parallel plates geometry at a frequency of 1 Hz was used. The initial applied maximum strain was 200% while keeping torque below 20 g cm to prevent breaking of the formed gel.

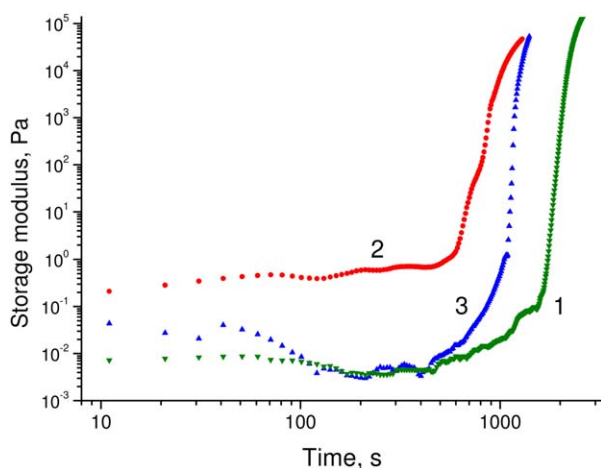


Figure 1. Shear storage modulus $G'(t)$ of the studied systems as a function of time during polymerization at $T = 80^\circ\text{C}$: 1 DGEBA-D230, 2 DGEBA-D230-TMOS, BF_3MEA , 3 DGEBA-D230-TMOS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The gel point was determined by using the multifrequency sweep measurement ranging from 1 to 64 rad s^{-1} and applying a power-law rheological behavior at the critical state, $G'(\omega) \sim G''(\omega) \sim \omega^n$.²⁴ The loss factor $\tan \delta$ is independent of measurement frequency at the gel point and therefore, the gelation was evaluated as a crossover of the $\tan \delta$ for different experimental frequencies during the polymerization.

Thermogravimetric Analysis (TGA)

TGA measurements were performed on Perkin Elmer Thermogravimetric Analyzer Pyris 1 in air atmosphere. The temperature interval of measurements was $30\text{--}880^\circ\text{C}$, with gradual temperature rise of $10^\circ\text{C min}^{-1}$ and gas flow 50 mL min^{-1} on samples of $\sim 10 \text{ mg}$.

RESULTS AND DISCUSSION

We have studied the epoxy-silica hybrids prepared by the nonaqueous sol-gel procedure initiated by BF_3MEA . The alkoxy-silanes TMOS and GTMS were employed for *in situ* generation of nanosilica and grafting of inorganic structures to an epoxy matrix. A comparison with the TEOS based hybrids studied previously²³ is included in order to highlight the TMOS benefits. Two types of epoxy-amine systems were used as hybrid matrices. The DGEBA-Laromin network, involving cycloaliphatic diamine, was used as a high- T_g matrix for the synthesis of high-performance hybrids. In addition, the model low- T_g DGEBA-Jeffamine D230 system, containing amino-terminated polyether D230, was employed to study the hybrid structure evolution and factors governing the non-aqueous sol-gel process in order to disclose relationships between reaction conditions, the hybrid structure and hybrid properties.

Thermomechanical properties of hybrids and their thermal stability were followed by DMA and TGA, respectively.

Formation of Epoxy-Silica Nanocomposites

Structure evolution at formation of the epoxy-silica hybrid under the nonaqueous conditions was monitored by

chemorheology. Figure 1 shows the rise of the storage modulus during build-up of the epoxy network DGEBA-D230 (curve 1) and the hybrid DGEBA-D230-TMOS (curves 2 and 3). The steep increase in the modulus indicates gelation of the mixture and the gel times are given in Table II. Figure illustrates that the gelation sets in earlier in the hybrids than in the neat epoxy network. Moreover, the hybrid network formation is faster if the sol-gel process is initiated with BF_3MEA (curve 2). It was proved²³ that the acceleration of the network build-up results from the covalent bonding between the formed silica and epoxy structures. Table II includes for comparison also the gel times of the previously studied "TEOS hybrids."²³ The results reveal a higher reactivity and shorter gel times in case of the TMOS hybrids with respect to the TEOS system.

Table II characterizes the formation-structure-property relationships in the DGEBA-D230-silica hybrids. It shows t_{gel} featuring rate of a hybrid network formation, the sol-gel conversion as characteristics of a silica structure in the hybrid and glass transition temperature T_g of the hybrids describing thermomechanical properties.

