

Properties of Epoxy Networks Derived from the Reaction of Diglycidyl Ether of Bisphenol A with Polyhedral Oligomeric Silsesquioxanes Bearing OH-Functionalized Organic Substituents

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ABSTRACT: A polyhedral oligomeric silsesquioxane (POSS), consisting mainly of a mixture of octahedra, nonahedra, and decahedra with bulky and flexible organic substituents, with three secondary hydroxyls per organic group, was used to modify epoxy networks produced by the homopolymerization of diglycidyl ether of bisphenol A in the presence of benzyldimethylamine. Several physical, thermal, and mechanical properties of the cured materials containing 0, 10, 30, and 50 wt % POSS were determined. The addition of POSS increased the elastic modulus and the yield stress measured in uniaxial compression tests, mainly because of the increase in the cohesive energy density produced by hydrogen bonding through the hydroxyl groups. A constant yield stress/elastic modulus ratio equal to 0.03 was observed for different POSS concentrations and test temperatures. The glass-transition temperature decreased with POSS addition because of the flexibility of organic branches present in the POSS structure and the decrease in the crosslink density (determined from the rubbery modulus). Although a combination of a reduction in the glass-transition temperature (plasticization) with an increase in the glassy modulus (antiplasticization) is a well-known phenomenon, what is original is that in this case it was not the result of the suppression (or reduction in intensity) of subglass relaxations but was produced by an increase in the cohesive energy density. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 41: 1451–1461, 2003

Keywords: crosslinking; epoxy; networks; polyhedral oligomeric silsesquioxane (POSS); thermosets

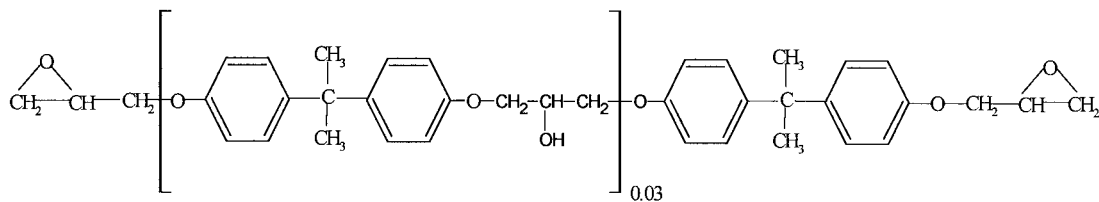
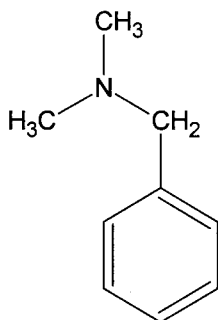
INTRODUCTION

Polyhedral oligomeric silsesquioxanes [POSS, or $(\text{RSiO}_{1.5})_n$, where $n = 6, 8, 10, \dots$] are nano-sized cage structures that can be incorporated into linear or thermosetting polymers to improve their thermal and oxidation resistance

and reduce flammability.^{1–11} According to the number of organic groups (R) bearing reactive functionalities, POSS can be classified as non-functional, monofunctional, or polyfunctional. Polyfunctional POSS can be polymerized to obtain polymer networks, with the POSS cage acting as the basic crosslinking unit.^{12–15} Epoxy networks have been synthesized from polyfunctional epoxy–POSS cages, either by photoinduced cationic polymerization¹² or by blending with an aliphatic diepoxide and curing with an aliphatic diamine.¹⁵

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**Epoxy Resin (DGEBA)****Initiator (BDMA)**

(a)

Figure 1. Chemical structures of (a) the epoxy monomer and tertiary amine and (b) a representative species of POSS (T_8).

This study addressed the synthesis and characterization of a new class of POSS-modified epoxy networks. The starting POSS consisted of a distribution of polyhedra, the main species being octahedra [$T_8 = (\text{RSiO}_{1.5})_8$], nonahedra [$T_9(\text{OH}) = (\text{RSi})_9\text{O}_{13}(\text{OH})$], and decahedra [$T_{10} = (\text{RSiO}_{1.5})_{10}$; R is a bulky organic substituent bearing three secondary hydroxyl groups]. The number of OH groups per cage was 24 for T_8 , 27 for $T_9(\text{OH})$, and 30 for T_{10} . The synthesis and characterization of this particular POSS was previously reported.^{16,17}

