

Synthesis and Characterization of Organic–Inorganic Hybrids Based on Epoxy Resin and 3-Glycidyloxypropyltrimethoxysilane

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Received 18 February 2003; accepted 23 September 2003

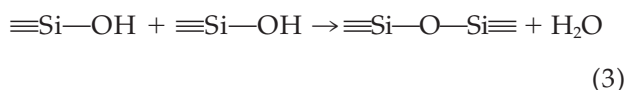
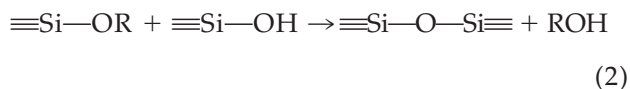
ABSTRACT: Organic–inorganic hybrid materials based on diglycidyl ether of bisphenol A (DGEBA) and 3-glycidyloxypropyltrimethoxysilane (GLYMO) were prepared, using a poly(oxypropylene) diamine Jeffamine D230 as a curing agent. Materials were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), infrared spectroscopy, swelling in tetrahydrofuran (THF), and Soxhlet extraction in THF. A dependence of the final conversion of epoxy groups and the final degree of organic phase crosslinking on inorganic phase content was found.

The inorganic phase presents a steric hindrance to full crosslinking of epoxy groups. It also immobilizes the organic chains and improves the temperature stability of hybrid materials. Products of GLYMO hydrolysis together with unreacted organic molecules lower the glass transition temperature of hybrid materials. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 498–505, 2004

Key words: nanocomposites; silicas; sol-gel process; structure; thermosets

INTRODUCTION

The study of organic–inorganic hybrids obtained by the sol-gel process is an expanding field of investigation. The main hypothesis of the research is that hybrid materials, with a very finely dispersed inorganic phase (on molecular or nano level), which is often interconnected three-dimensionally with the organic polymer, have superior properties compared to composites obtained via classical routes such as blending polymers with inorganic fillers or fibers. In the sol-gel process, the inorganic phase is formed *in situ*, by hydrolysis and condensation of metal (usually silicon) alkoxides, by the following reactions, where R represents an alkyl group:¹



Hydrolysis and condensation reactions are catalyzed by acid or base catalysts. The great flexibility of the sol-gel process enables preparation of organic–inorganic hybrids with diverse organic components.^{2–9}

In this work, organic–inorganic hybrids based on epoxy resins are prepared. Epoxy resins are high-performance polymers with a wide area of application, which could be further expanded by modifying properties of the final material. Several workers obtained hybrid materials based on epoxy resin using the sol-gel process and reported their properties.^{8,10–18} In this work, 3-glycidyloxypropyltrimethoxysilane (GLYMO) was used as an inorganic precursor for preparation of epoxy–silica hybrids. GLYMO is an organofunctional alkoxy silane monomer that can undergo both the sol-gel polymerization of the alkoxy groups and curing of the epoxy functionality to form a hybrid network with covalent bonds between organic and inorganic phases. Sol-gel polymerization of GLYMO consists of hydrolysis and condensation of methoxysilane groups and formation of silsesquioxane structures, $\text{RSiO}_{3/2}$.^{19–21}

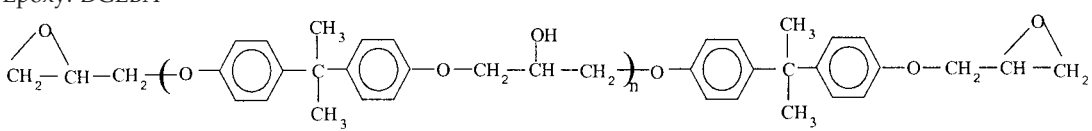
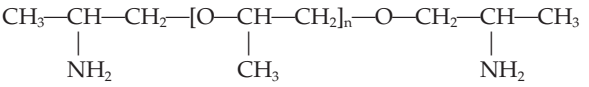
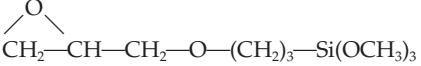
EXPERIMENTAL

