Epoxy networks based on solutions of silsesquioxanes functionalized with 3-glycidoxypropyl groups in diglycidylether of bisphenol A (DGEBA)

Adriana N. Mauri, Carmen C. Riccardi, Roberto J. J. Williams (✉)

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, (7600) Mar del Plata, Argentina
e-mail: williams@fi.mdp.edu.ar

Summary

In previous publications we reported the synthesis and characterization of silsesquioxanes derived from the hydrolytic condensation of (3-glycidoxypropyl) trimethoxysilane (GPMS) using diglycidylether of bisphenol A (DGEBA) as a solvent [1,2]. The reaction product has aliphatic epoxy groups supplied by the silsesquioxane and aromatic epoxy groups supplied by the solvent. Solutions containing 0, 25 and 50% aliphatic epoxy groups, were cured with different hardeners: methyltetrahydrophthalic anhydride (MTHPA), ethylenediamine (EDA) and benzyldimethylamine (BDMA). Silsesquioxane-modified epoxy networks showed a significant increase in the elastic modulus in the rubbery state, the abrasion resistance and the development of strain hardening in uniaxial compression tests.

Introduction

The synthesis of high-molar-mass silsesquioxanes based on (3-glycidoxypropyl) trimethoxysilane (GPMS), using diglycidylether of bisphenol A (DGEBA) as a solvent, has been described in recent papers [1,2]. These silsesquioxanes may be described by the generic formula $[RSiO_{1.5-x-y}(OH)_{2x}(OCH_3)_{2y}]_n$, where R = (3-glycidoxypropyl), is an aliphatic epoxy group. A multimodal distribution of molar masses was observed by size exclusion chromatography (SEC), with relative maxima at about M = 1400, 4500 and 24000, based on polystyrene standards. The integrity of

epoxy rings supplied by GPMS and DGEBA, during the synthesis, as well as the presence of residual (OCH$_3$) groups, was confirmed by ^{1}H NMR [2].

The resulting solution may be regarded as a silsesquioxane-modified DGEBA, where the modifier supplies flexible organic structures (aliphatic epoxy groups), covalently bonded to relatively rigid inorganic structures (usually visualized as combinations of incompletely condensed polyhedra and ladder-like fragments [2]). Epoxy networks were obtained from solutions containing 0, 25 and 50% of epoxy groups supplied by the silsesquioxane, using different hardeners: methyltetrahydrophthalic anhydride (MTHPA), ethylenediamine (EDA) and benzyldimethylamine (BDMA). Dynamic mechanical analysis, uniaxial compression and abrasion tests were performed on the resulting epoxy networks, to analyze the main effects produced by the incorporation of the silsesquioxane in the formulation.

Experimental

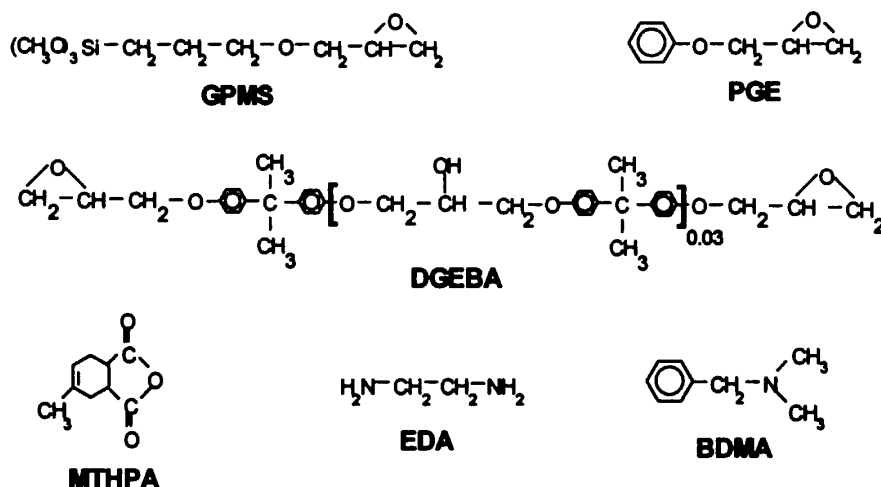*Synthesis of the silsesquioxane in a DGEBA solution*

Figure 1. Chemical structures of the silane (GPMS), the bifunctional epoxy monomer (DGEBA) and different hardeners: an anhydride (MTHPA), a diamine (EDA) and a tertiary amine (BDMA)

The synthesis has been described in detail elsewhere [1,2]. Briefly, (3-glycidoxypropyl)trimethoxysilane (GPMS, Sigma; Fig. 1) was hydrolytically

condensed in three steps. The first one was carried out in tetrahydrofuran (THF) solution at 50 °C during 24 h, using HCOOH (0.1 N) as catalyst and keeping the molar ratio $H_2O/Si = 3$. The second step was performed by adding diglycidylether of bisphenol A (DGEBA, MY790 Ciba; Fig.1), in an amount such that 25% or 50% of the epoxy groups were contributed by the silsesquioxane. The hydrolytic condensation was continued for another 24 h at 70 °C (THF and other volatiles were removed in this step). The final step was performed using the following heating schedule: 3 h at 75 °C, 6 h at 105 °C, and 6 h at 140 °C, leading to the final product.

