PREPARATION OF EPOXY-BASED ORGANIC-INORGANIC HYBRIDS BY SOL-GEL PROCESS

Jelena Macan, Hrvoje Ivanković, Marica Ivanković, Helena Jasna Mencer
Faculty of Chemical Engineering and Technology, University of Zagreb
HR-10001 Zagreb, Marulićev trg 19, p.p. 177, Croatia

Abstract: Epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) and poly(oxypropylene) diamine Jeffamine D230 was modified by adding modified silicon alkoxide, 3-glycidyloxypropyltrimethoxysilane (GLYMO), in the reaction mixture. Inorganic phase inside the organic matrix is formed by sol-gel process, which includes hydrolysis and condensation of alkoxy groups of GLYMO. Thus obtained hybrid organic-inorganic materials were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), infrared spectroscopy, swelling in tetrahydrofuran (THF) and Soxhlet extraction in THF. It was found that both the final conversion of epoxy groups and the final degree of cross-linking in the material depend on content of inorganic phase in the hybrid material. Epoxy groups of GLYMO were found to react only with primary amine. The inorganic phase presents a steric hindrance to full cross-linking of epoxy groups. The organic chains are also immobilised by the inorganic phase, and its presence improves the temperature stability of hybrid materials. Products of GLYMO hydrolysis combined with lesser degree of cross-linking in organic matrix lower the glass transition temperature of hybrid materials.

Key words: nanocomposites, silica, sol-gel process, structure, thermosets

1. INTRODUCTION

The organic-inorganic hybrids obtained by sol-gel process have gained increasing attention of researches. The main hypothesis of the research is that hybrid materials, with inorganic phase dispersed on molecular or nano level and often interconnected with the polymeric matrix, have superior properties compared to classical polymer composites. In sol-gel process, inorganic phase is formed *in situ*, by hydrolysis and condensation of silicon alkoxides by following reactions, where R represents an alkyl group [1]:

$$\equiv\text{Si-OR} + H_2O \Leftrightarrow \equiv\text{Si-OH} + \text{ROH} \qquad (1)$$

$$\equiv\text{Si-OR} + \equiv\text{Si-OH} \rightarrow \equiv\text{Si-O-Si}\equiv + \text{ROH} \qquad (2)$$

$$\equiv\text{Si-OH} + \equiv\text{Si-OH} \rightarrow \equiv\text{Si-O-Si}\equiv + H_2O \qquad (3)$$

Hydrolysis and condensation reactions are acid or base catalysed. The great flexibility of sol-gel process enables preparation of organic-inorganic hybrids with diverse organic components [2-9].

In this work, preparation of organic-inorganic hybrids based on epoxy resins is described. Epoxy resins are high-performance polymers with wide area of application, which could be further expanded by modifying properties of the final material. In this work, 3-glycidyloxypropyltrimethoxysilane (GLYMO) was used as inorganic precursor for preparation of epoxy-silica hybrids. GLYMO is an organofunctional alkoxysilane 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.

2. EXPERIMENTAL

Organic-inorganic hybrid materials were synthesized from an epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Epikote 828 EL, Shell Chemicals) with the epoxy equivalent weight of 190 g/mol, and 3-glycidyloxypropyltrimethoxysilane (GLYMO, 98%, Aldrich Chemicals), with poly(oxypropylene) diamine (Jeffamine D230, Huntsman Corporation) as a curing agent for epoxy and as a basic catalyst of GLYMO hydrolysis. The materials were used as received.

DGEBA/Jeffamine and GLYMO/Jeffamine systems with a stoichiometric amount of Jeffamine D230 (30 phr and 23.8 phr, respectively) were prepared. To prepare hybrid materials, DGEBA and GLYMO were blended in weight ratios of 1:2; 1:1; and 2:1 at room temperature, with a stoichiometric amount of Jeffamine D230 added as a curing agent. Designations of all four hybrids and pure epoxy-amine system are listed in Table I. Curing was effected at room temperature, making use of air humidity for GLYMO hydrolysis. The materials were postcured for 24 h at 120°C in an oven.

