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Synthesis of oligomeric silsesquioxanes functionalized with (β-carboxyl)ester groups and their use as modifiers of epoxy networks

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Abstract

A silsesquioxane functionalized with (β-carboxyl)ester groups was synthesized by reacting a silsesquioxane functionalized with secondary hydroxyls with a stoichiometric amount of an acid anhydride. The reaction could be carried out to completion as shown by FTIR spectra and SEC chromatograms. The carboxyl-functionalized silsesquioxane was composed of polyhedra with 8–11 Si atoms, containing two (β-carboxyl)ester groups per organic branch (from 16 to 22 carboxyl groups per molecule). It was a stable glassy product at room temperature and could be dissolved in a variety of organic solvents. It was used as a modifier of epoxy networks based on diglycidylether of bisphenol A (DGEBA) cured with 4-(dimethylamino)pyridine (DMAP). A complete reaction of epoxy groups was observed in a higher temperature range than in the formulation devoid of the functionalized silsesquioxane. This was explained by the reversible complexation of the tertiary amine with (β-carboxyl)ester groups. The addition of the silsesquioxane produced a decrease in the crosslink density explained by the presence of transesterification and chain transfer reactions, and a maximum in the elastic modulus measured at room temperature, explained by a combination of variations of cohesive energy density and the magnitude of β-relaxations.

Keywords: Silsesquioxanes; Poly(silsesquioxanes); COOH-functionalized silsesquioxanes; Epoxy-acid reaction; Epoxy networks

1. Introduction

Silsesquioxanes are usually synthesized by the hydrolytic condensation of organotrialkoxysilanes, $RSi(OR')_3$, performed in the presence of an acid or base as catalysts. The resulting *n*-mers have a generic formula $R_nSi_nO_{1.5n-x}(OH)_{2x}$, and may vary from polyhedra of formula $(RSiO_{1.5})_n$ ($n =$ even number $\geqslant 6$), denoted as T_n or polyhedral oligomeric silsesquioxanes (POSS), to partially condensed (but completely hydrolyzed) species designed as $T_n(OH)_m$, where $T = RSiO_{1.5-m/2n}$. The maximum value of m is equal to $2 + n$ representing a chain without intramolecular cycles.

The introduction of appropriate functionalities in the organic branch (R) has been used to obtain a

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large variety of organic–inorganic hybrid materials. In previous studies we have reported the one-step synthesis and characterization of narrow distributions of perfect and imperfect polyhedra bearing secondary hydroxyls in the organic branches (hydroxyl-functionalized silsesquioxanes, OH–SSO) [1–3], and their use as modifiers of epoxy networks [4,5]. On the other hand, carboxylic acids are useful functionalities to attach to silsesquioxanes to provide ion-exchange resins for scavenging heavy metals and organic amines [6], but also as multifunctional monomers to synthesize different types of cross-linked networks. A simple way to generate carboxylic acid functionalities is through the reaction of the secondary hydroxyls present in the OH–SSO, with acid anhydrides, leading to (β-carboxyl)ester groups (carboxyl-functionalized silsesquioxanes, COOH–SSO).

In this paper, the synthesis and characterization of oligomeric silsesquioxanes functionalized with (β-carboxyl)ester groups will be reported and their use as modifiers of epoxy networks will be analyzed.

2. Experimental

2.1. Synthesis of the silsesquioxane containing (β-carboxyl)ester groups

The organotriethoxysilane with secondary hydroxyls in the organic group was synthesized by reacting (3-aminopropyl)triethoxysilane (APS, Sigma, 98% purity) with phenylglycidylether (PGE, Aldrich, 99% purity), in a molar ratio PGE/APS = 2. The reaction was carried out in bulk, at 50 °C for 24 h under vacuum, attaining complete conversion [3]. The hydrolytic condensation was performed by dissolving 1 g of the resulting product in 1.5 ml tetrahydrofuran (THF) and adding HCOOH 85 wt% (molar ratios: HCOOH/Si = 3, H_2O/Si = 1.35). Formic acid acts both as a catalyst and as reactant, promoting the condensation through the formation of sililformates as intermediate species [7,8]. The reaction was carried out at 50 °C for 24 h allowing continuous evaporation of volatiles and leading to a silsesquioxane (OH–SSO) containing two secondary hydroxyls per organic branch (Fig. 1a).