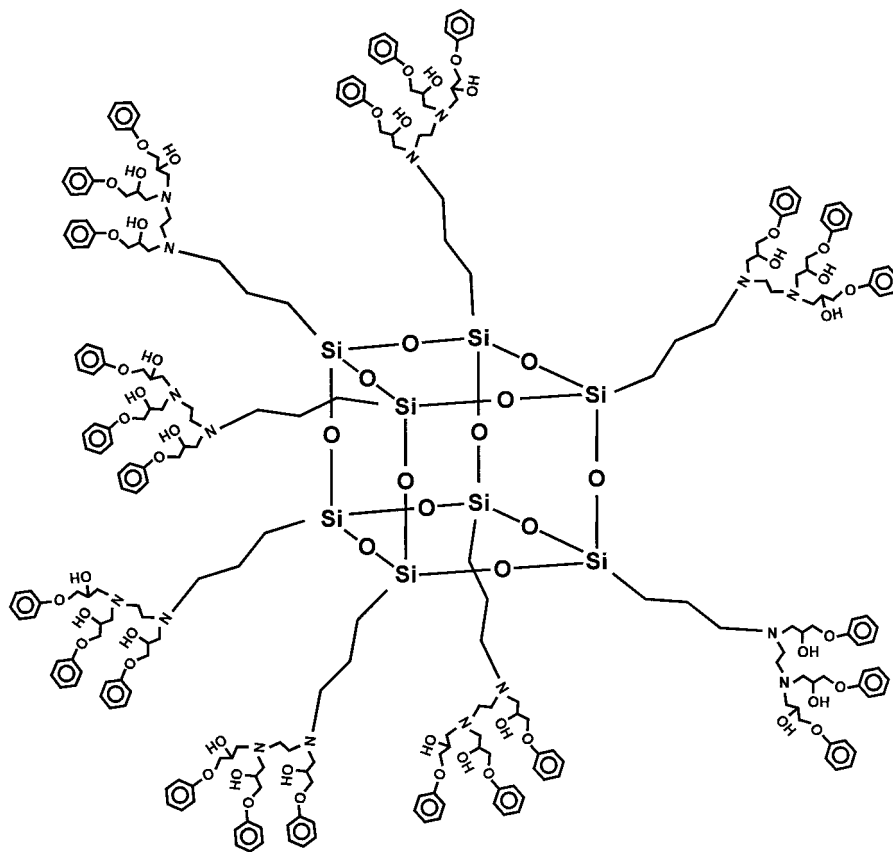
The epoxy network was built up by the reaction of the synthesized POSS with diglycidyl ether of bisphenol A (DGEBA) in the presence of a tertiary amine. The amine acted either as a catalyst of the epoxy-hydroxyl reaction with the regeneration of the OH group¹⁸ or as an initiator of the epoxy homopolymerization.^{19,20} In this last reaction, a chain-transfer step to the R'OH groups of POSS produced the covalent bonding of both monomers. Termination steps with the generation of terminal double bonds and extra OH groups were also present in this complex reaction mechanism.¹⁹⁻²³

The aim of this study was to examine the physical and mechanical properties of this class of POSS-modified epoxy networks as a function of the POSS mass fraction in the initial formulation.

EXPERIMENTAL

Materials and Sample Preparation

The chemical structures of the epoxy monomer, the tertiary amine, and a representative species of POSS are shown in Figure 1. The epoxy monomer, based on DGEBA (MY790, Ciba), had an epoxy equivalent weight of 174 g/mol. The 0.03 index in the repeating unit means that the epoxy monomer was a mixture of 97 mol % of the pure DGEBA and 3 mol % of the monomer with an index in the repeating unit equal to 1. The tertiary amine was benzyltrimethylamine (BDMA; Aldrich), used at a concentration of 0.06 mol/mol of epoxy groups. POSS was synthesized according to a procedure previously described.^{16,17} The main species were T_8 [structure shown in Fig.



T₈

(b)

Figure 1. (Continued from the previous page)

1(b)], $T_9(\text{OH})$, and T_{10} . It was an amorphous material with a glass-transition temperature ($T_g = 14\text{ }^\circ\text{C}$). The hydroxyl equivalent weight of POSS was 201.4 g/mol of C—OH.

Formulations containing 0, 10, 30, and 50 wt % POSS (A0 to A5 in Table 1) were cured for 3 h at 80 °C and then cured for 3 h at 120 °C. We machined the specimens for subsequent mechanical characterization from the molded materials (plates or cylinders) to reach their final dimensions and improve the surface finishing.

T_g

The T_g values of the cured samples were determined with differential scanning calorimetry

(DSC; Pyris 1, PerkinElmer). The onset of the transition during a heating scan at 10 °C/min, under nitrogen, was the selected value.

Mass Density (ρ)

The ρ values were determined with conventional pycnometry in water. Eight to ten determinations were carried out for each of the different cured formulations.

Elastic Modulus (E_G) and Yield Stress (σ_Y) in the Glassy State

The E_G and σ_Y values of the different cured samples in the glassy state were determined from

Table 1. Compositions of POSS-Modified Epoxy Networks

Sample	DGEBA (g)	POSS (g)	BDMA (g)	BDMA/Epoxy (Molar Ratio)	C-OH/Epoxy (Molar Ratio)
A0	95.6	—	4.4	0.06	0.015
A1	86.4	9.6	4.0	0.06	0.111
A3	67.8	29.1	3.1	0.06	0.386
A5	48.9	48.9	2.2	0.06	0.880

uniaxial compression tests with an Instron 4467 universal testing machine provided with a thermal chamber. Tests were performed between flat dies at 1 mm/min with cylindrical specimens (length = 8 mm and diameter = 5 mm) machined out from the cured materials. Four to eight specimens were used for every formulation. The measurements were carried out at 20 °C for all formulations and additionally at 30, 40, 50, 55, and 60 °C for the sample containing the highest mass fraction of POSS (A5). The compressive stress was calculated with the following equation:

$$\sigma = P(1 - e)/A_0 \quad (1)$$

where P is the load, A_0 is the initial cross-sectional area, and e is the strain determined from the crosshead displacement (corrected for the machine compliance). The curves of the true stress (σ) versus the true strain (ϵ) exhibited a maximum stress followed by a strain softening before the strain hardening observed at large deformations. E_G was obtained from the initial slope, and σ_Y was obtained from the maximum value before strain softening.