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. 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. Dynamic DSC experiments were also performed to determine the glass transition temperature, T_g, of the completely cured material. 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 1000°C at a heating rate of 10 Kmin^{-1} in a nitrogen gas flow. FTIR spectra of pure ingredients and postcured hybrid samples were obtained on a Nicolet Magna-IR 760 FT-IR. Each spectrum from 4000 to 600 cm^{-1} was averaged over 16 scans at 4 cm^{-1} resolution. The liquid samples were coated on NaCl plates.

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.

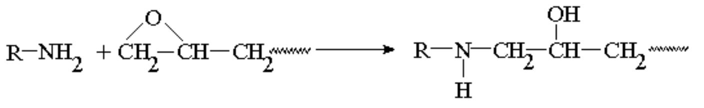
3. RESULTS AND DISCUSSION

The residual heats of reaction for the investigated systems after curing at room temperature for certain periods of time, as determined by dynamic DSC characterization, are shown in Fig. 1. For all investigated systems residual heat of curing is seen to decrease, and its maximum shift towards higher temperatures. An endothermic relaxation peak superposed on T_g of epoxy-amine matrix is observed for systems G0E1, G1E2 and G1E1, but not in the hybrid systems with higher GLYMO content. Only epoxy resin G0E1 has noticeable residual heat of curing even after 30 day curing at room temperature, indicating quenching of crosslinking reaction due to vitrification. Systems G1E2, G1E1 and G2E1 are completely crosslinked after 3 days of curing at room temperature, and G1E0 after 4 days. In Table I, the heats of curing for freshly prepared mixtures and the temperatures of exothermic peaks are listed. Peak temperature increases with GLYMO content.

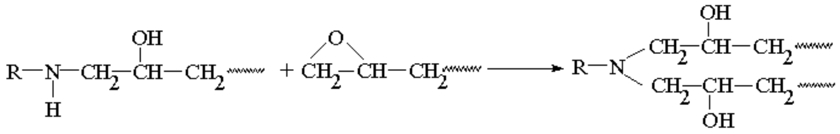
Table I. *Composition and Properties of Prepared Materials*

Material	GLYMO/ DGEBA mass ratio	DSC maxima T_{max} [°C]	ΔH_T [Jg^{-1}]		α_{max}	Q_{max}	Soxhlet [mass %]	T_g [°C]
			meas.	theor.				
G0E1	0/1	127	448	448	1.00	0.366	0.0	---
G1E2	1/2	138	331	363	0.91	0.466	0.0	72.0
G1E1	1/1	145	247	321	0.77	0.458	0.7	82.1
G2E1	2/1	155	255	278	0.92	0.354	0.0	84.9
G1E0	1/0	177	180	194	0.93	0.207	0.0	89.1

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:



$$R{-}NH_2 + \overset{O}{CH_2{-}CH}{-}CH_2{\sim\sim} \longrightarrow R{-}\underset{H}{N}{-}CH_2{-}\overset{OH}{CH}{-}CH_2{\sim\sim} \qquad (4)$$



$$R{-}\underset{H}{N}{-}CH_2{-}\overset{OH}{CH}{-}CH_2{\sim\sim} + \overset{O}{CH_2{-}CH}{-}CH_2{\sim\sim} \longrightarrow R{-}N\begin{cases} CH_2{-}\overset{OH}{CH}{-}CH_2{\sim\sim} \\ CH_2{-}\underset{OH}{CH}{-}CH_2{\sim\sim} \end{cases} \qquad (5)$$