Silsesquioxane-modified epoxy networks

Three different series of silsesquioxane-modified epoxy networks were prepared.

The first series was produced by adding a stoichiometric amount of methyltetrahydrophthalic anhydride (MTHPA, HY 918 Ciba; Fig. 1) and 0.04 moles of benzyldimethylamine (BDMA, Sigma; Fig. 1), per mol of epoxy groups, as initiator of the epoxy-anhydride polymerization. The following cure schedule was used: 24 h at 70 °C, 3 h at 75 °C, 6 h at 105 °C and 6 h at 140 °C. The resulting materials will be denoted as A(0), A(25) and A(50), where the number between parenthesis indicates the percentage of epoxy groups supplied by the silsesquioxane; e.g., A(0) means the unmodified DGEBA - MTHPA system.

The second series was obtained by using a stoichiometric amount of ethylenediamine (EDA, Sintorgan; Fig. 1). The cure schedule was 1 h at 50 °C and 2 h at 120 °C. The resulting materials will be called B(0), B(25) and B(50), depending on the percentage of epoxy groups supplied by the silsesquioxane.

The third series was obtained by the homopolymerization of epoxy functionalities initiated by the addition of 0.06 moles of BDMA per mol of epoxy groups. The cure was performed by heating 6 h at 120 °C. This led to samples C(0), C(25) and C(50).

Mass fractions of the silsesquioxane in every formulation are shown in Table 1.

Dynamic-mechanical thermal analysis (DMTA)

Plaques for subsequent dynamic mechanical characterization were obtained in a mold consisting of two glass plates coated with siliconized paper, spaced by a 2.5-mm rubber cord, and held together with clamps. Specimens with dimensions 20 mm x 3.3

mm x 2.5 mm, were machined from the plaques. Dynamic mechanical spectra were obtained with a Perkin-Elmer DMA-7 system, operating at 1 Hz in the three-point-bending mode at a heating rate of 10 °C min^{-1}.

Abrasion resistance

Specimens with dimensions 6 mm x 25 mm x 50 mm were machined from plaques obtained using a 6-mm rubber cord as spacer. Their abrasion resistance was determined using a dry sand / rubber wheel apparatus (ASTM G65-91, Procedure D). Four to six samples of every formulation were tested.

Uniaxial compression

Cylindrical compression-test specimens with a diameter D = 4 mm and a length L = 6 mm, were machined from plaques obtained using a 6-mm rubber cord as spacer. They were deformed under uniaxial compression between metallic plates lubricated with molybdenum disulphide, in a Shimadzu Autograph S55-C universal testing machine. The crosshead displacement rate was 1 mm min^{-1} and the actual displacement was measured using an LVDT placed very close to the specimen. The true strain was obtained as the natural logarithm of the initial length divided by the instantaneous length while the true stress was defined in terms of the instantaneous cross-sectional area, obtained assuming a constant volume deformation. At least three samples of every formulation were tested and a very good reproducibility was obtained.

Results and discussion

From DMTA results, the following parameters were determined: glass transition temperature (T_g), defined as the maximum in tan δ; glassy modulus at 25 °C (E'_G); and rubbery modulus at T_g + 30 °C (E'_R). Table 1 shows the values obtained for every sample and Figures 2 to 4 illustrate the influence of the silsesquioxane (SSQO) addition on E' vs. T curves for each one of the series.

A single tan δ peak was observed for every silsesquioxane-modified epoxy network, meaning that no phase separation was produced. The glass transition temperature was slightly shifted either to lower or higher temperatures due to a counterbalance between

the flexibility associated with the aliphatic epoxy groups and the increase in crosslink density and rigidity introduced by the inorganic structures. The rubbery modulus exhibited a significant increase with the crosslink density, related to the mass fraction of silsesquioxane in the formulation. For B(50) and C(50), the difference between the glassy modulus and the rubbery modulus was less than one decade.

Table 1. Glass transition temperature defined at the maximum in tan δ (T_g), glassy modulus at 25 °C (E'_G), rubbery modulus at T_g + 30 °C (E'_R), and average weight loss in the abrasion tests, Δw, for the different materials.