The mechanism of the nonaqueous sol-gel process involves protolysis of the alkoxy-silane agent, TMOS or TEOS, initiated by BF_3MEA and/or by OH groups in the DGEBA molecule.²³ This initiation occurs in the first synthesis step (see Experimental). The sol-gel conversions and distribution of Q_i structural units after protolysis under different initiation conditions were determined by ^{29}Si NMR. The results are given in Table III showing a comparison between TMOS and TEOS as well as the effect of BF_3MEA on initiation of the sol-gel process. Table proves the higher TMOS reactivity compared to TEOS. While only 13% of TEOS reacted during the protolysis step ($Q_0 = 0.87$), in the case of TMOS it was more than 50% ($Q_0 = 0.48$). Moreover, Q_2 units determined in the TMOS mixture after protolysis reveal a presence of short polysiloxane chains. In contrast, only low molecular weight products, like disiloxanes characterized by Q_1 units, were formed in the TEOS mixture. The results disclose that TMOS conversion during protolysis is higher even in the absence of BF_3MEA . The sol-gel reaction is initiated in this case by OH groups of DGEBA.²³

The initiation of the nonaqueous sol-gel process is a crucial stage. An extent of TMOS protolysis in this initial synthesis step strongly affects the following silica structure evolution within a hybrid. The final sol-gel condensation conversion, $(\alpha_{\text{Si}})_{\text{hybrids}}$ in both "TEOS and TMOS hybrids" is given in Table II. The comparison of the results in Tables II and III shows that conversions in the hybrids well correlate with the conversions of the pre-reacted mixtures in the first synthesis step, $(\alpha_{\text{Si}})_{\text{protolysis}}$, revealing an importance of the initiation stage. Also in the hybrids, the conversion of TMOS is higher compared to TEOS even in the case of the reaction without BF_3MEA . The conversion $\alpha_{\text{Si}} = 0.72$ in the network DGEBA-D230-TMOS, BF_3MEA is close to that in the classic "aqueous hybrids" DGEBA-D2000-TEOS, which is in the range $0.79\text{--}0.85$.²⁵ The curing partially under air atmosphere (see Experimental) is another way of the "non aqueous sol-gel process" initiation. The results disclose that an air humidity promotes the sol-gel reactions and slightly

Table II. Formation-Structure-Property Characteristics of the Hybrids Based on DGEBA-D230 Epoxy Network; Gelation Time, Sol-Gel Conversion and T_g Values

System	t_{gel}^a (min)	$(\alpha_{Si})_{hybrid}$	T_g^b (°C)
DGEBA-D230	34	-	91
DGEBA-D230-TEOS	52	0.19	68
DGEBA-D230-TEOS, air	-	-	62, 75
DGEBA-D230-TEOS, BF ₃ MEA	33	0.46	82
DGEBA-D230-TMOS	20	0.51	71, 95
DGEBA-D230-TMOS, air	-	0.54	101
DGEBA-D230-TMOS, BF ₃ MEA	15	0.72	107
DGEBA-D230-TMOS, BF ₃ MEA, air	-	-	120

^aFor t_{gel} determination see Experimental.

^b T_g determined from position of the $\tan \delta$ curve maximum, two T_g values correspond to the two-phase system.

raises the “TMOS hybrid” sol-gel conversion as well as the hybrids T_g values as discussed below (Table II).

The important benefit of the nonaqueous sol-gel procedure consists in a slower reaction enabling a structure control in order to avoid a phase separation.²³ Although TMOS is a much faster silica precursor than TEOS, the structure evolution is under control and well homogeneous hybrids are produced. Figure 2 illustrates the transparent DGEBA-Laromin-TMOS hybrid containing 80% TMOS.

The best properties and homogeneity was achieved by using the coupling agent GTMS. TEM micrographs of the GTMS containing nanocomposites and the reference epoxy network are shown in Figure 3. The results reveal silica aggregates of the size about 70 nm dispersed in the epoxy matrix and composed of primary particles of ~10 nm in diameter [Figure 3(b,c)]. The epoxy matrix [Figure 3(a)] does not display any heterogeneity.

Thermomechanical Properties of the Hybrids

In the previous work dealing with the “TEOS hybrids”²³ it was proved that a covalent bonding between simultaneously formed silica structures and an epoxy network occurs by the reaction of SiOH in silica and C—OH in an epoxy system. This interphase grafting finally leads to crosslinking of epoxy chains through the silica domains. Formation of the hard silica nanofiller structures and the mentioned crosslinking resulted in a rise of the storage modulus above glass transition. Despite this reinforcement, however, the T_g of the hybrids were not improved or even declined with respect to the epoxy network due to a plasticizing effect of soft incompletely cured silica structures. The higher sol-gel conversion in the “TMOS hybrids” is expected to result in the improved properties. The enhancement of the hybrids thermomechanical behavior is the main goal of the work. For this purpose we monitored thermomechanical properties of the hybrids of various compositions prepared under different nonaqueous conditions.

Table III. Distribution of Q_i Units and Condensation Conversion After the TEOS and TMOS Protolysis Under Nonaqueous Conditions

System	Q_0^a	Q_1	Q_2	$(\alpha_{Si})_{protolysis}$
DGEBA-TEOS, BF ₃ MEA (ref. 23)	0.87	0.13	0	0.05
DGEBA-TMOS	0.54	0.39	0.07	0.13
DGEBA-TMOS, BF ₃ MEA	0.48	0.41	0.11	0.175

^a Q_i is the mole fraction of the Q_i structural units.

