EPOXY NETWORKS MODIFIED BY MULTIFUNCTIONAL POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS) CONTAINING AMINE GROUPS

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The hydrolytic condensation of a precursor synthesized by the reaction of equimolar amounts of (3-aminopropyl)triethoxysilane and phenylglycidylether led to a distribution of polyhedral oligomeric silsesquioxanes (POSS) containing 8–11 Si atoms, functionalized with amine groups. About 57% of the NH functionalities were active for reaction with epoxy groups. The multifunctional amine-POSS was used to modify an epoxy network obtained by the homopolymerization of diglycidylether of bisphenol A initiated by benzyldimethylamine. The main effect of POSS modification was an increase in both the glassy and rubbery modulus explained, respectively, by the increase in cohesive energy and crosslink densities.

Keywords: amine-functionalized POSS, dynamic-mechanical analysis, epoxy network, silsesquioxane

Introduction

Polyhedral oligomeric silsesquioxanes (POSS), of generic formula $(RSiO_{1.5})_n$ (n=6, 8, 10…) or T_n, are nanosized cage structures that can be incorporated into linear or thermosetting polymers to improve thermal and mechanical properties. The definition may be extended to include imperfect polyhedra, $T_n(OH)$ (n=7, 9, 11…), containing one free SiOH group in the structure. Depending on the number of organic groups bearing reactive functionalities, POSS can be classified as non-functional, monofunctional or multifunctional.

The polymerization of diglicidylether of bisphenol A (DGEBA) with a monofunctional amine-POSS bearing one propylamine group and seven isobutyl groups was studied by differential scanning calorimetry (DSC) [1]. Multifunctional amine-POSS were employed as co-monomers to produce epoxy networks, either by reaction with DGEBA [2–4], or with a variety of epoxy monomers including multifunctional epoxy-POSS [3]. The incorporation of multifunctional amine-POSS to epoxy networks produced an increase in crosslink density and improved thermal properties (increases in the glass transition temperature and the thermal stability and reduction of the coefficient of thermal expansion).

The aim of this manuscript is to analyze thermal and mechanical properties of epoxy networks modified with a multifunctional amine-POSS consisting mainly of a distribution of T_n and $T_n(OH)$ structures

with n=8–11. This particular POSS was synthesized in one step by the hydrolysis and condensation of a precursor obtained by reacting equimolar amounts of phenylglycidylether and (3-aminopropyl)triethoxysilane [5]. This led to a product containing flexible organic branches bearing hydroxyl groups together with a statistical distribution of primary, secondary and tertiary amine groups. Epoxy networks were obtained from formulations containing an excess of DGEBA and a tertiary amine, by a combination of epoxy-amine reactions and epoxy homopolymerization. Thermal and mechanical properties of POSS-modified epoxies were compared with those of the neat epoxy network.

Experimental

Materials

Synthesis of the multifunctional amine-POSS

In the first step, equimolar amounts of (3-aminopropyl)triethoxysilane (APS, Sigma, 98% purity) and phenylglycidylether (PGE, Aldrich, 99% purity), were reacted in bulk, at 50°C under vacuum, during 24 h, attaining complete conversion [5, 6]. The reaction product is composed of three different species (Fig. 1). Assuming equal reactivities of primary and secondary amino groups, the relative amount of these species is: 25% APS, 50% APS-PGE and 25% APS-PGE$_2$.
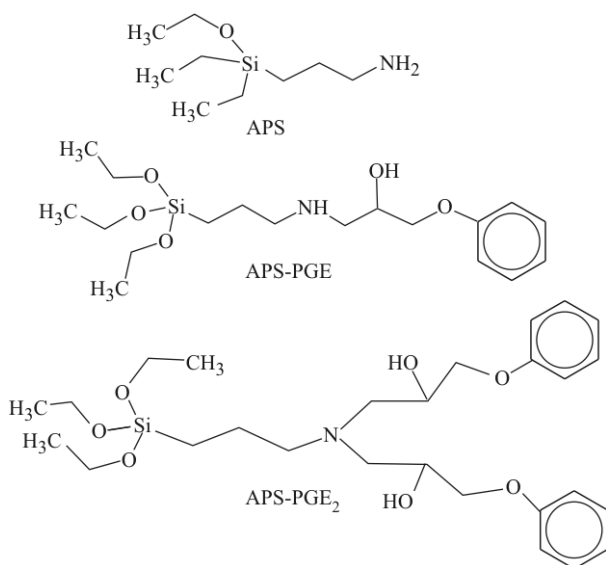
Fig. 1 Chemical structure of the precursor of the multi-functional amine-POSS