Materials

An epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Epikote 828 EL, Shell Chemicals) with the epoxy equivalent weight of 190 g/mol and GLYMO (98%, Aldrich Chemicals) were used to synthesize organic–inorganic hybrid materials. Poly(oxypropylene)

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TABLE I
Chemical Structure of the Materials Used

Epoxy: DGEBA

Curing agent: Poly(oxypropylene)diamine Jeffamine D230

Silica: 3-glycidyloxypropyltrimethoxysilane (GLYMO)


diamine (Jeffamine D230, Huntsman Corp.) was used as a curing agent for epoxy and as a basic catalyst of GLYMO hydrolysis. The materials were used as received. Chemical structures of the ingredients used are displayed in Table I.

Sample preparation

DGEBA/Jeffamine and GLYMO/Jeffamine systems with a stoichiometric amount of Jeffamine D230 (30 and 23.8 phr, respectively) were prepared. Mixtures were stirred at room temperature in a closed vessel for 90 min. To prepare hybrid materials, DGEBA and GLYMO were blended in weight ratios of 1 : 2, 1 : 1, and 2 : 1 at room temperature in a closed vessel for 90 min. A stoichiometric amount of Jeffamine D230 was added as a curing agent. The mixtures were stirred for another 60 min and then poured into a Teflon mold. Designations of all four hybrids and pure epoxy-amine system are listed in Table II.

Curing was affected at room temperature (from 1 to 30 days), making use of air humidity for GLYMO hydrolysis. The materials were postcured for 24 h at 120°C in an oven.

Characterization

The curing kinetics of investigated systems were studied by means of differential scanning calorimetry

(DSC) under dynamic heating rate of 10 Kmin⁻¹ on a Netzsch DSC 200 differential scanning calorimeter operating in a temperature range between -100 and 500°C in a nitrogen atmosphere. The sample was heated from room temperature to 240°C. The total heat of reaction, ΔH_T , is estimated by drawing a straight line connecting the base line before and after the peak and integrating the area under the peak. The digitized data were acquired by a computer and transferred to a PC for further treatment.

Dynamic DSC experiments were also performed to determine the glass transition temperature, T_g , of the completely cured material. The sample was heated from room temperature to 250°C at 10 Kmin⁻¹ and then cooled in the DSC cell to 0°C at 10 Kmin⁻¹ and immediately reheated to 250°C at 10 Kmin⁻¹. T_g was taken as the midpoint of the endothermic step transition.

Loss of weight of samples postcured at 120°C was measured by thermogravimetric analysis (TGA), using a Netzsch thermoanalyzer STA 409. Samples were heated from room temperature to 1,000°C at a heating rate of 10 Kmin⁻¹ in a nitrogen gas flow and synthetic air flow.

FTIR spectra of pure ingredients and postcured hybrid samples were obtained on a Nicolet Magna-IR 760 FT-IR. Each spectrum from 4,000 to 600 cm⁻¹ was averaged over 16 scans at 4 cm⁻¹ resolution. The liquid samples were coated on NaCl plates. Solid sam-

TABLE II
Composition and Properties of Prepared Materials (Values of ΔH_T are Expressed per Gram of Reaction Mixture)

Material	GLYMO/DGEBA mass ratio	DSC maxima T_{max} (°C)	ΔH_T (meas.) (Jg ⁻¹)	ΔH_T (theor.) (Jg ⁻¹)	α_{max}	Q_{max}	Soxhlet extracted (mass %)
G0E1	0/1	127	448	448	1.00	0.366	0.0
G1E2	1/2	138	331	363	0.91	0.446	0.0
G1E1	1/1	145	247	321	0.77	0.458	0.7
G2E1	2/1	155	255	278	0.92	0.354	0.0
G1E0	1/0	177	180	194	0.93	0.207	0.0