A comparison of thermomechanical properties of the hybrids DGEBA-Laromin-silica prepared both from TMOS and TEOS is presented in Figure 4, showing the storage modulus G' and loss factor $\tan \delta (=G''/G')$ as functions of temperature. The synthesis of hybrids was initiated with BF₃MEA and the composition of both systems corresponds to the theoretical silica content of 5.4 wt %. As discussed above, the TEOS hybrid has a higher modulus with respect to the epoxy network, however, the glass transition temperature T_g is not changed (curve 2). In contrast, by using TMOS a significant enhancement of thermomechanical properties was achieved. The T_g of the hybrid raised by 40°C and the rubbery modulus is by an order of magnitude higher compared to that of the neat network (curve 3). In addition, the figure illustrates the effect of a curing temperature T_C because of a high curing conditions sensitivity of the nonaqueous sol-gel process. The common curing regime used for the epoxy system is not sufficient for hybrids, that had to be cured at a higher temperature, $T_C = 210^\circ\text{C}$. Figure 4 presents a substantial drop of T_g by 30–40°C as well as moduli of the hybrids prepared at a lower temperature $T_C = 190^\circ\text{C}$ (curves 4, 5).

The reinforcement of the DGEBA-Laromin epoxy network by silica formed from TMOS is very efficient and the modulus above glass transition raises as TMOS content increases in

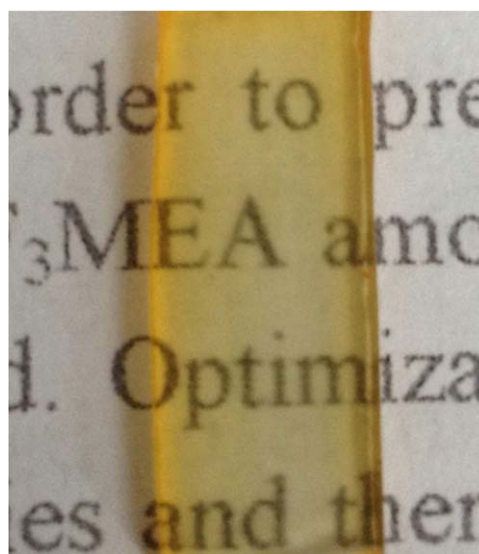


Figure 2. Photo of the hybrid DGEBA-Laromin-TMOS (80%), BF₃MEA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

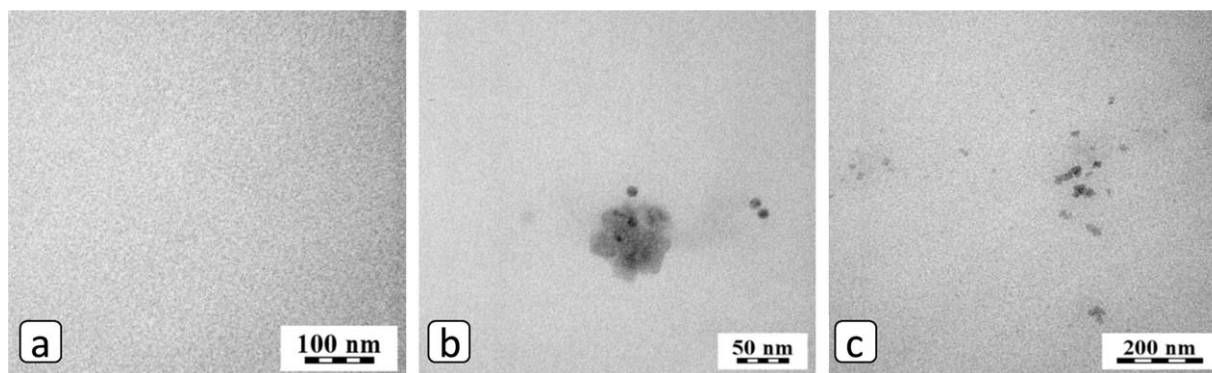


Figure 3. TEM micrographs of (a) epoxy network DGEBA-D230 and (b, c) DGEBA-D230-TMOS (14)-GTMS (0.3), BF_3MEA nanocomposite.

Figure 5(a). T_g values, however, go through a maximum at 14% TMOS (curve 3). At a higher TMOS amount the glass transition becomes less distinct and T_g declines as shown in Figure 5(b). This thermomechanical behavior can be explained as follows:

The silica-epoxy grafting leads to a restriction of the epoxy network chains mobility. This is manifested by a shift of T_g to higher values and drop of the loss factor $\tan \delta$ amplitudes due to a reducing fraction of the relaxing polymer chains. Moreover, broadening of the loss peaks occurs because of a wide distribution of the corresponding relaxation times. The hybrid containing 40% TMOS (i.e., 15 wt % silica) has an almost indistinct T_g and a very high modulus up to 260°C (curve 5) revealing a strong immobilization of the epoxy chains. Moreover, it indicates a good dispersion of silica structures within the matrix because 15 wt % of silica, corresponding to ~ 10 vol %, is sufficient to completely restrict the epoxy matrix and likely to percolate through the hybrid. The high TMOS content in the hybrid implies in addition to a more extensive covalent bonding between phases, also formation of undercured silica structures. An incomplete curing is more likely at a high alkoxy-silane content due to severe sterical hindrances for the sol-gel reactions within a densely crosslinked epoxy matrix.^{23,26,27} The small relaxation peak at 140°C corresponds to a small fraction of a polymer, which is plasticized by soft less cured inorganic structures. The effect is much more pronounced in the hybrid with 60 % TMOS. In this case the T_g is decreased by 40°C due to a great amount of low-cured plasticizing products. The hypothesis of plasticization with undercured silica domains was proved by postcuring the sample for 1 h at 250°C. Figure reveals the marked properties improvement; T_g raises by 80°C (curve 7).