The multifunctional amine-POSS was synthesized by dissolving the precursor synthesized in the first step in tetrahydrofuran (THF, 1 g of precursor per 1.5 mL of solvent), adding water in a molar ratio $H_2O/Si=3$, and heating at 50°C during 24 h, allowing continuous evaporation of volatiles. The resulting product was dissolved in dichloromethane and washed three times with equal volumes of water. The solvent was eliminated by heating at 80°C for 1 h at atmospheric pressure followed by 5 min under vacuum.

Reaction of the multifunctional amine-POSS with epoxy monomers

A solution containing 66.7 mass% POSS in PGE was prepared at 45°C. The tube was transferred to a thermostat held at 100°C and the evolution of the epoxy conversion as a function of time was followed by Fourier-transformed infrared spectroscopy (FTIR, Genesis II, Mattson), in the transmission mode, using acetone solutions of samples extracted at different times. The final epoxy conversion (x) was determined by the decrease of the absorbance of the epoxy peaks located at 915 and 863 cm^{-1} with respect to the reference band of the aromatic ring at 1600 cm^{-1}:

$$x=1-[(A_i(t)A_{1600}(0)/A_i(0)A_{1600}(t)] \qquad (1)$$

where the subscript i refers either to the peak at 915 or 863 cm^{-1}.

Solutions of POSS in diglycidylether of bisphenol A (DGEBA, Der 332 Dow, EEW=174.3 g), containing different concentrations of POSS, were cured in the DSC (Shimadzu, DSC-50), at 5°C min^{-1}. The glass transition temperatures (mid-point of the

change in the specific heat) of the cured products were determined during second scans at the same rate.

Methods

Characterization of the multifunctional amine-POSS

The characterization of the molar mass distribution of the synthesized POSS was performed using UV-MALDI-TOF mass spectrometry, as described in a previous publication [5]. Its glass transition temperature (T_g) was determined by differential scanning calorimetry (Shimadzu DSC-50), as the mid-point of the change in the specific heat with temperature at a scanning rate of 5°C min^{-1}.

Cure and characterization of POSS–DGEBA formulations containing an epoxy excess

Formulations containing 0 to 20 mass% POSS in DGEBA were cured in the presence of benzyldimethylamine (BDMA, Aldrich), using 0.06 mol BDMA per mol of epoxy groups. Cure was performed in a mold with the following thermal cycle: 4 h at 80°C followed by 3 h at 120°C.

To compare the relative rates of epoxy-amine reaction and epoxy homopolymerization initiated by BDMA, both POSS-DGEBA and DGEBA-BDMA formulations were cured in the DSC at 80°C.

Glass transition temperatures of POSS-modified epoxies were determined by DSC at a 5°C min^{-1} heating rate. Dynamic mechanical analysis was performed using a PerkinElmer DMA-7 device. Tests were carried out at 1 Hz in the three-point bending mode. Dimensions of the specimens, machined from the cured plates, were: length=20 mm (span=15 mm), width=3 mm and thickness=2 mm. Runs were carried out at 5°C min^{-1} under nitrogen.