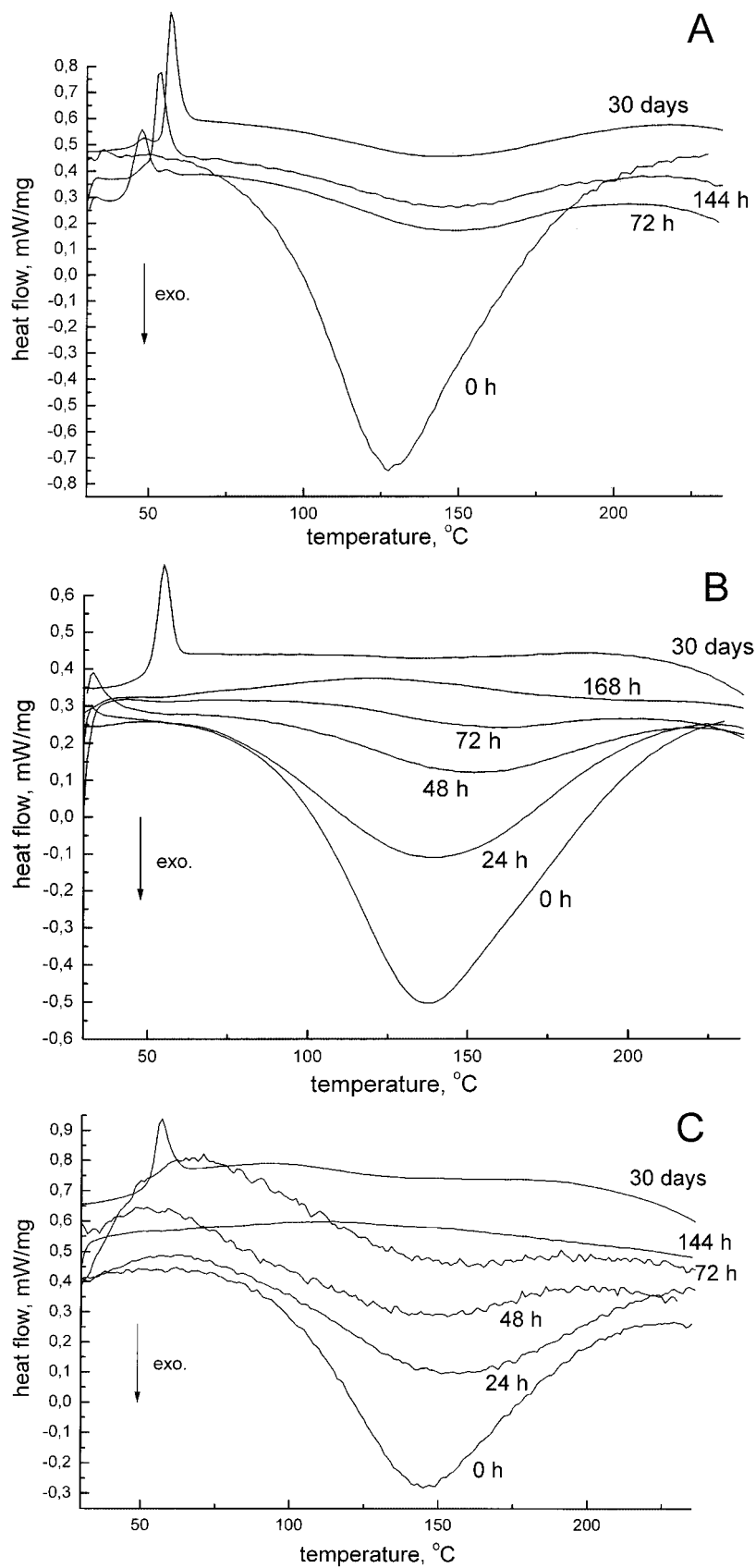


Figure 1 DSC thermograms of samples cured at room temperature for listed time, heated with 10 Kmin^{-1} : (A) G0E1; (B) G1E2; (C) G1E1; (D) G2E1; (E) G1E0.