The initiation of the nonaqueous sol-gel process was shown to be a crucial step in controlling evolution of the silica structure in hybrids featured by the sol-gel conversion. Determination of the effect of initiation conditions on the hybrids final properties is of a high importance in order to optimize the hybrids synthesis. This investigation was performed by using the model hybrid based on the DGEBA-D230 network cured at 190°C.

Figure 6 presents thermomechanical behavior of the DGEBA-D230-silica hybrids prepared under different conditions with

respect to initiation of the sol-gel process. The effect of BF_3MEA and an influence of the air humidity on hybrid properties are shown. Both “TEOS and TMOS hybrids” were studied and T_g values of the corresponding systems are given in Table I.

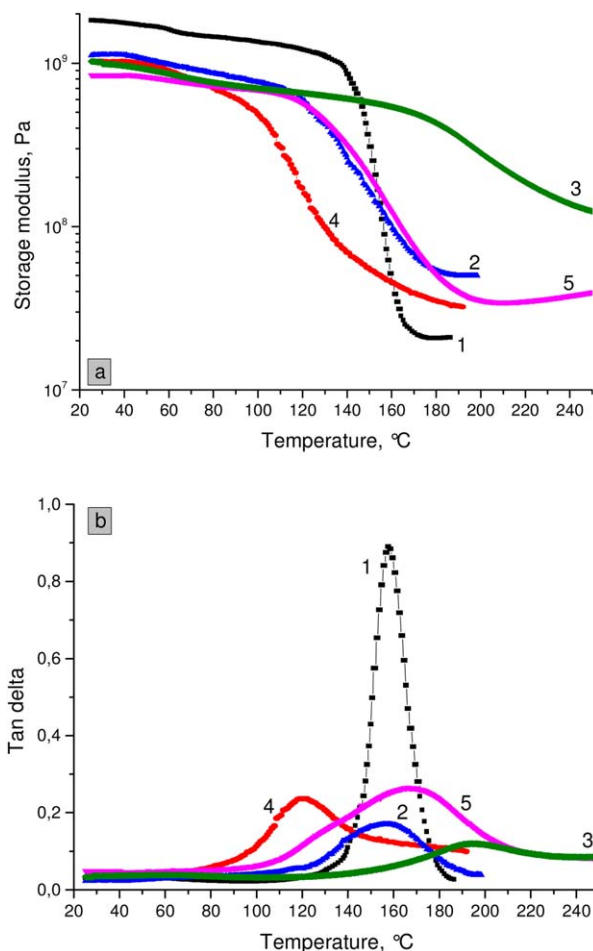


Figure 4. Storage modulus (a) and loss factor $\tan \delta$ (b) of the DGEBA-Laromin based hybrids as functions of temperature: 1 DGEBA-Laromin, 2 DGEBA-Laromin-TEOS (18) $T_C = 210^\circ\text{C}$, 3 DGEBA-Laromin-TMOS (14) $T_C = 210^\circ\text{C}$, 4 DGEBA-Laromin-TEOS (18) $T_C = 190^\circ\text{C}$, 5 DGEBA-Laromin-TMOS (14) $T_C = 190^\circ\text{C}$. Constant BF_3MEA amount. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