Results and discussion

Characterization of the multifunctional amine-POSS

The multifunctional amine-POSS was an amorphous solid with a T_g=30°C. Its characterization was performed by UV-MALDI-TOF mass spectrometry, as reported in a previous publication [5]. Main species were perfect polyhedra: T_8, T_{10}, imperfect polyhedra: $T_9(OH)$, $T_{11}(OH)$, and other structures exhibiting a large fraction of intramolecular cycles: $T_9(OH)_3$, $T_{10}(OH)_2$. For every one of these species there was a distribution of molar masses that depended on the number of moles of PGE bonded to the structure. For example, for T_n or $T_n(OH)_m$ the particular species present in the highest concentration contained n PGE units, as results from the 1:1 molar ratio of PGE and

APS employed in the synthesis. However, a statistical distribution of species containing $(n+j)$ PGE units with j varying from about –3 to about +3, was found. The average equivalent mass of the multifunctional amine-POSS expressed per equivalent of amine hydrogens was 261 g, calculated on the basis of the initial stoichiometry and the almost complete conversion attained in the polycondensation reaction.

Due to the fact that amine groups are aliphatic and to the presence of hydroxyl groups in the POSS structure that act as catalysts of the epoxy-amine reaction, we can expect a relatively high reactivity of the multifunctional amine-POSS with either PGE or DGEBA.

The consumption of epoxy groups was followed by FTIR for a solution with 66.7 mass% POSS in PGE, kept at 100°C. This solution contained a theoretical excess of amine equivalents (molar ratio NH/epoxy=1.15), implying that a full conversion of epoxy groups could be expected. Figure 2 shows the decrease in the absorbance of characteristic peaks of the epoxy group at 915 and 863 cm^{-1}. Spectra obtained for samples cured for more than 30 min did not show any further significant decrease of both bands meaning that a significant residual fraction of unreacted epoxy groups was present under these conditions.

The use of the peak at 915 cm^{-1} to monitor epoxy conversion has been the subject of some controversy in the literature since the paper by Dannenberg and Harp [7], stating that some other group apart from the epoxy does also contribute to this band. Although a variation of the molar absorption coefficient with conversion was also postulated [8], the more likely explanation of the problems in the use of the 915 cm^{-1} band is the overlapping with a non-reactive
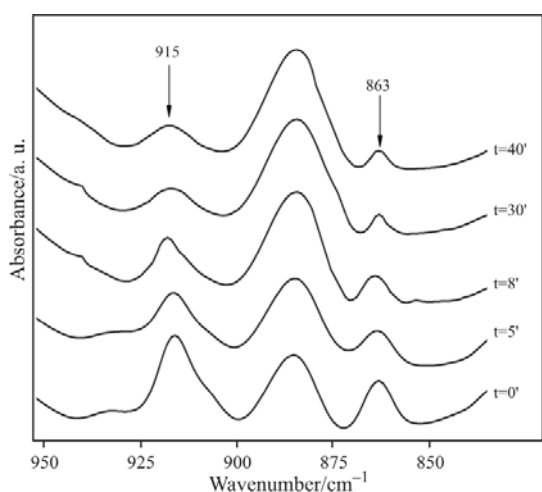
peak [8, 9]. However, for some epoxy systems this problem was not present as the band completely disappeared at full epoxy conversion [10–12]. In our case, the possibility of using the peak at 915 cm^{-1} to determine the conversion of epoxy groups was in principle validated by the fact that the use of the peak at 863 cm^{-1} led to the same maximum conversion with a value close to 0.65. This maximum conversion was not produced by a vitrification process (due to the high fraction of residual PGE the glass transition temperature of the blend was located below room temperature). Therefore it was concluded that about 65/115= 57% of the NH groups present in POSS were available for reaction with PGE units. The equivalent mass of the multifunctional amine-POSS based on active NH groups was calculated as 460 g eq^{-1}.