Secondary hydroxyls were converted into (β-carboxyl)ester groups by reaction with a stoichiometric amount of 4-methyl tetrahydrophthalic anhydride (MTHPA, HY 918 Ciba) in a THF solution. The reaction was carried out at 50 °C for 24 h in closed tubes. Then THF was eliminated by heating at 80 °C for 2 h at atmospheric pressure, followed by another 2 h at the same temperature under vacuum. The resulting silsesquioxane (COOH–SSO) containing two (β-carboxyl)ester groups per organic branch (Fig. 1b), was ground and stored as a yellow glassy powder.

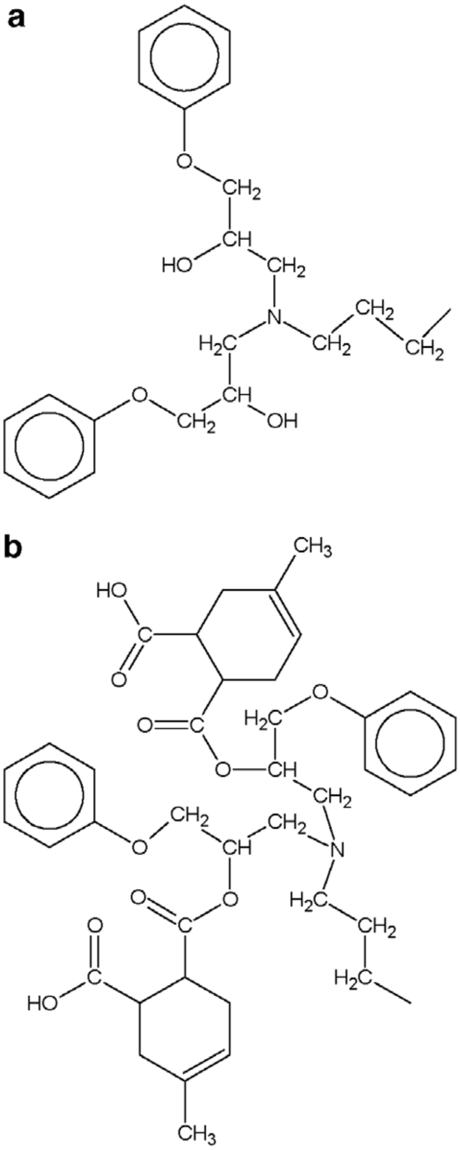

Fig. 1. Chemical structures of the organic branches of silsesquioxanes functionalized with: (a) secondary hydroxyls and (b) (β-carboxyl)ester groups.

2.2. Epoxy networks modified by COOH–SSO

The epoxy monomer was based on diglycidylether of bisphenol A (DGEBA, Der 332 Dow, equivalent weight of 174.3 g per mol of epoxy groups). The epoxy network was obtained using 4-(dimethylamino)pyridine (DMAP, Fluka, 98% purity, m.p. 111–114 °C), as catalyst of the epoxy-acid reaction and initiator of the epoxy homopolymerization. For every formulation a molar ratio DMAP/epoxy group = 0.08, was used that led to full conversion of epoxy groups and a maximum crosslink density in the neat epoxy-tertiary amine system [9].