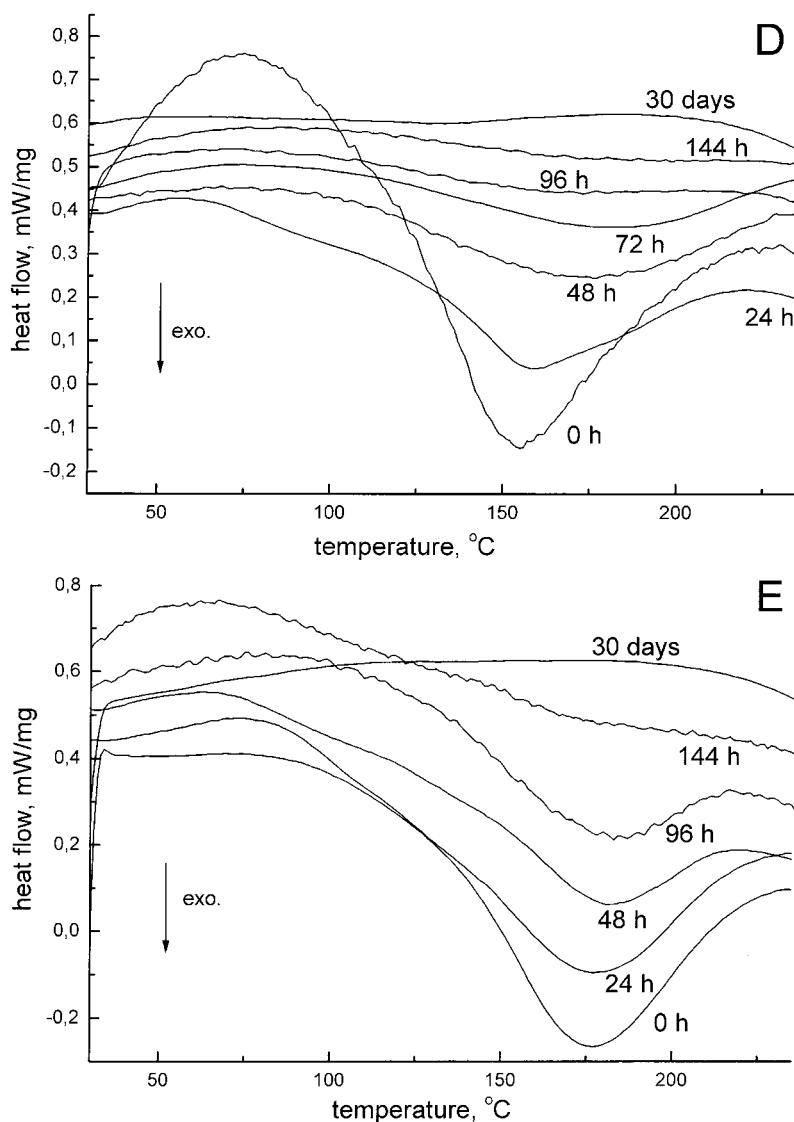


Figure 1 (Continued from the previous page)

ples were mixed with dry KBr, ground into fine powder, and pressed into pellets.

The equilibrium degree of swelling for postcured materials in tetrahydrofurane (THF) was measured volumetrically, at room temperature. Soluble components of postcured materials were extracted by Soxhlet extraction in refluxing THF and characterized by FTIR.

RESULTS AND DISCUSSION

Heat of reaction and degree of crosslinking

Figure 1 shows the residual heats of reaction for the investigated systems after different curing times at room temperature, as determined by dynamic DSC characterization. It can be seen that for all investigated systems residual heat of curing decreases, and its max-

imum shifts toward higher temperatures. For systems G0E1, G1E2, and G1E1 an endothermic peak is observed, which is superposed on T_g of an epoxy-amine matrix. Since curing temperature, T_c , is lower than the maximum glass transition temperature, $T_{g^{max}}$ of the epoxy resin (89°C, see Fig. 3), in time T_g becomes equal to T_c , and the system vitrifies. Further curing after vitrification causes a slow increase of T_g with the annealing time and structural relaxation in the matrix. When the material is heated to temperatures above T_g , the endothermic peak appears as a consequence of those relaxation processes. Under these conditions residual curing starts just beyond the endothermic relaxation peak.²² In the hybrid systems with higher GLYMO content (G2E1 and G1E0) endothermic relaxation peak does not appear. As can be seen from thermograms in Figure 1, only epoxy resin G0E1 has