Fracture Toughness

The critical stress intensity factor in plane strain (K_{IC}) was determined with single-edge-notched specimens (B (thickness) = 6 mm, W (width) = 12 mm, L (length) = 60 mm). Tests were performed according to the ASTM D 5045-93 standard. After a notch was made at the center of the sample with a reciprocating saw, a sharp crack of length a , close to 6 mm ($a/W = 0.5$), was initiated by the tapping of a fresh razor blade within the sample at room temperature. The specimens were tested in a three-point bending mode at a crosshead speed of 10 mm/min. The reported results are the means of at least nine samples. K_{IC} was calculated from load–displacement curves:

$$K_{IC} = (P_{\max}/BW^{1/2})f(a/W) \quad (2)$$

where P_{\max} is the maximum load at failure and $f(a/W)$ is an expression accounting for the geometry of the sample, given in ASTM Standard D 5045.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical spectra were obtained with a PerkinElmer DMA-7 system operating at 1 Hz in the three-point bending mode at a heating rate of 10 °C/min. The dimensions of the specimens were $B = 3.1$ mm, $W = 2.3$ mm, and $L = 20$ mm (span = 15 mm). Selected values of the static and dynamic pressure were 0.8 MPa and 0.2 MPa, respectively. Under these conditions, the response of DMA was very sensitive in the range of the rubbery modulus (E_R) but not so sensitive in the range of E_G (the latter was obtained from uniaxial compression tests). DMA curves were used to obtain E_R at 160 °C (at least 60 °C above T_g) and to analyze subglass relaxations.

RESULTS AND ANALYSIS

A summary of the properties of the different POSS-modified epoxy networks is shown in Table 2. In the following sections, the observed trends are analyzed.

T_g

DSC thermograms of the different POSS-modified epoxy networks are shown in Figure 2. A single and neat T_g is observed for every formulation without any evidence of physical aging. For sample A5, the presence of another glass transition at about 170 °C may be inferred from the DSC trace shown in Figure 2. However, DMA thermograms (Fig. 3) do not show any evidence of this second glass transition, which must then be ascribed to a nonlinear baseline in the corresponding DSC thermogram.

Table 2. Properties of POSS-Modified Epoxy Networks

Sample	T_g (°C)	E_R (160 °C) (MPa)	ρ (g/cm ³)	E_G (GPa)	σ_Y (MPa)	K_{IC} (MPa m ^{1/2})
A0	100	48	1.180	2.80	84	0.56
A1	81	40	1.198	2.97	88	0.51
A3	75	29	1.215	3.23	94	0.39
A5	64	19	1.224	3.43	100	0.32

The addition of POSS produces a significant decrease in T_g of the cured specimens. This may be explained by two concurrent factors: (1) the decrease in crosslink density (associated with the decrease in E_R) produced by the increase in the rate of chain-transfer steps and (2) the flexibility of the organic branches of POSS cages ($T_g = 14$ °C for pure POSS).

Crosslink Density

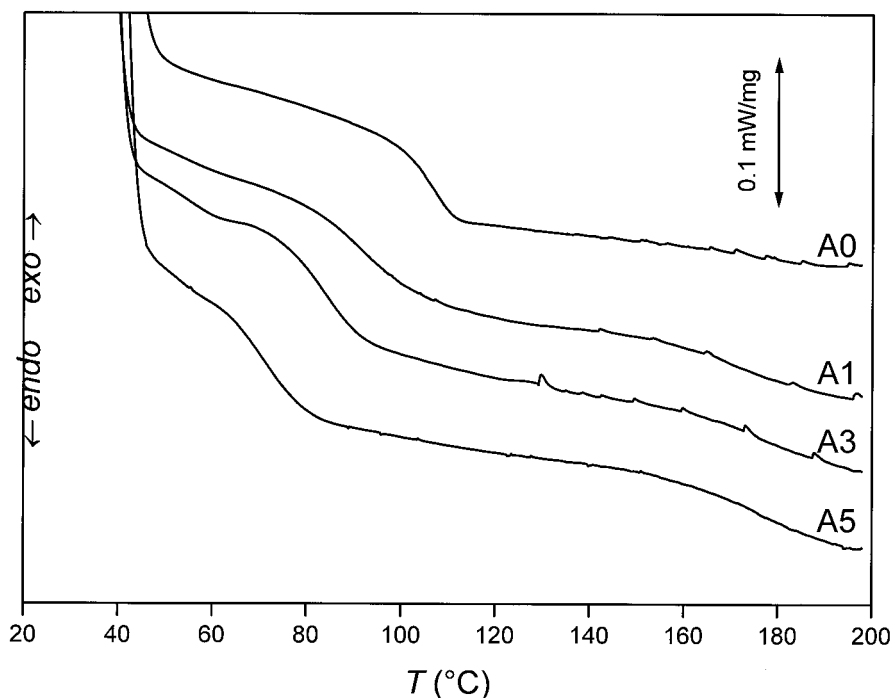
The variation of the storage modulus with temperature, obtained from DMA tests, is shown in Figure 3. As explained in the Experimental section, test conditions were selected so that quantitative values in the rubbery region could be obtained. In this region, E_R increases linearly with temperature according to the theory of ideal rubbers:

$$E_R = 3\phi \nu_e RT \quad (3)$$

where ϕ is the front factor, which takes into account every factor that distinguishes thermosets from ideal rubbers (e.g., the short length of elastic chains); ν_e is the concentration of elastic chains (mol/cm³); R is the gas constant; and T is the absolute temperature.

The value of ϕ may, in principle, be obtained from the behavior of model networks. An analysis of reported values revealed that eq 3 leads to good predictions of E_R , with ϕ varying in the range of $0.4 < \phi < 1.6$.²⁴ A value of $\phi = 1$ may, therefore, be used for a good order-of-magnitude prediction.²⁵⁻²⁷

With the experimental values of E_R reported in Table 2, the concentration of elastic chains could be determined. The corresponding values are indicated in Table 3.


Figure 2. DSC thermograms of POSS-modified epoxies.

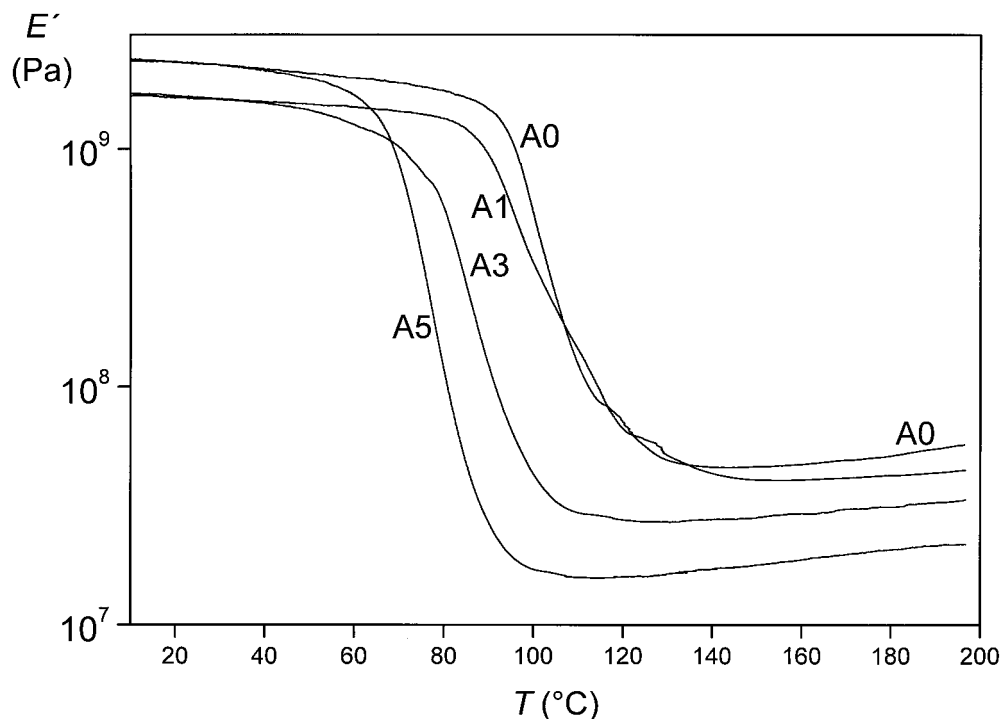


Figure 3. Storage modulus (E') as a function of temperature for the different formulations.

To express the crosslink density in terms of unit mass, we must estimate ρ values at 160 °C. From the experimental ρ values at 20 °C, reported in Table 2, ρ values at 160 °C could be estimated with typical values of the volumetric expansion coefficients of epoxies in the glassy state (α_G) and in the rubbery state (α_R). The following values were used: $\alpha_G = 3 \times 10^{-4} \text{ K}^{-1}$ and $\alpha_R = 6 \times 10^{-4} \text{ K}^{-1}$.²⁴ Estimated ρ values at 160 °C, in the rubbery state, are given in Table 3. This enabled the calculation of the crosslink density per unit mass (ν) and of the molar ratio of elastic chains per DGEBA unit. These values are also indicated in Table 3.

In the homopolymerization of DGEBA, both epoxides are opened, acting as bifunctional groups. If primary chains were of infinite length, every DGEBA molecule would originate two trifunctional crosslinks [two CH groups bonded to

three elastic chains: (1) $-\text{CH}_2-\text{O}-$, (2) $-\text{O}-\text{CH}_2-$, and (3) $-\text{CH}_2-\text{O}-\phi-\text{C}(\text{CH}_3)_2-\phi-\text{O}-\text{CH}_2-$). Therefore, the maximum value of the molar ratio of elastic chains with respect to DGEBA units is 3 (3/2 elastic chains issuing for both crosslinks). However, as the length of the primary chains is very short because of the significant rate of chain-transfer and chain-termination steps,²⁰ the actual value of this molar ratio should be significantly less than 3. The estimated value for sample A0 is 1.45 (Table 3), which represents a correct order of magnitude. The molar ratio of elastic chains per DGEBA unit decreases with POSS addition as a result of the increase in the rate of chain-transfer steps to the secondary hydroxyls present in the POSS structure.