The COOH–SSO was dissolved in acetone (0.5 g/ml) and the desired amount of DGEBA was added with gentle stirring to obtain a homogeneous solution. The ratio of COOH–SSO/DGEBA was varied to give a molar ratio of COOH/epoxy groups in the range comprised between 0 and 0.25. The solvent was eliminated by heating at 80 °C for 6 h. The solution was cooled to 55 °C and the appropriate amount of DMAP was dissolved. The polymerization was performed following two different thermal cycles: (a) in the cell of a differential scanning calorimeter (DSC) from room temperature to 200 °C, at 5 °C/min and (b) in small molds to obtain samples for mechanical characterization, heating for 3 h at 80 °C, 3 h at 120 °C, and 30 min at 165 °C.

2.3. Characterization techniques

The equivalent weight of secondary OH groups in the OH-functionalized silsesquioxane was determined by reaction with an excess of *p*-toluenesulfonyl isocyanate (Aldrich, 96% purity), adding an excess of dibutylamine (Anedra, 98% purity) to quench the remaining isocyanate groups, and back-titrating with HCl.

Size exclusion chromatography (SEC) was performed in a Knauer K-501 device using a set of Phenomenex 5 μ-columns: 50 A, 100 A and M2, and a refractive index detector (Knauer K-2301). THF was used as a carrier at 1 ml/min.

Fourier-transformed infrared (FTIR) spectra were obtained with a Genesis II-Mattson device in the transmission mode. Soluble samples were coated on NaCl windows from THF solutions. Crosslinked products were ground and mixed with spectroscopic-grade KBr.

Differential scanning calorimetry (DSC) was performed using a Shimadzu DSC-50 device, at a scanning rate of 5 °C/min under nitrogen flow. Reaction heats were measured during a first scan up to 200 °C and glass transition temperatures were determined in a second scan (mid-point of the change in the specific heat).

Dynamic mechanical thermal analysis (DMTA) was performed using a Perkin–Elmer DMA-7 device provided with a cooling system with liquid air. Runs were carried out at 1 Hz in the three-point bending mode at a heating rate of 7 °C/min. Dimensions of the specimens were: length = 20 mm (span = 15 mm), width = 3 mm and thickness = 2 mm. The rubbery modulus was determined at a temperature 50 °C higher than the end of the glass transition.

Uniaxial compression tests were performed at 20 °C using an Instron 4467 universal testing machine. Tests were performed between flat dies at 1 mm/min with cylindrical specimens (length = 11 mm and diameter = 6.6 mm). The elastic modulus was obtained using four to six specimens for every formulation.

3. Results and discussion

3.1. Characterization of OH–SSO and COOH–SSO

A detailed characterization of OH–SSO was performed by matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectrometry (UV-MALDI-TOF MS), and reported in a previous paper [3]. Main species were T_8, T_9(OH), T_{10}, $T_{10}(OH)_2$, and T_{11}(OH) (a $T_n(OH)_m$ species has $2n$ secondary hydroxyls and mSiOH groups). No evidence of stable Si–O–C bonds formed by reaction of SiOH groups with secondary hydroxyls was observed in this product (when acid formic was replaced by NaOH as a catalyst of the hydrolytic condensation, stable Si–O–C bonds were observed in the resulting silsesquioxane [3]). Therefore, OH–SSO is characterized by the presence of a narrow distribution of perfect and imperfect polyhedra containing from 16 to 22 secondary hydroxyls per molecule. A small concentration of species with a lower number of Si atoms was also present in the mass spectra. Titration of the secondary hydroxyls gave 4.78×10^{-3} mol OH per gram of OH–SSO, a value that is very close to the one calculated for a completely condensed species (for T_{10} the theoretical value is 4.87×10^{-3} mol OH per gram).