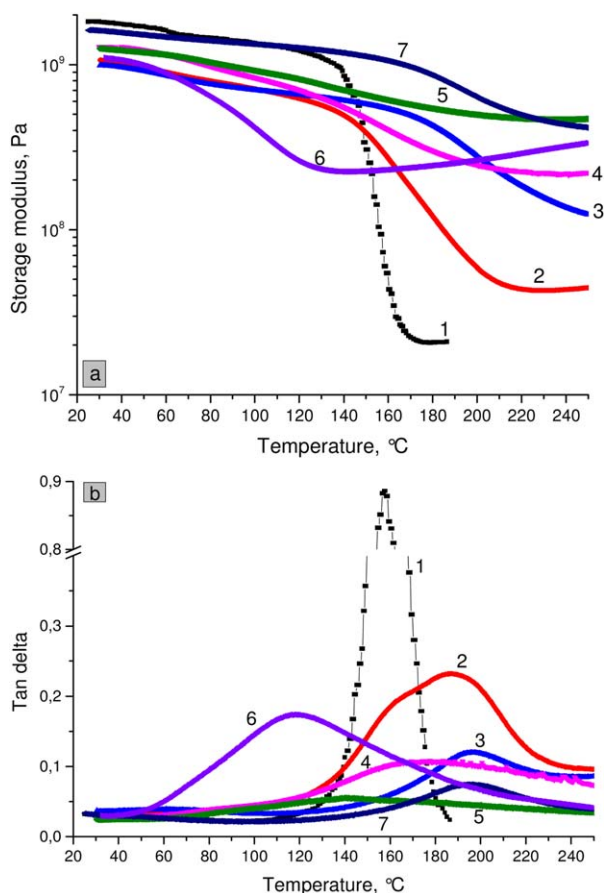


Figure 5. Storage modulus (a) and loss factor $\tan \delta$ (b) of the DGEBA-Laromin hybrids containing different amount of TMOS, curing temperature $T_C = 210^\circ\text{C}$: 1 0%, 2 7%, 3 14%, 4 25%, 5 40%, 6 60%, 7 60%—postcuring at $T_C = 250^\circ\text{C}$. Constant BF_3MEA amount. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

While the “TMOS hybrid” prepared in the presence of BF_3MEA (curve 2) exhibits a significant improvement both in T_g and modulus with respect to the epoxy network (curve 1), the TEOS based system shows a drop of T_g (curve 3) due to a low sol-gel conversion (see Table II). The poor properties of the “TMOS hybrid” prepared in the absence of BF_3MEA reveal the importance of the BF_3MEA initiation. In this case a two phase system is formed which is characterized by two loss factor peaks in figure (curve 4). In addition to the polymer phase of a low T_g , which is plasticized by the unreacted TMOS and undercured siloxanes, there is a polymer fraction partly immobilized by better cured silica structures.

The reaction under air atmosphere presents a limiting case of a transition between the aqueous and nonaqueous sol-gel procedures. The figure discloses that the “TMOS hybrid” prepared under air humidity without BF_3MEA (curve 5) exhibits properties which are close to those of the hybrid initiated with BF_3MEA . In contrast, “TEOS hybrid” prepared under air humidity does not show any improvement of properties (see Table II). The best thermomechanical properties were achieved by curing the hybrid under air humidity in the presence of BF_3MEA . The corresponding hybrid shows the T_g rise by 30°C

and the high modulus (curve 6). Consequently, in the inert atmosphere the BF_3MEA complex is necessary for the initiation of the non-aqueous sol-gel process. Otherwise the hybrids of poor properties are produced. However, in the case of TMOS, the sol-gel reactions are promoted by air humidity even in the absence of BF_3MEA to form hybrids of improved properties unlike TEOS which is unreactive under the air humidity.

The hybrids thermomechanical properties and T_g values well correlate with the rate of hybrids formation featured by t_{gel} and sol-gel conversions in the hybrids as presented in Table II. The higher rate of the hybrid network formation results in the better cured silica structures and higher T_g of the hybrid.

A homogeneous nanofiller dispersion in a matrix and a strong interphase interaction are known to be principal factors determining nanocomposite properties. As mentioned above, an interphase bonding exists in the TMOS containing epoxy hybrid due to $\text{SiOH} + \text{COH}$ reactions. In addition, according to the common approach, we employed the coupling agent GTMS to promote an interphase grafting. GTMS is incorporated into an epoxy-amine network by the reaction of glycidyl group with an amine crosslinker. Simultaneously, silsesquioxanes (SSQO) are formed by the sol-gel process producing inorganic domains

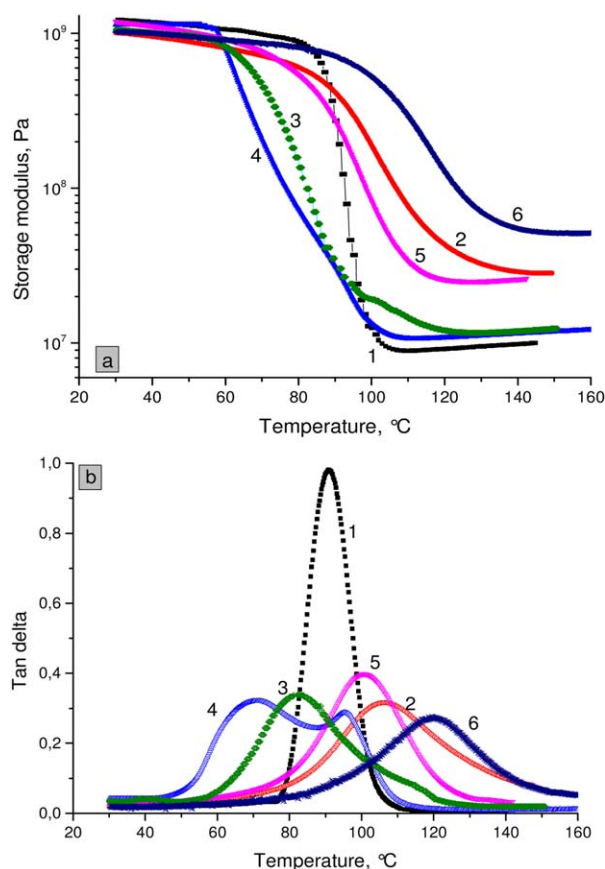


Figure 6. Storage modulus (a) and loss factor $\tan \delta$ (b) as functions of temperature of the DGEBA-D230 based hybrids prepared under different initiation conditions 1 DGEBA-D230, 2 DGEBA-D230-TMOS, BF_3MEA ; 3 DGEBA-D230-TEOS, BF_3MEA ; 4 DGEBA-D230-TMOS, inert; 5 DGEBA-D230-TMOS,Air; 6 DGEBA-D230-TMOS, BF_3MEA ,Air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