In one of the first reviews related to the influence of crosslinks on the physical properties of

Table 3. Crosslink Density of POSS-Modified Epoxy Networks

Sample	ν_e (mol/cm ³)	ρ_R (160 °C) (g/cm ³)	ν (mol/g)	Elastic Chains/DGEBA
A0	4.44×10^{-3}	1.112	3.99×10^{-3}	1.45
A1	3.70×10^{-3}	1.123	3.29×10^{-3}	1.33
A3	2.68×10^{-3}	1.125	2.38×10^{-3}	1.22
A5	1.76×10^{-3}	1.142	1.54×10^{-3}	1.10

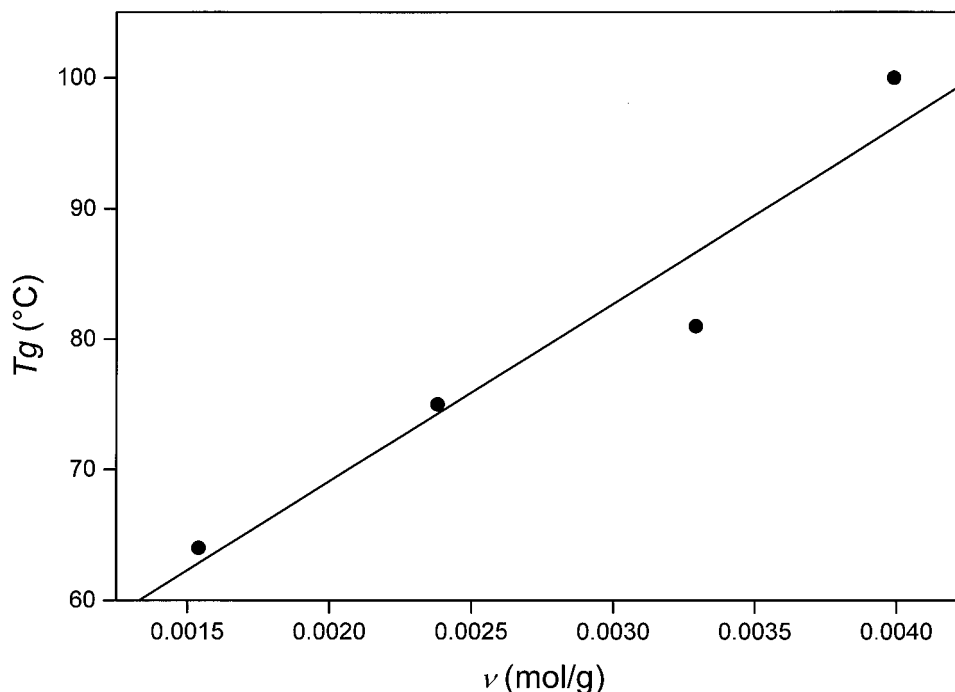


Figure 4. T_g of POSS-modified epoxy networks versus ν .

thermosetting polymers, Nielsen²⁸ proposed the following equation relating T_g to the crosslink density:

$$T_g = T_{g0} + 3.9 \times 10^4 \nu \quad (4)$$

where T_{g0} represents the glass-transition temperature of the uncrosslinked polymer. As Nielsen pointed out, the equation accounts only for the shift in T_g due to crosslinking; the shift due to changes in composition (copolymer effect) is not explained. The suitability of Nielsen's equation for predicting T_g values of several nonstoichiometric epoxy-amine networks was analyzed.²⁹ It was found that the equation gave an excellent prediction for high- T_g networks in which the change in crosslink density with composition was much more important than the copolymer effect. However, for low- T_g networks built up from flexible monomers (one or both), the slope $dT_g/d\nu$ was significantly lower (from 0.7×10^4 to 1.5×10^4), giving evidence of the significant effect of the change in composition with respect to the variation of the crosslink density.

Figure 4 shows T_g of POSS-modified epoxy networks plotted as a function of ν . The best linear fitting was given by

$$T_g(^{\circ}\text{C}) = 41.9 + 1.36 \times 10^4 \nu \quad (5)$$

By comparison with other results reported for epoxy networks,²⁹ it may be concluded that the decrease in T_g produced by POSS addition mainly originates in the copolymer effect (the high flexibility of the organic branches of POSS), rather than from the decrease in the crosslink density of the resulting networks.

Properties in the Glassy State

A representative set of uniaxial compression tests carried out at 20 °C for the different samples is shown in Figure 5. The addition of POSS increases both E_G and σ_Y . The average values of these parameters are shown in Table 2.

Factors affecting E_G are well established.²⁴ The unrelaxed modulus determined below subglass transitions (measured either at low temperatures or at high frequencies) is only dependent on the cohesive energy density (CED), which may be estimated through a group contribution method.³⁰ The relaxed value of E_G , determined at room temperature, incorporates the effect produced by subglass transitions (mainly the β transition).