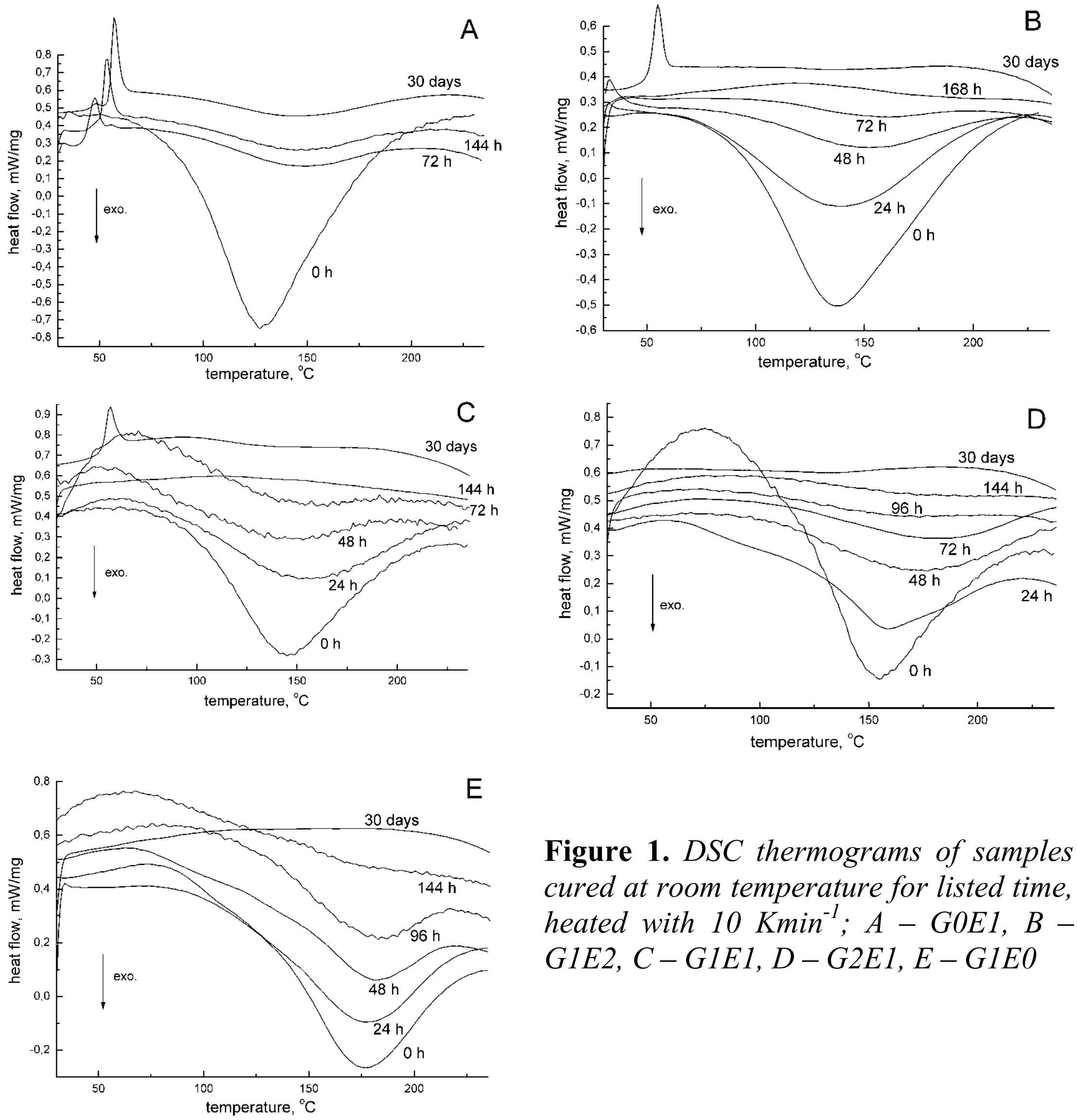


Figure 1. *DSC thermograms of samples cured at room temperature for listed time, heated with 10 Kmin^{-1}; A – G0E1, B – G1E2, C – G1E1, D – G2E1, E – G1E0*