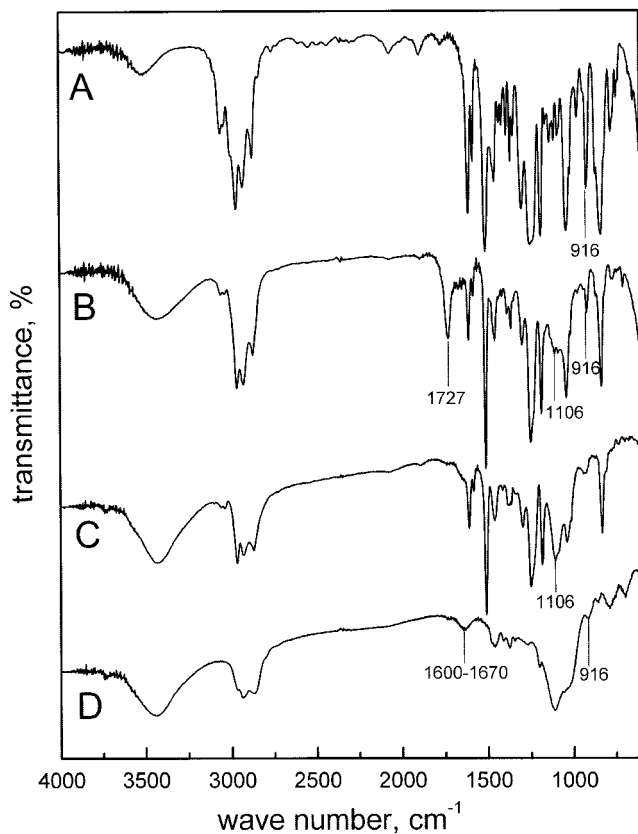
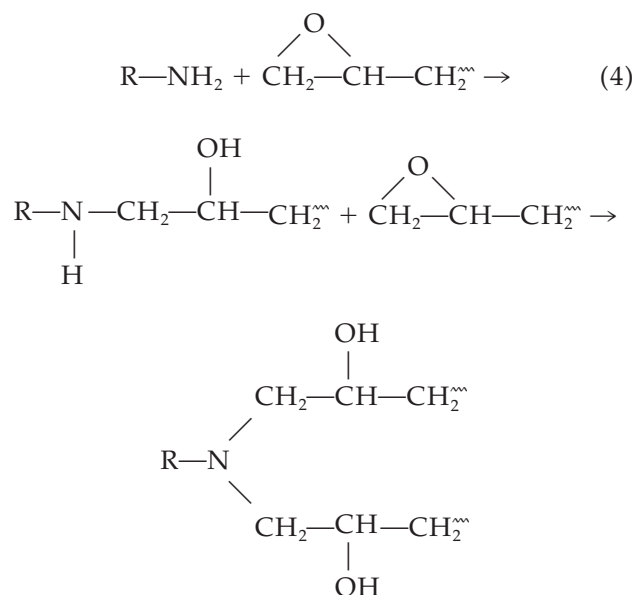


Figure 2 FTIR spectra: (A) DGEBA; (B) extracted component of G1E1; (C) fully cured G0E1; (D) fully cured G1E0.

noticeable residual heat of curing even after 30-day curing at room temperature, indicating quenching of the crosslinking reaction due to vitrification. Systems

G1E2, G1E1, and G2E1 are completely crosslinked after 4 days of curing and after 5 days for G1E0. In Table II, the heats of curing for freshly prepared mixtures and the temperatures of exothermic peaks are listed. Peak temperature increases with GLYMO content.