From the analysis of group contributions to the CED value, it is clear that hydrogen-bond donor groups, such as alcohols or amides, have an especially high contribution to cohesion, whereas hy-

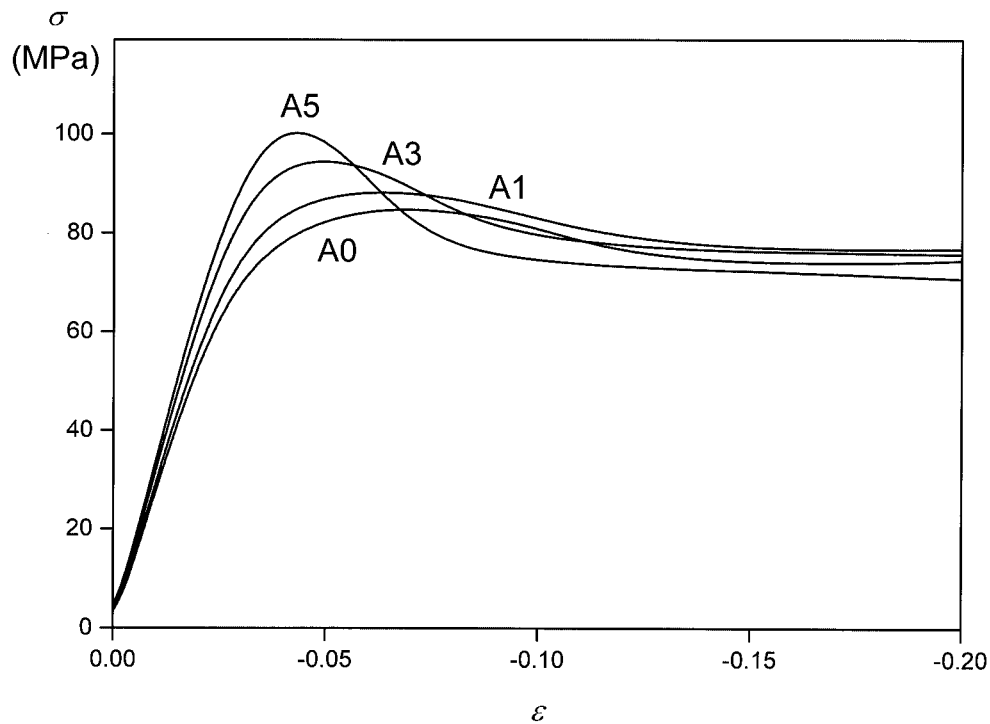


Figure 5. Set of uniaxial compression tests at 20 °C for the different samples (σ vs ϵ).

drocarbons display the lowest cohesivity.²⁴ CED values were estimated with Fedor's group contributions³⁰ for a DGEBA unit with both epoxy

groups opened to generate polyether chains (an idealized structure of sample A0) and for the cubes (T_8) present in the distribution of POSS

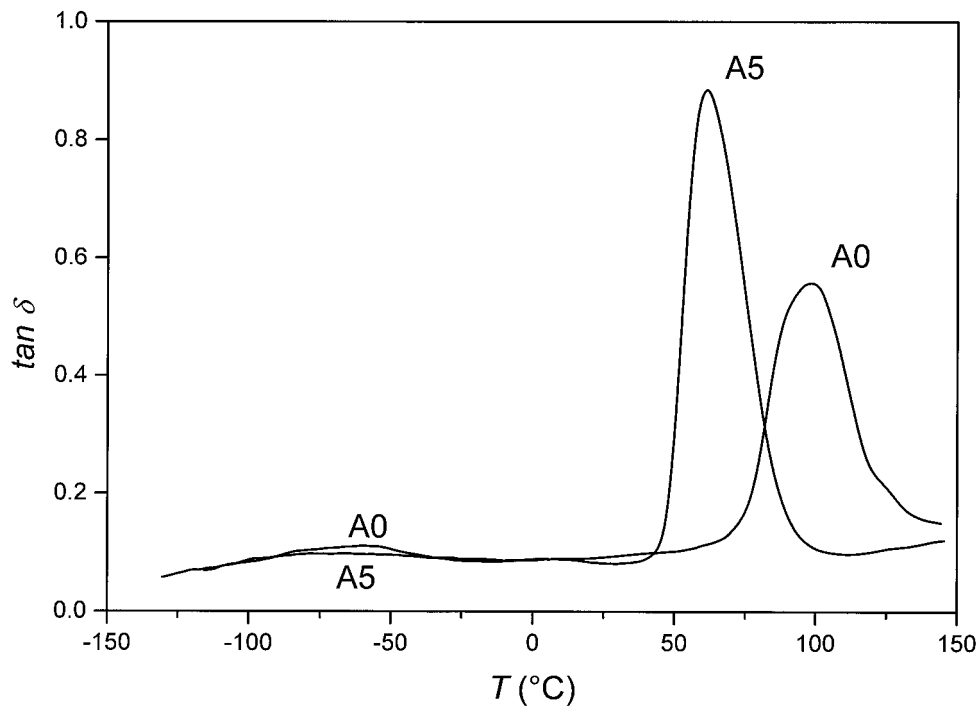


Figure 6. Dynamic mechanical spectra of samples A0 and A5 at 1 Hz.