Heat of curing for G0E1 converted into joules per equivalent of epoxide is 113.4 kJ/mol, which is in accordance with value for epoxy-amine reaction found in literature [10]. This also suggests that both primary and secondary amine groups of Jeffamine react, which is confirmed by FTIR, as shown in Fig.2. If the spectra of uncured DGEBA (Fig.2A) and completely cured epoxy G0E1 (Fig.2C) are compared, the complete disappearance of characteristic epoxide band at 916 cm^{-1} and appearance of band at 1106 cm^{-1} as a result of epoxy crosslinking is visible. Heat of epoxy-amine curing reaction for the G1E0 system was determined, supposing that the influence of sol-gel process is negligible in the fresh mixtures [11]. Resulting value of 52.6 kJ/mol suggests that only 47%, or approximately half, of epoxy groups of GLYMO reacted with amine. FTIR of completely crosslinked G1E0 (Fig.2D) indicates that in the G1E0 system the primary amine-epoxide reaction is dominant, since the spectrum still shows the presence of unreacted epoxide, as well as the broad band in 1600-1670 cm^{-1} interval characteristic of secondary amine groups. Presence of broad overlapping bands between 1000 and 1200 cm^{-1} confirms the existence of silicon-oxide network formed by sol-gel process inside the material.

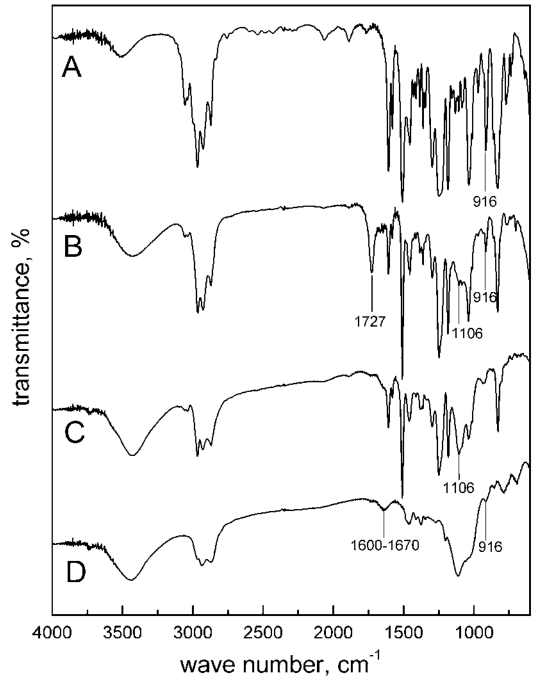


Figure 2. *FTIR spectra; A – DGEBA, B – extracted componet of G1E1, C – fully cured G0E1, D – fully cured G1E0*

Presuming that total heat of curing for G0E1 corresponds to 100% conversion of epoxy groups, and taking 56.7 kJ/mol (50% of 113.4 kJ/mol) to be theoretical heat of reaction for G1E0, theoretical total heats of reaction were calculated for all systems, and maximum conversion, $\alpha_{\max}$, was calculated according to the following equation:

$$\alpha_{\max} = \frac{\Delta H_T(meas.)}{\Delta H_T(theor.)} \qquad (6)$$

Theoretical total heats of cure and maximum conversions for all systems are displayed in Table I. Maximum conversion increases in order G1E1<G1E2<G2E1<G1E0. The higher maximum conversion suggests higher level of crosslinking in the material. This is confirmed by the results of swelling in tetrahydrofurane (THF). Equilibrium degree of swelling, $Q_{\max}$, was calculated according to equation (7) [12], where V_0 is the initial volume, and $V_{\max}$ the equilibrium swollen volume of the specimen. The results are also given in Table I. As was expected, materials with higher conversion/crosslinking have lower equilibrium degree of swelling. Soxhlet extraction of all materials by THF showed that only G1E1 contains soluble component, identified by FTIR (Fig.2B) to be oligomer of DGEBA.

$$Q_{\max} = \frac{V_{\max} - V_0}{V_{\max}} \qquad (7)$$

Incomplete crosslinking in the hybrid systems is probably caused by steric hindrances between the organic and inorganic component. Glass transitions of all 5 materials are listed in Table I. Glass transition shifts towards lower temperatures with increased content of inorganic phase, to finally disappear in G1E0. This is caused by lower degree of crosslinking in hybrid materials, as well as by plasticizing effect of the products of GLYMO hydrolysis and condensation [13].