DSC was used to reassure the validity of the equivalent mass determined for the multifunctional amine-POSS. Blends of the amine-POSS with DGEBA were prepared using molar ratios r=epoxy/NH equal to 0.92, 1 and 1.07, on the basis of an equivalent mass of 460 g/eq for the amine-POSS. These blends were cured in the DSC and the respective glass transition temperatures were obtained in second scans. Resulting values were T_g=42°C for r=0.92, T_g=54°C for r=1, and T_g=47°C for r=1.07. This trend is consistent with the estimated equivalent mass of the multifunctional amine-POSS and reassures the validity of the FTIR analysis. Figure 3 shows the first DSC scan for the stoichiometric sample (r=1) that contains 72.5 mass% POSS. Figure 4 shows the second DSC scan of the same sample leading to a T_g of 54°C.

Now, the question is why are there only 57% of the NH groups of the amine-POSS available for reaction with epoxy groups? The answer might be related to the fact that fully condensed silsesquioxanes containing free aminopropyl groups are not stable rela-
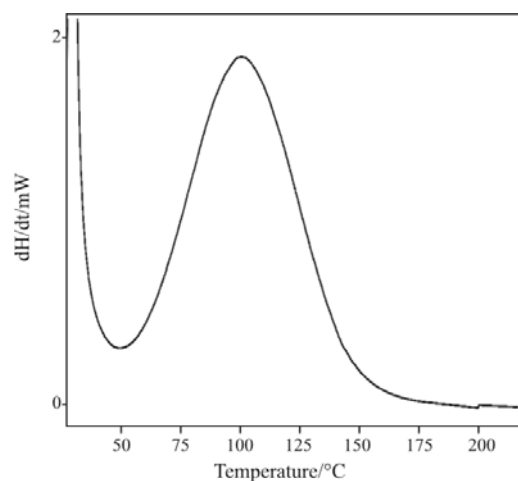

Fig. 2 FTIR spectra in the region 850–950 cm^{-1} showing characteristic peaks of the epoxy group at 915 and 863 cm^{-1}, for a solution with 66.7 mass% POSS in PGE, kept at 100°C for 0 to 40 min

Fig. 3 DSC scan of a stoichiometric POSS-DGEBA blend containing 72.5 mass% POSS
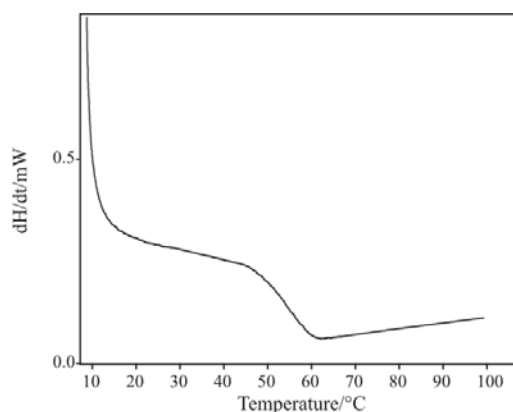
Fig. 4 Second DSC scan after the first scan shown in Fig. 3

Fig. 5 Isothermal DSC scan at 80°C for a POSS-DGEBA blend with 10 mass% POSS

tive to incompletely condensed frameworks (they decompose to an ill-defined gel) [13]. In these compounds, primary amine groups are possibly present as ionic species $SiO^- NH_3^+$, a fact that can also take place in the amine-functionalized POSS synthesized in this study. Ammonium salts will not react as fast as free amines with the electrophilic epoxy groups. Therefore, the formation of ammonium salts decreases the actual fraction of NH groups that is available to react with epoxies. From the statistical distribution of organic branches shown in Fig. 1, it results that 50% of the NH functionalities are present in secondary amine groups and the remaining 50% pertain to primary amine groups (25% of primary amines containing 2 NH functionalities per group). If only secondary amine groups had been available for reaction, the maximum limiting conversion for the selected stoichiometry would have been 0.575, slightly less than the experimental value (0.65). An increase in the fraction of secondary amines with respect to the ideal value can result from a negative substitution effect in the epoxy-amine reaction during the synthesis of the precursor (e.g, the secondary amine reacts at a slower rate than the primary amine).