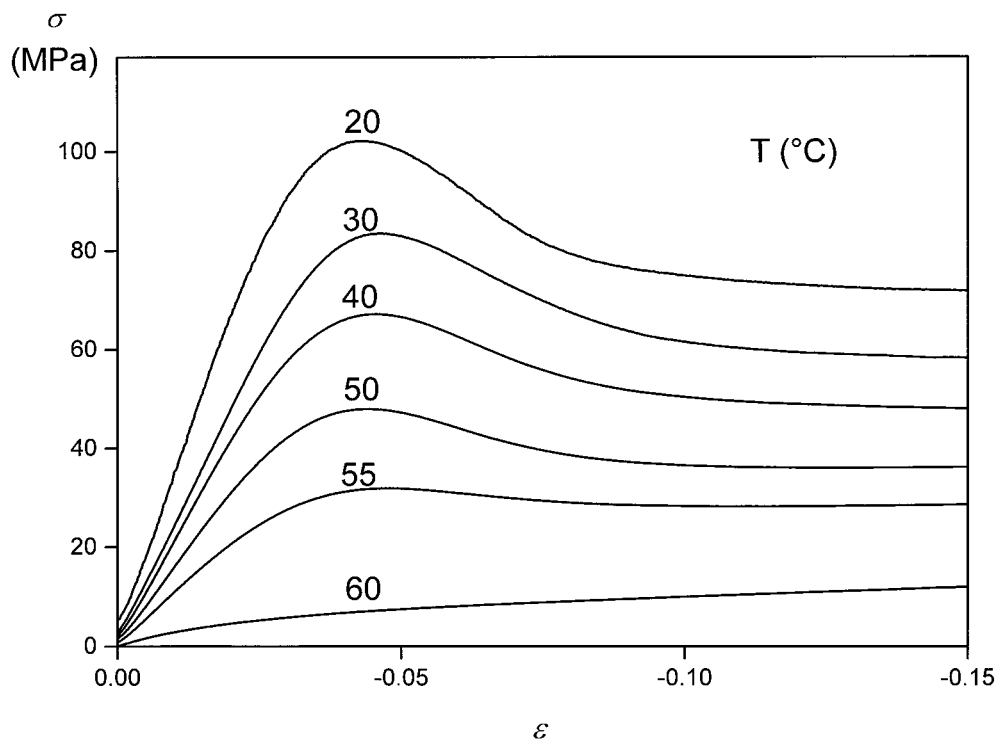


Figure 7. Set of uniaxial compression tests for sample A5 at different temperatures (σ vs ϵ).

species. The resulting values were CED (DGEBA with opened epoxides) = 401 MPa and CED (T_g) = 571 MPa. Therefore, the increase in the CED may explain the observed increase in E_G by the presence of POSS in the epoxy network.

The influence of POSS addition on the intensity of subglass relaxations was also investigated. Figure 6 shows the dynamic mechanical spectra of samples A0 (without POSS) and A5 (with 50 wt % POSS). Subglass relaxations exhibit comparable intensities in both samples, and this means that the main factor accounting for the increase in E_G by the presence of POSS is the increase in the CED.

Therefore, adding POSS to the initial formulation led to a decrease of T_g (plasticization), accompanied by an increase in E_G (antiplasticization). This is a typical phenomenon common to polymers exhibiting a strong β transition well separated from the α transition.²⁴ In these cases, the explanation of the antiplasticization phenomenon is the reduction of the intensity of the β relaxation produced by the modification of the network structure. However, for the POSS-modified epoxy networks analyzed in this study, the antiplasticization effect is related to the significant increase in the cohesive energy produced by POSS addition.

σ_Y exhibits a behavior similar to that of E_G (Table 2). Brown³¹ stated that, for glassy polymers, any variable that increases E_G also increases σ_Y and that the ratio σ_Y/E_G is a constant value in the range of 1/60 to 1/30 (Brown's rule). Although exceptions for this trend have been reported,³² Brown's rule seems to be valid for our POSS-modified epoxy networks. The ratio σ_Y/E_G is indeed a constant value equal to 0.03 or 1/33. It is concluded that σ_Y is mainly affected by the CED of the polymer networks.

The behavior of the POSS-modified epoxy network with 50 wt % POSS (A5) is of particular interest because it exhibits the highest room-temperature σ_Y , combined with the lowest T_g . As no yielding is expected at temperatures close to $T_g = 64$ °C, a high sensitivity of σ_Y with temperature in the 20–64 °C temperature range is expected for this sample.

Figure 7 shows a set of uniaxial compression tests for sample A5 at different temperatures in the range of 20–60 °C. At 60 °C, no definite yielding was observed. The average values of E_G and σ_Y for different temperatures are shown in Table 4.