Several reviews on the mechanism and kinetics of epoxy-amine reactions are available.²³⁻²⁶ It is generally agreed that, in the epoxy-amine systems in which amine is present in stoichiometric quantity, the two-stage addition of amine to epoxy is the most important reaction:



This reaction is catalyzed by Lewis acids, phenols, and alcohols. The hydroxyl groups generated by the

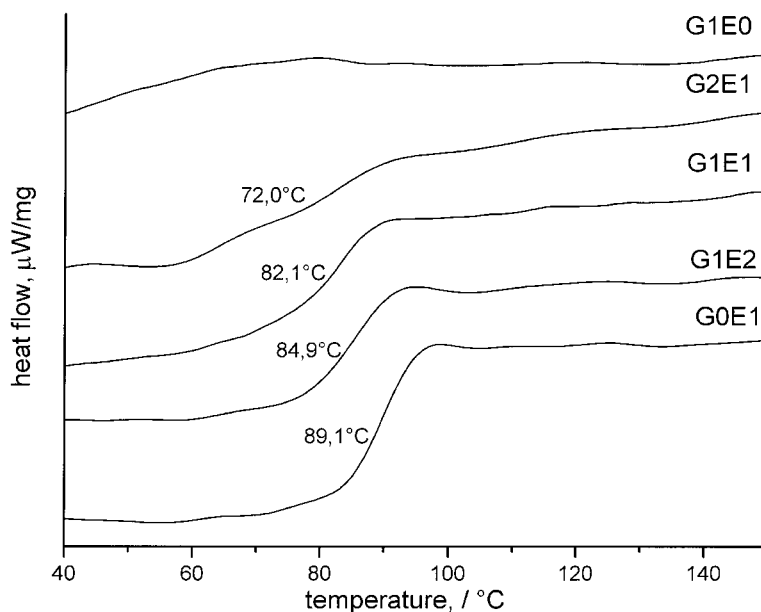


Figure 3 Comparison of glass transition temperatures for investigated materials.

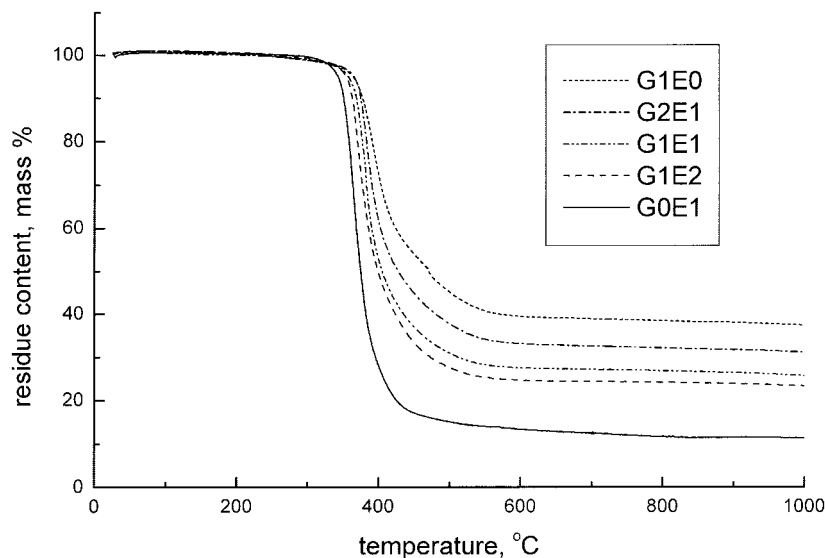


Figure 4 TGA curves of investigated materials, heated with 10 Kmin^{-1} in nitrogen atmosphere.

amine-epoxide addition are active catalysts themselves, so the curing reaction usually shows an accelerating rate in its early stages, typical of auto catalysis. If the heat of curing for G0E1 is converted into joules per equivalent of epoxide, the resulting value of 113.4 kJ/mol is in accordance with the value for epoxy-amine reaction found in literature.²⁷ This also suggests that both primary and secondary amine groups of Jeffamine react. This is confirmed by results of FTIR, shown in Figure 2. If the spectra of uncured DGEBA [Fig. 2(A)] and completely cured epoxy G0E1 [Fig. 2(C)] are compared, the complete disappearance of characteristic epoxide band at 916 cm^{-1} and appearance of band at $1,106 \text{ cm}^{-1}$ characteristic of the $=\text{CH}-\text{OH}$ group formed as a result of the epoxy ring opening in reaction with amine [eq. (4)] is visible.