POSS-DGEBA-BDMA formulations

To avoid practical problems associated to the high viscosity of stoichiometric POSS-DGEBA blends as well as to produce an increase in the maximum T_g of the final networks, we investigated the possibility of employing the multifunctional amine-POSS as a modifier of an epoxy network produced by the homopolymerization of DGEBA initiated by BDMA.

First we compared the relative rates of the epoxy-amine reaction and the epoxy homopolymerization initiated by BDMA. For this purpose, binary formulations of POSS-DGEBA or DGEBA-BDMA were cured in the DSC at 80°C. Figure 5 shows the scan for the POSS-DGEBA for-
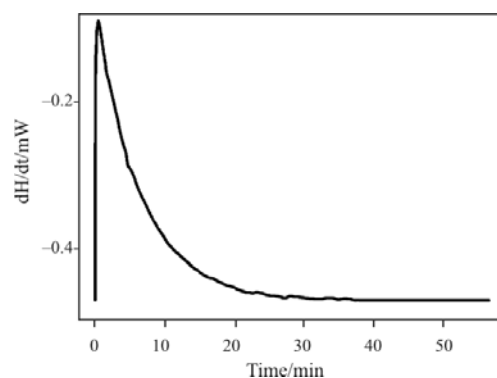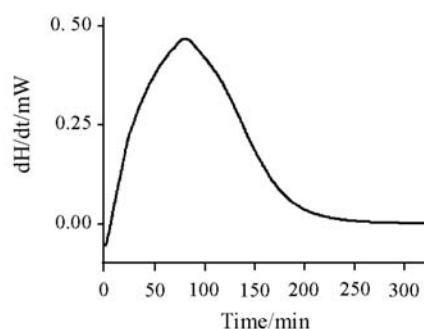

Fig. 6 Isothermal DSC scan at 80°C for a DGEBA-BDMA formulation

mulation containing 10 mass% POSS while Fig. 6 shows the scan for the DGEBA-BDMA formulation. While the epoxy-amine reaction proceeds at a very fast rate (most of the reaction takes place in about 20 min), the homopolymerization reaction occurs at a much slower rate. Therefore, during the cure of POSS-DGEBA-BDMA formulations in the heated mold, with a first part of the cycle at 80°C, the grafting of DGEBA units to POSS species will occur first, followed by a slow homopolymerization of the excess epoxy groups.

Formulations containing 0 to 20 mass% POSS in DGEBA were cured in the presence of BDMA, in a concentration of 0.06 mol/mol of epoxy groups, following the thermal cycle described in the experimental section. Glass transitions temperatures of the cured samples were determined by DSC (Fig. 7). Resulting values were comprised in the range 100–110°C, very close to the value of the neat epoxy. This is the consequence of a balance between the increase in cross-link density produced by POSS addition and the intrinsic flexibility supplied by the organic branches present in the POSS structure. As shown in Fig. 4, increasing the POSS amount to 72.5 mass% led to a T_g of 54°C, indicating that at this percentage the flexibility of POSS arms plays a major role on the value of the glass transition temperature.
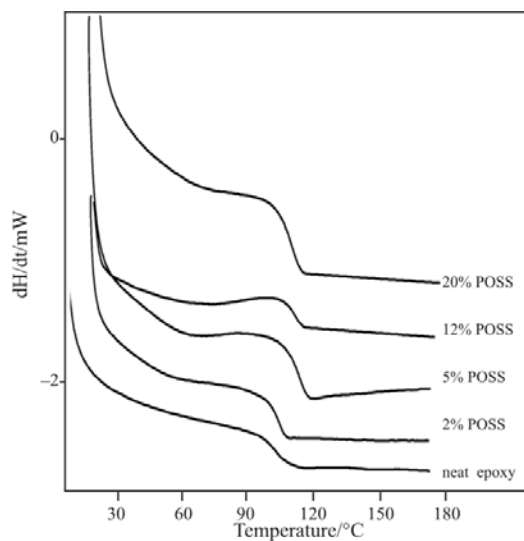
Fig. 7 Glass transition temperatures of epoxies containing 0 to 20 mass% POSS cured in the presence of BDMA