The ratio of σ_Y to E_G , σ_Y/E_G , is constant and equal to 0.03 in the entire temperature range. This is a clear indication of the neat glassy behavior up to 55 °C. A sharp transition to a rubbery behavior is

Table 4. Properties in the Glassy State for Sample A5 as a Function of Temperature

Temperature (°C)	E_G (GPa)	σ_Y (MPa)
20	3.43	100
30	2.53	84
40	2.10	67
50	1.56	48
55	1.11	32

observed with the temperature increasing by 5 °C (manifested by the stress–strain curve at 60 °C). The sharp decrease of both σ_Y and E_G at T_g constitutes a significant property of the POSS-modified epoxy network containing 50 wt % POSS.

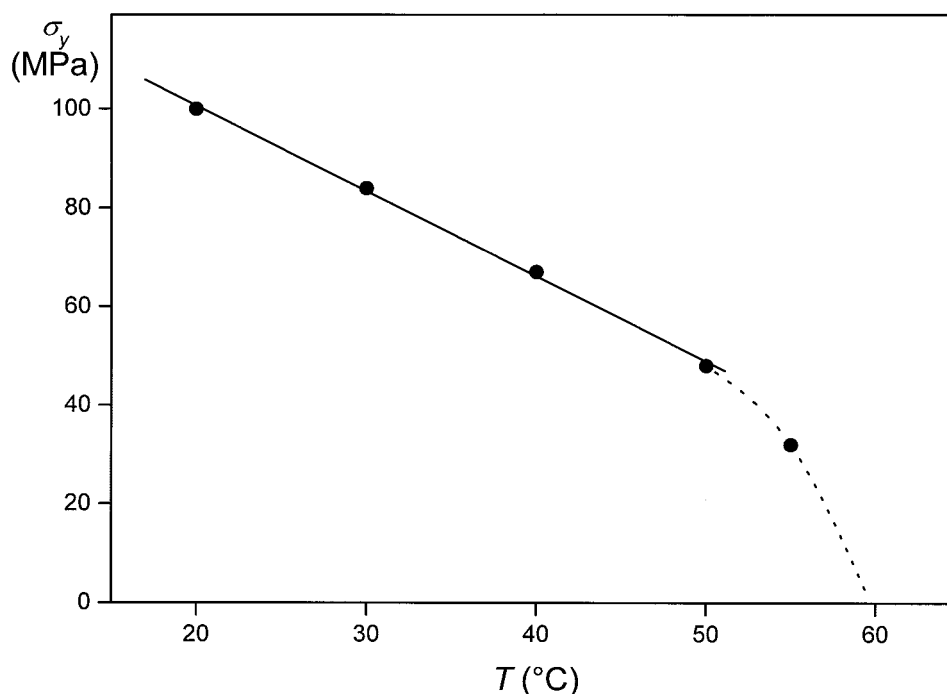
Figure 8 shows a linear variation of σ_Y of sample A5 with temperature, in the 20–50 °C range, with a slope equal to -1.73 MPa/K. A linear variation of σ_Y with T has been observed for several polymer networks in a range of temperatures close to T_g .^{24,33–35} The sensitivity of σ_Y with temperature for the family of POSS-modified epoxy networks is higher than values reported for anhydride-cured and diamine-cured epoxies, which range from -0.5 to -1.5 MPa/K, but lower than values reported for styrene-crosslinked vinyl ester resins (-2.0 MPa/K).^{34,35}

Regarding the fracture resistance of this family of modified epoxies, Table 2 shows that K_{IC} decreases with POSS addition. This is explained by the corresponding increase in σ_Y , which leads to a decrease in the size of the plastic zone around the crack tip. This leads to a reduction of the energy dissipated during crack propagation.^{36,37}

CONCLUSIONS

A POSS with bulky and flexible organic branches, bearing three secondary hydroxyls per branch, was used to modify epoxy networks built up by the homopolymerization of epoxides in the presence of tertiary amines. Covalent bonding between POSS and the epoxy network was produced either by the direct reaction of secondary hydroxyls with epoxides or by chain-transfer steps in the course of the tertiary amine-initiated homopolymerization of epoxides.

The addition of POSS increased the stiffness and σ_Y values of the epoxy network, mainly because of the increase in the CED produced by hydrogen bonding through the hydroxyl groups. A constant σ_Y/E_G ratio equal to 0.03 was observed for different POSS concentrations and test temperatures. T_g decreased with POSS addition because of the flexibility of organic branches present

**Figure 8.** σ_Y as a function of temperature for sample A5.

in the POSS structure and the decrease in the crosslink density. The former factor was more important than the latter, as inferred from the application of Nielsen's empirical equation. Although a combination of a reduction in T_g (plasticization) and an increase in E_G (antiplasticization) is a well-known phenomenon, what is original is the fact that, for the class of POSS-modified epoxy networks investigated in this study, it was not the result of the suppression (or reduction in intensity) of the β relaxation but was produced by an increase in the CED.

An interesting property of the network containing 50 wt % POSS (sample A5) is the high temperature sensitivity of the mechanical behavior in the vicinity of the glass transition. At 55 °C, it behaved as a glassy material with an E_G value of 1.11 GPa and a σ_Y value of 32 MPa. However, at 60 °C, it exhibited a rubbery behavior in uniaxial compression tests. The temperature range in which this behavior was observed can, in principle, be shifted to room temperature with an increase in the initial amount of POSS.

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