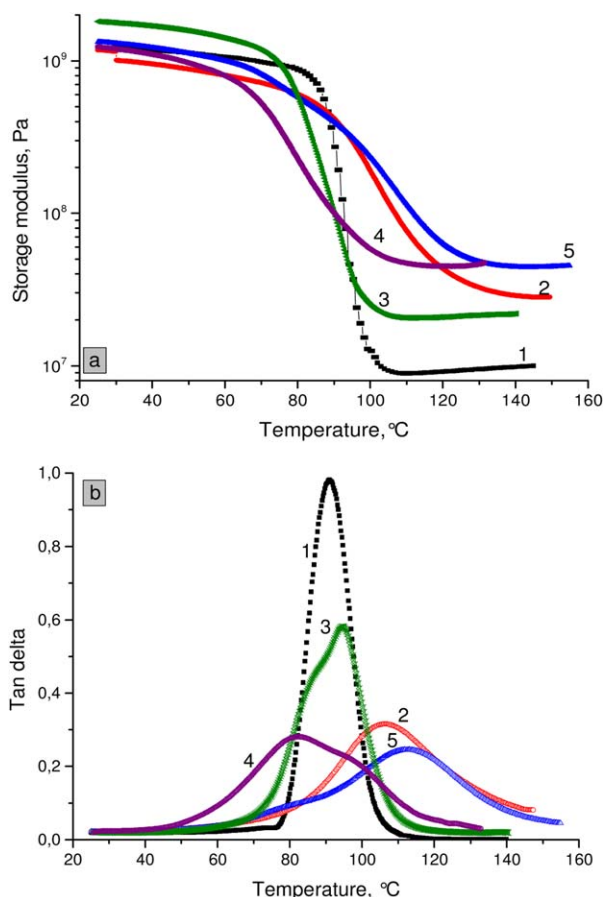


Figure 7. Storage modulus (a) and loss factor $\tan \delta$ (b) as functions of temperature of the DGEBA-D230 based hybrids containing TMOS or/and GTMS 1 DGEBA-D230, 2 DGEBA-D230-TMOS(14), 3 DGEBA-D230-GTMS(0.1), 4 DGEBA-D230-GTMS(0.3), 5 DGEBA-D230-TMOS(14)-GTMS(0.1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which are bound to epoxy network chains. Finally, these domains interconnect the network chains thus functioning as SSQO junctions increasing the hybrid network crosslinking density.^{15,28,29}

Figure 7 compares the reinforcing effect of TMOS (curve 2) and GTMS (curves 3, 4) in the hybrid network based on DGEBA-D230. The rise of the hybrids rubbery moduli is slightly more pronounced in the GTMS containing systems, taking into account the theoretical silica content (see Table I). This is a manifestation of the interphase grafting and the hybrid crosslinking via inorganic domains, which is more efficient by using the coupling agent. However, T_g values are lower in the “GTMS hybrids.” GTMS undergoes slow sol-gel reactions under non-aqueous conditions and the formed SSQO structures are severely undercured when reacted at 190°C.²³ Mainly at a high GTMS content ($x=0.3$) T_g drops due to incomplete curing and the network plasticization (curve 4). In contrast, T_g raises with respect to the epoxy network in the “TMOS hybrid” despite low T_c (curve 2). The stronger limitation of the SSQO structure growth from GTMS is likely due to the covalent incorporation

in the epoxy network thus being more confined than silica structures formed from TMOS.

The efficient epoxy-inorganic phase grafting by GTMS and the better evolution of inorganic domains within the hybrid in the case of TMOS suggest a hybrid design as a combination of both alkoxysilane reagents. Figure 7 illustrates the best enhancement of properties in the hybrid DGEBA-D230-TMOS(14)-GTMS(0.1), BF_3MEA (curve 5).

On the basis of the results of the model system we have prepared the high- T_g heat resistant hybrid by using DGEBA-Laromin epoxy network as a matrix. The hybrid was cured at 230°C, which was proved to be sufficient for GTMS to form well developed SSQO domains, while the curing at 250°C already causes some polymer decomposition. The combination of TMOS and GTMS in hybrids leads to outstanding properties at a low inorganic phase content as illustrated in Figure 8. The hybrid DGEBA-Laromin-TMOS(14)-GTMS(0.1) with a silica amount of 7.6 wt % has a very indistinct glass transition and a high modulus up to 300°C; $G' = 335$ MPa at 300°C (curve 5).