A dynamic mechanical characterization of cured materials with 0 and 10 mass% POSS is shown in Fig. 8. The incorporation of POSS to the epoxy network produced a significant increase in the glassy modulus. At 25°C values were 2.04 GPa for the neat epoxy and 2.53 GPa for the network modified with 10 mass% POSS. There are two main factors that determine the value of the elastic modulus at room temperature. One is the cohesive energy density (CED) and the other one is the magnitude of sub-vitreous relaxations below room temperature [14]. The small intensity of sub-glass relaxations in epoxy networks synthesized with BDMA as initiator [15], indicates that the increase in CED by POSS addition must be the cause of the increase in the glassy modulus. Hydrogen-bond donor groups, such as alcohols or amines, present in the POSS structure, increase CED and, consequently, the glassy modulus of the POSS-modified epoxy.

The cross-link density of the POSS-modified epoxy networks is affected by two factors. On the one hand, the addition of a multifunctional amine monomer should increase cross-link density. But, on the other hand, OH groups present in the POSS structure are chain transfer agents in the anionic polymerization of epoxy groups [12, 15]. Propagating chains with an alkoxide end group terminate by abstracting a proton from the OH group regenerating an alkoxide group that initiates a new chain. This reaction produces an extra grafting of POSS to the epoxy network. However, it reduces the length of primary polyepoxy chains and decreases the crosslink density. As the rubbery modulus is proportional to the crosslink density, it may be used to infer which of both effects is predominant. Experimental values showed a slight increase in the rubbery modulus
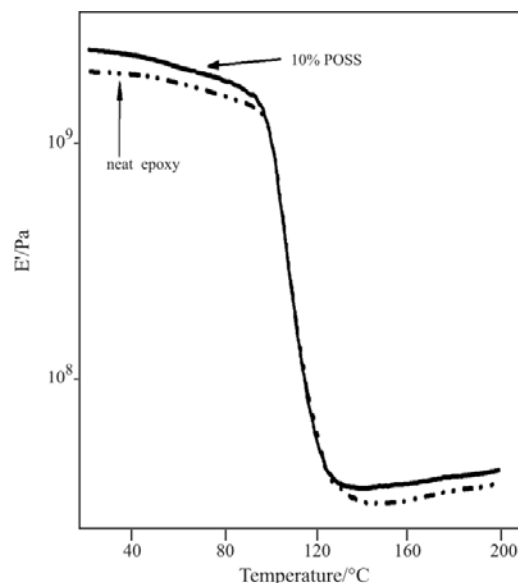

Fig. 8 DMA characterization of the cured epoxies containing 0 and 10 mass% POSS

(measured at T_g+60°C) with the amount of POSS, from 29 MPa for the neat epoxy to 34 MPa for the network modified with 10 mass% POSS. Therefore, the multifunctionality provided by the POSS monomer prevailed over the chain transfer action produced by their OH groups.

Conclusions

A multifunctional amine-POSS with main species consisting of perfect and imperfect polyhedra containing 8–11 Si atoms was obtained in one step starting from a precursor synthesized by the equimolar reaction of (3-aminopropyl)triethoxysilane and phenylglycidylether. It was found that about 57% of the NH functionalities were available for reaction with epoxy groups under typical conditions. We speculated that this fraction corresponds to the secondary amine groups and that primary amines are present as ammonium salts and do not react with epoxy groups.

The multifunctional amine-POSS was used to modify an epoxy network obtained by the anionic homopolymerization of diglycidylether of bisphenol A in the presence of benzyldimethylamine. The grafting of POSS to DGEBA units occurred in a first step followed by the slow homopolymerization of the epoxy excess. The main effect of POSS modification was an increase in the glassy modulus explained by the increase in the cohesive energy density produced by the presence of H-donor groups in the organic branches of the POSS structure, and a slight increase in the rubbery modulus produced by an increase in crosslink density.

Acknowledgements

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