Material	% aliphatic epoxies	mass% SSQO	E'_G (GPa)	T_g (°C)	E'_R (MPa)	Δw (mg)
A(0)	0	0	2.8	125	32	66
A(25)	25	12	3.2	123	53	54
A(50)	50	25	2.9	100	80	53
B(0)	0	0	1.9	113	35	79
B(25)	25	22	1.6	113	98	41
B(50)	50	45	1.3	104	187	43
C(0)	0	0	2.2	76	18	146
C(25)	25	23	2.0	89	69	90
C(50)	50	47	1.4	86	156	61

Table 1 shows the weight loss of every material in the abrasion test. The addition of the silsesquioxane produced a significant increase in the abrasion resistance (a decrease in the weight loss), particularly for series C where the unmodified formulation exhibited a very low abrasion resistance.

A correlation has been found between the abrasive wear rate of many polymers and the reciprocal of the product of the breaking strength and the elongation to break, as determined from conventional tensile tests [3]. Uniaxial compression tests are more useful than tensile tests for studying the stress - strain curve at large strains. As the stress is compressive, tensile fracture is suppressed and plastic yielding can be obtained in a material that under most conditions is brittle.
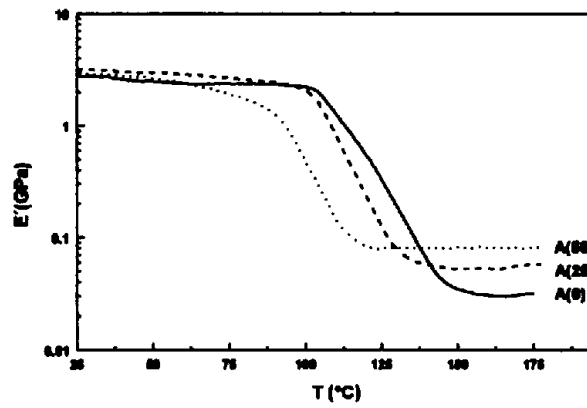
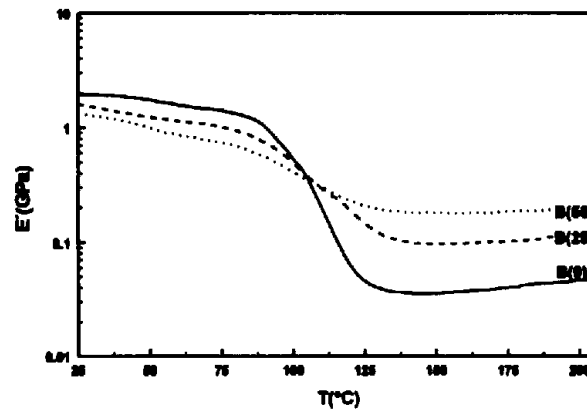**Figure 2.** E' vs. T curves for epoxy-anhydride formulations

Figure 3. E' vs. T curves for epoxy-diamine formulations
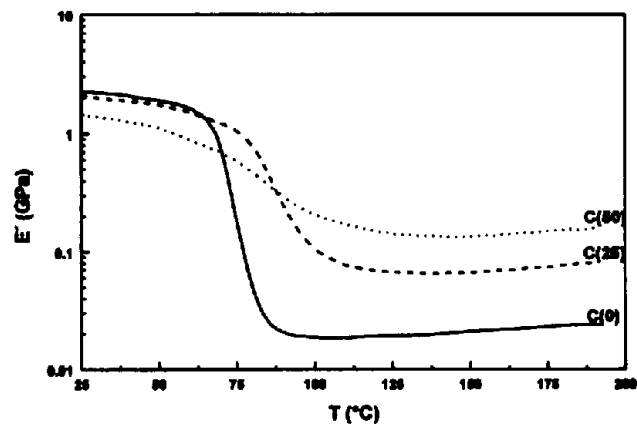