The epoxy group in GLYMO reacts with the amino groups as shown earlier. Supposing that the influence of the sol-gel process is negligible in the fresh mixtures,¹² the heat of the epoxy-amine curing reaction for the G1E0 system was determined and converted to joules per equivalent mole. The resulting value of 52.6 kJ/mol suggests that only 47%, or approximately half, of epoxy groups of GLYMO reacted with amine. The

FTIR spectrum of completely crosslinked G1E0 [Fig. 2(D)] still shows the presence of unreacted epoxide, as well as the broad band in the $1,600\text{--}1,670 \text{ cm}^{-1}$ interval, characteristic of amine groups. Therefore it was presumed that the reaction of epoxy rings with primary amines is dominant, while the reactivity of secondary amine groups is significantly decreased due to steric hindrances of the rigid inorganic network. Presence of broad overlapping bands between $1,000$ and $1,200 \text{ cm}^{-1}$ confirms the existence of a silicon-oxide network formed by the sol-gel process inside the material.

Presuming that molar heat of curing for G0E1 (113.4 kJ/mol) corresponds to complete conversion of epoxy groups, maximum conversion, α_{max} for G0E1 was taken to be 1.00. For G1E0, the theoretical molar heat of reaction was taken to be 56.7 kJ/mol (50% of 113.4 kJ/mol), following the supposition that only one half of amine groups can react with epoxy, and the theoretical heat of reaction per gram of reactive mixture was calculated accordingly. Theoretical heats of reactions for systems G1E2, G1E1, and G2E1 were then calculated by simple linear combination of heats of

TABLE III
Residue Content and Temperature of DTG Maxima

Material	Residue content (mass %)			DTG maxima ($^{\circ}\text{C}$)	
	N_2 atmosphere	Air atmosphere	Calculated	N_2 atmosphere	Air atmosphere
G0E1	11.32	0.04	0.00	363	384, 408, 581
G1E2	23.31	6.29	6.72	369	390, 397, 669
G1E1	25.63	9.11	10.14	382	396, 453, 693
G2E1	31.09	14.15	13.59	383	401, 456, 644
G1E0	37.38	28.25	20.54	394, 471	401, 467

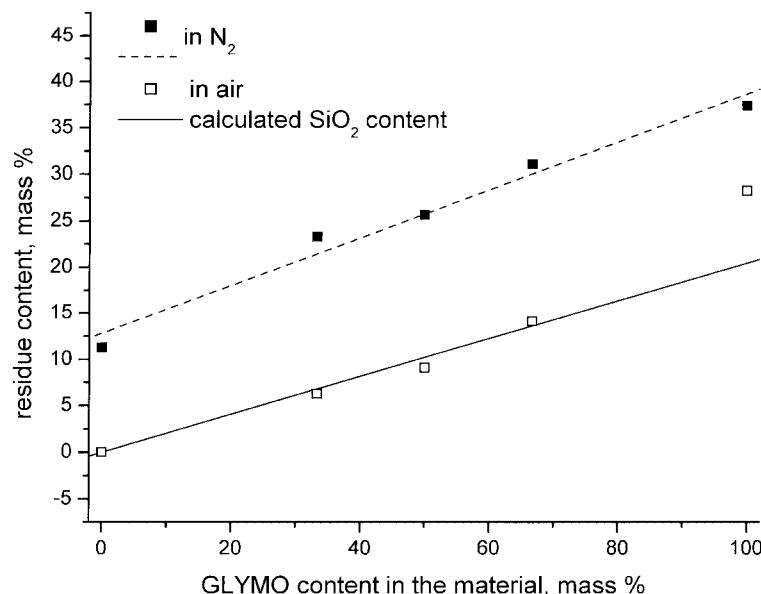


Figure 5 Residue content as a function of GLYMO content in material.

reaction for G1E0 and G0E1, and α_{\max} was calculated according to the following equation:

$$\alpha_{\max} = \frac{\Delta H_T(\text{meas.})}{\Delta H_T(\text{theor.})} \quad (5)$$

Theoretical total heats of cure and maximum conversions for all systems are displayed in Table II. Maximum conversion increases in order G1E1 < G1E2 < G2E1 < G1E0.