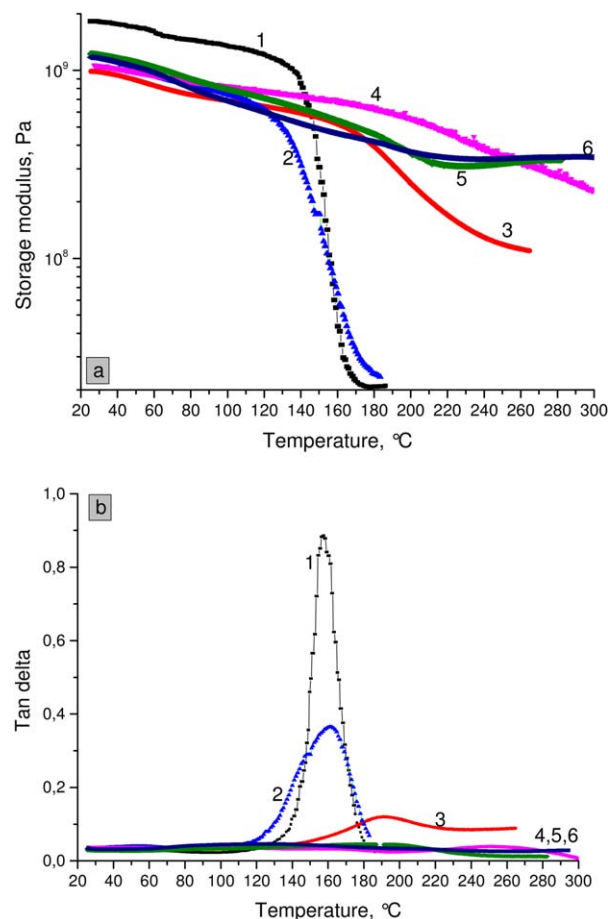


Figure 8. Storage modulus (a) and loss factor $\tan \delta$ (b) of the DGEBA-Laromin based high- T_g hybrids as functions of temperature 1 DGEBA-Laromin, 2 DGEBA-Laromin-GTMS(0.1); 3 DGEBA-Laromin-TMOS(14); 4 DGEBA-Laromin-GTMS(0.3); 5 DGEBA-Laromin-TMOS(14)-GTMS(0.1); 6 DGEBA-Laromin-TMOS(14)-GTMS (0.3). Constant BF_3MEA content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

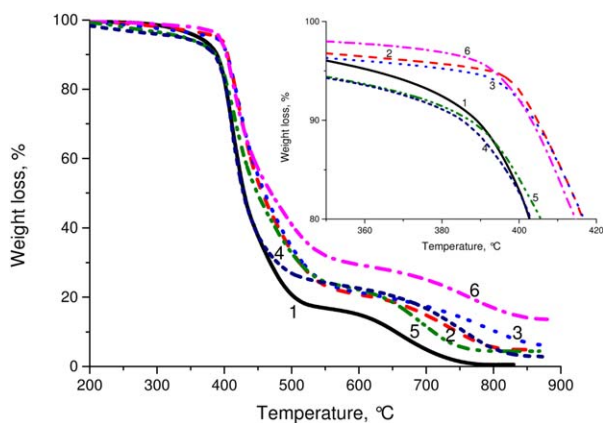


Figure 9. TGA plot of the epoxy network and the hybrids in air 1— DGEBA-Laromin; 2 -- DGEBA-Laromin-TMOS(14),BF₃MEA; 3 DGEBA-Laromin-TMOS(14),Air; 4 ---- DGEBA-Laromin-TMOS(14),i-ner; 5 --- DGEBA-Laromin-TEOS(18),BF₃MEA; 6 ——— DGEBA-Laromin-TMOS(14)-GTMS(0.2),BF₃MEA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The increasing GTMS content in the hybrid DGEBA-Laromin-TMOS(14)-GTMS(0.3) leads to a vanishing of the glass transition before the polymer decomposition (curve 6). Only a very small polymer fraction relaxes in a low-temperature region as revealed by the small amplitudes of the loss factor curves in Figure 8(b). This behavior results from a very strong interfacial interaction and a complete immobilization of epoxy chains by bonding to inorganic structures.

The figure shows also the individual effects of both alkoxy-silanes revealing a synergy of their combination in the hybrid. Reinforcement of the epoxy network with TMOS (14), corresponding to 5.4% silica, provides a limited grafting resulting in T_g rise by 35°C (curve 3). However, a severe decline of mechanical properties occurs above 200°C disclosing a lack of the sufficiently strong interfacial interaction. As to the effect of GTMS, the figure displays an appreciable properties dependence on the content of the coupling agent. No properties improvement, only a slight transition broadening, occurs after incorporation of a small amount of GTMS in the hybrid DGEBA-Laromin-GTMS(0.1) (curve 2). Figure illustrates a dramatic increase in the high-temperature modulus as GTMS amount raises; the curve 4 corresponds to the hybrid with GTMS content, $x = 0.3$, i.e. 6.6 wt % equivalent silica. The interphase interaction and

crosslinking are more efficient and the modulus is higher compared to the TMOS containing hybrid. However, also in this case a drop of the modulus sets in above 200°C. Only the combination of both alkoxy-silanes even at small contents, TMOS (14) and GTMS (0.1), results in the hybrid which maintains the mechanical properties up to 300°C without worsening. Obviously, there is a synergy effect. GTMS is very efficient in an interphase grafting and homogenization of the system, while it is low reactive. The TMOS high sol-gel reactivity ensures formation of well developed silica structures even under conditions of the nonaqueous procedure; however an extent of interphase grafting is low. The combination thus leads to the strong grafting with well cured structures because of cocondensation of silica and SSQO domains. Very likely a percolation of the inorganic structures through the hybrid occurs and the bicontinuous epoxy-silica/SSQO hybrid is formed.