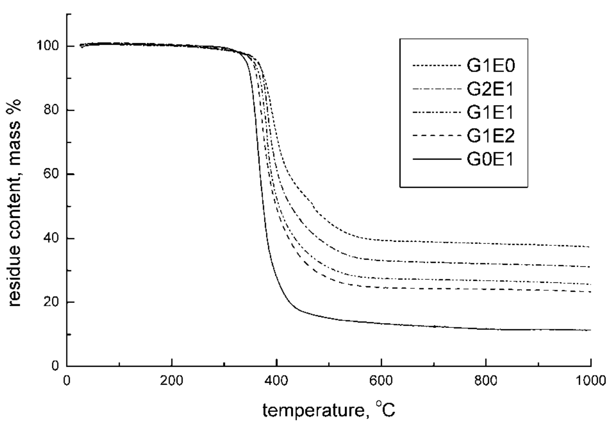


Figure 3. *TGA curves of investigated materials, heated with 10 Kmin^{-1} in nitrogen atmosphere*

TGA thermograms for the investigated system obtained in a nitrogen environment are shown in Figure 3. The degradation temperature at which drastic weight loss occurs increases with the increase of the GLYMO content in the investigated blends.

4. CONCLUSIONS

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 tetrahydrofurane (THF) and Soxhlet extraction in THF. Maximum conversion of epoxy groups and the degree of crosslinking increase in the order G1E1<G1E2<G2E1<G1E0. This is probably caused by steric hindrances between the organic and inorganic component, coupled with organic chain immobilisation upon inorganic phase. Epoxy groups of GLYMO react primarily with primary amines, while the reaction with secondary amines is negligible. Soluble uncrosslinked component of hybrid materials does not contain inorganic phase. Presence of inorganic phase results in lowering of glass transition temperature in hybrid materials, due to lesser degree of crosslinking and plasticizing influence of products of sol-gel process. TGA showed that inorganic phase increases thermal stability of hybrid materials, shifting the degradation to higher temperatures.

References

1. R. C. Mehrotra, in *Chemistry, Spectroscopy and Applications of Sol-Gel Glasses*, R. Reisfeld and C. K. Jørgensen, Ed., Springer-Verlag, Berlin, 1992, p. 1.
2. B. M. Novak, *Adv. Mater.*, **5** (1993) 422
3. E. Girardreydet, T. M. Lam and J. P. Pascault, *Macromol. Chem. Phys.*, **195** (1994) 149
4. J. E. Mark, *J. Appl. Polym. Sci.*, **58** (1995) 1135
5. C. L. Jackson, B. J. Bauer, A. I. Nakatani and J. D. Barnes, *Chem. Mater.*, **8** (1996) 727
6. J. E. Mark, *Polymer*, **38** (1997) 4523
7. D. W. McCarthy, J. E. Mark and D. W. Schaefer, *J. Polym. Sci. Part B Polym. Phys.*, **36** (1998) 1167
8. L. Matejka, O. Dukh and J. Kolarik, *Polymer*, **41** (2000) 1449
9. W. Zhou, J. E. Mark, M. R. Unroe and F. E. Arnold, *J. of Appl. Polym. Sci.*, **79** (2001) 2326
10. J. M. Barton, in *Epoxy Resins and Composites I*, K. Dusek, Ed., Advances in Polymer Science vol. 72, Springer-Verlag, Berlin, 1985, p. 112.
11. A. Serier, J. P. Pascault and T. M. Lam, *J. Polym. Sci. Part A Polym. Chem.*, **29** (1991) 209
12. H. J. Mencer and Z. Gomzi, *European Polym. J.*, **30** (1994) 33
13. L. Mascia and T. Tang, *J. Sol-Gel Sci. Technol.*, **13** (1998) 405