The higher maximum conversion suggests a higher level of organic phase crosslinking in the material. This is confirmed by the results of swelling in THF. Equilibrium degree of swelling, Q_{\max} , was calculated according to eq. (6),²⁸ where V_0 is the initial volume and V_{\max} is the equilibrium swollen volume of the specimen. The results are also given in Table II. As was expected, materials with higher conversion/crosslinking have a lower equilibrium degree of swelling.

$$Q_{\max} = \frac{V_{\max} - V_0}{V_{\max}} \quad (6)$$

Soxhlet extraction of all materials by THF showed that only G1E1 contains a soluble component, identified by FTIR [Fig. 2(B)] to be an oligomer of DGEBA. The band at $1,727 \text{ cm}^{-1}$ is a result of THF polymerization during the extraction, as proven by blank extraction.

Contribution of the inorganic phase to crosslinking density in hybrid materials is certainly significant. The formation of a silicon-oxide network in all hybrid materials was confirmed by IR spectroscopy, but fur-

ther conclusions require additional research, which will be the focus of future work.

Glass transition

Glass transitions of all five materials are compared in Figure 3. With increased content of inorganic phase, glass transition shifts toward lower temperatures, and finally disappears in G1E0. This is caused by the already established lower degree of organic phase crosslinking in hybrid materials compared to unmodified epoxy resin. Also, products of GLYMO hydrolysis and condensation are retained inside the polymer matrix, acting as plasticizers.¹⁵

Thermogravimetric analysis

TGA thermograms for the investigated system obtained in a nitrogen environment are shown in Figure 4. The degradation temperature at which drastic weight loss occurs increases with the increase in the GLYMO content in the investigated blends, as shown by peak values of derivated thermograms (DTG) listed in Table III. DTG peaks for the investigated systems obtained in a synthetic air environment are also listed in Table III, and while the degradation kinetics in an oxidizing atmosphere is obviously more complicated, it shows the same trend toward higher degradation temperatures. The residues at $1,000^\circ\text{C}$ after degradation in an oxidizing atmosphere are a measure of the amount of silica present in the hybrids, and the values obtained experimentally are comparable to calculated values of SiO_2 content in hybrids. Only G1E0 residue

mass deviates remarkably from the calculated value, since the organic component, being partially entrapped in a dense inorganic network, cannot fully oxidize. This is also obvious from the color of the residue, which is grayish-black instead of white. The residue mass at 1,000°C after degradation in nitrogen atmosphere shows linear dependence on the inorganic content of hybrids, as shown in Figure 5. The increase is steeper than that of calculated SiO₂ content, showing that presence of the inorganic phase additionally increases the degradation resistance of hybrid materials.

CONCLUSION

Organic-inorganic hybrid materials based on DGEBA and GLYMO were prepared, using a poly(oxypropylene) diamine Jeffamine D230 as a curing agent. Materials were studied by DSC, TGA, infrared spectroscopy, swelling in THF, and Soxhlet extraction in THF. Maximum conversion of epoxy groups, and also the degree of organic phase crosslinking, increase in the order G1E1 < G1E2 < G2E1 < G1E0. This is probably caused by steric hindrances between the organic and inorganic components, coupled with organic chain immobilization upon the inorganic phase. Epoxy groups of GLYMO react primarily with primary amines, while the reaction with secondary amines is negligible due to steric hindrances of the rigid inorganic network. The soluble uncrosslinked component of hybrid materials does not contain inorganic phase. Presence of the inorganic phase results in lowering of glass transition temperature in hybrid materials, due to a lesser degree of crosslinking and the plasticizing influence of products of the sol-gel process. TGA showed that the inorganic phase increases thermal stability of hybrid materials, shifting the degradation to higher temperatures. Residue mass increases linearly with the content of inorganic phase, except for G1E0, where the organic phase trapped inside a dense inorganic network cannot completely combust.

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