Thermal Stability

The incorporation of the silica *in situ* formed from TMOS into the epoxy network results in a significant enhancement of thermal stability. Figure 9 and Table IV present the results of thermal gravimetric analysis (TGA) of the DGEBA-Laromin based hybrids. The thermal stability was characterized by the temperature T_5 , at which 5% loss of mass occurs in the air atmosphere.

The TGA results show a dramatic difference between “TEOS” and “TMOS” hybrids. While the TEOS based hybrid exhibits a reduction of thermal stability with respect to the epoxy network, the thermal stability of DGEBA-Laromine-TMOS hybrids considerably enhances. The best results were achieved in the hybrids containing both TMOS and GTMS. The hybrid DGEBA-Laromin-TMOS(14)-GTMS(0.2) displays a rise of the thermal stability by 31°C (curve 6). Also the second decomposition step corresponding to the high temperature thermal oxidative degradation is shifted in the hybrid by ~100°C to higher temperatures. The residue which remained after analysis (in the air) is by 50% higher than the theoretical content of the inorganic phase (see Table IV) indicating a considerable char formation. This high residue reveals that a part of a polymer phase is well protected from thermal and thermal oxidative degradation due to strong interphase interaction in the hybrid and formation of a silica layer on a polymer surface.

The hybrid prepared without BF₃MEA shows a pronounced drop of decomposition temperature T_5 by 50–60°C compared

Table IV. Thermal Stability of the Epoxy Network and the Hybrids

System	T_5^a	Experimental residue (%)	Calculated residue (%)
DGEBA-Laromin	362	0.52	0
DGEBA-Laromin-TEOS(18), BF ₃ MEA	341	4.4	5.4
DGEBA-Laromin-TMOS(14)	335	2.8	5.4
DGEBA-Laromin-TMOS(14), air	384	6.1	5.4
DGEBA-Laromin-TMOS(14), BF ₃ MEA	392	4.9	5.4
DGEBA-Laromin-TMOS(14),BF ₃ MEA, $T_C = 190^\circ\text{C}$	379	4.8	5.4
DGEBA-Laromin-TMOS(14),GTMS(0.2), BF ₃ MEA	393	13.6	9.8

^a T_5 – 5 % loss of mass occurs.

to the “initiated hybrids.” This sample exhibits a lower residue than the theoretical one due to incompletely cured silica. Only small improvement of thermal stability was observed in the systems cured at a low temperature, $T_C = 190^\circ\text{C}$. In contrast, a relatively high thermal stability was achieved in the hybrids reacting partially under air atmosphere (see Experimental) even without BF_3MEA . The corresponding hybrid, moreover, has a slightly higher residue. We assume that a protective skin silica layer of a higher sol–gel conversion is formed on the surface in the air humidity atmosphere.

CONCLUSIONS

The high- T_g , heat resistant and transparent epoxy-silica hybrids have been prepared by the nonaqueous sol–gel process initiated with borontrifluoride monoethylamine. The hybrids containing a low amount of the *in situ* generated silica (~ 10 wt %) show indistinct T_g and the high modulus (335 MPa) up to 300°C . The thermal stability of the hybrids characterized by T_5 value (temperature of 5% mass loss) increased by $\sim 30^\circ\text{C}$ with respect to the epoxy network and the high temperature thermal-oxidative degradation was delayed by $\sim 100^\circ\text{C}$. The outstanding thermo-mechanical properties result from a very strong interphase interaction by covalent bonding leading to a complete immobilization of epoxy network chains and formation of the silica skin protective layer during a thermo oxidative hybrid degradation.

The epoxy network DGEBA-cycloaliphatic diamine (Laromin) was used as an organic matrix, TMOS as a precursor of silica formed by the sol-gel process and the coupling agent GTMS was employed to strengthen the interphase interaction. We took advantage of the synergy combination of both alkoxysilanes. The best properties were achieved in the hybrid of the following composition: DGEBA-Laromin-TMOS(14)-GTMS(0.1).

The model hybrid based on the network DGEBA-D230 was used to study the basic factors governing the nonaqueous sol–gel process. The results enabled to reveal the formation–structure–properties relationships in order to optimize the hybrid composition and conditions of the nonaqueous synthesis. The nonaqueous technique was employed due to better control of the structure evolution compared to the classical sol–gel process facilitating the synthesis of homogeneous transparent hybrids.

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