Figure 4. E' vs. T curves for epoxy-tertiary amine formulations

Figures 5 to 7 show true stress vs. true strain curves for the three families of materials. Materials B(50), C(25) and C(50), that exhibit a high increase in the abrasion resistance, also show a rapid orientation hardening effect that masks any possible strain softening [4]. The lower the yield stress the higher the orientation hardening effect produced by the silsesquioxane addition. Although the abrasion resistance should not be uniquely related to the orientation hardening effect, both properties are related to the increase in the energy necessary to produce large deformations, e.g., to detach parts of the sample in an abrasion test.
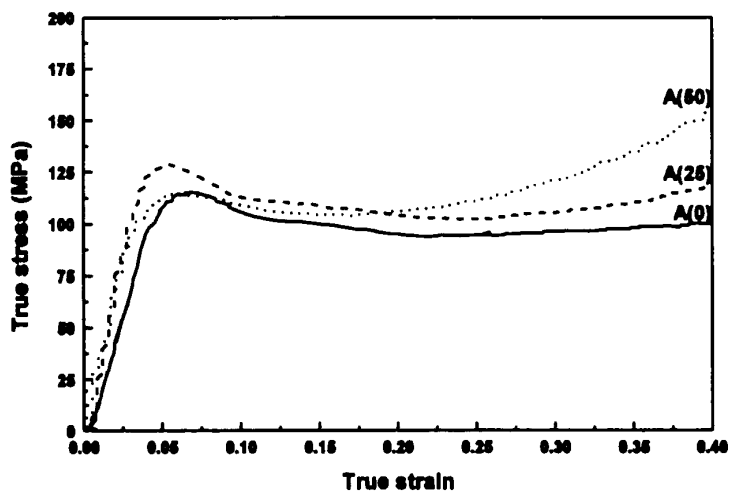

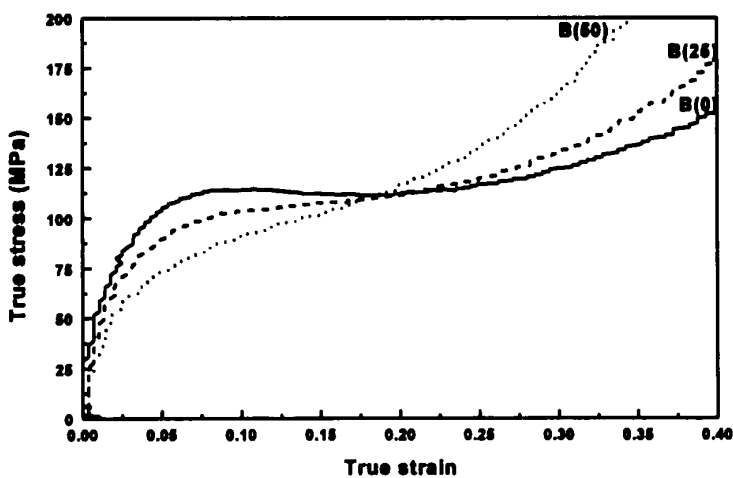**Figure 5.** True stress vs. true strain for epoxy-anhydride formulations

Figure 6. True stress vs. true strain for epoxy-diamine formulations
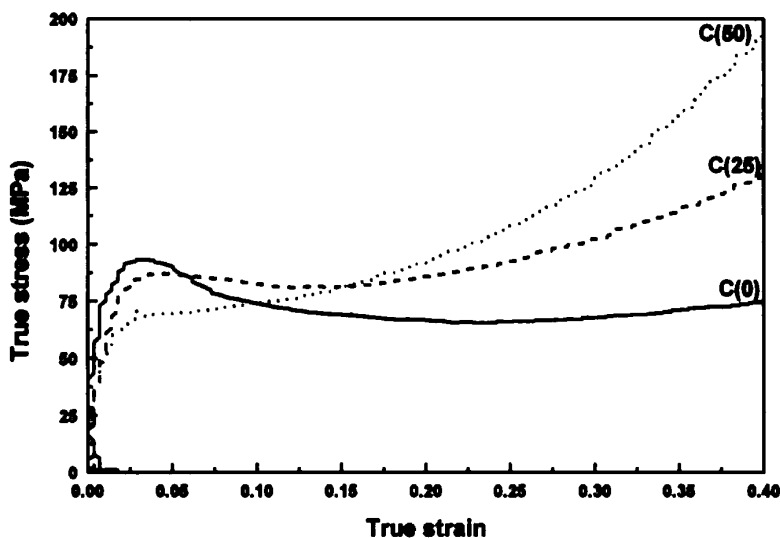
530

Figure 7. True stress vs. true strain for epoxy- tertiary amine formulations

Conclusions

Main effects produced by the incorporation of a silsesquioxane functionalized with aliphatic epoxy groups, in typical epoxy formulations were: a) a significant increase in the rubbery modulus associated to the increase in crosslink density, b) a significant increase in the abrasion resistance, and c) a rapid orientation hardening observed in uniaxial compression tests. Both b) and c) are related to the increase in the energy necessary to produce large deformations.

References

1. Mauri AN, Riccardi CC, Williams RJJ (2000) Macromol Symp 151:331
2. Eisenberg P, Erra-Balsells R, Ishikawa Y, Lucas JC, Mauri AN, Nonami H, Riccardi CC, Williams RJJ (2000) Macromolecules 33:1940
3. Lancaster JK (1973) Plast & Polym 41:297
4. Haward RN (1973) The post-yield behaviour of amorphous plastics. In: Haward RN (ed) The physics of glassy polymers. Applied Science Publisher, London:pp340-393