The reaction between the secondary hydroxyls of OH–SSO with MTHPA was followed by FTIR. Fig. 2 shows FTIR spectra of OH–SSO and MTHPA in the 1450–2000 cm^{-1} wavenumber region. Characteristic bands of the anhydride group are present at 1778 and 1858 cm^{-1}, in a region where OH–SSO has no bands. Fig. 3 shows FTIR

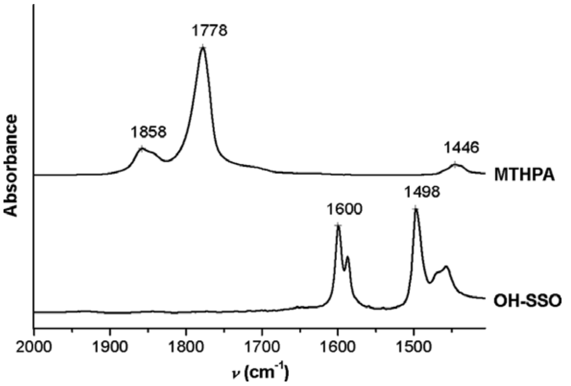

Fig. 2. FTIR spectra of MTHPA and OH–SSO in the 1450–2000 cm^{-1} region.

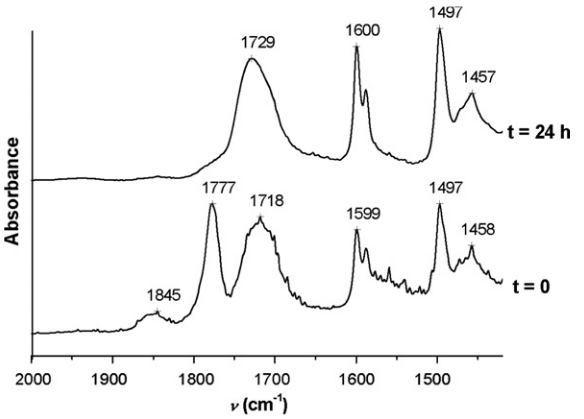

Fig. 3. FTIR spectra of the reaction product between stoichiometric amounts of MTHPA and OH–SSO, shortly after mixing and after 24 h reaction.

spectra of the stoichiometric solution of MTHPA and OH–SSO, shortly after mixing and after 24 h reaction. The reaction proceeds at a fast rate as indicated by the presence of a new band at 1718 cm^{-1} in the initial solution. This peaks includes the C=O stretching vibration of ester and carboxyl groups. After 24 h reaction the characteristic bands of the anhydride had disappeared and were replaced by a broad C=O stretching band with a maximum at 1729 cm^{-1}. This evidences that the reaction between MTHPA and OH–SSO could be carried out to completion leading to the desired COOH–SSO.

SEC chromatograms (Fig. 4) provided similar evidence. Shortly after mixing peaks of OH–SSO and MTHPA are present in the chromatogram. The main peak of OH–SSO includes species with 8 to 11 Si atoms while there are also two smaller peaks of species with a lower number of Si atoms.

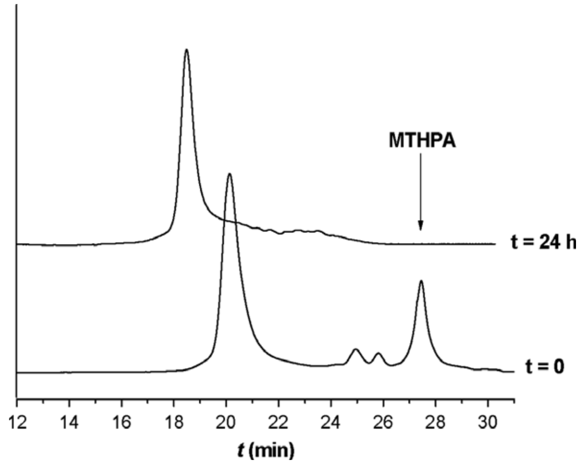

Fig. 4. SEC chromatograms of the reaction product between stoichiometric amounts of MTHPA and OH–SSO, shortly after mixing and after 24 h reaction.

After 24 h reaction the peak of MTHPA completely disappeared and peaks of COOH–SSO appeared at lower retention times than those of OH–SSO because of the large increase in the molar masses (the transformation of 20 hydroxyl groups of T_{10} into 20 (β-carboxyl)ester groups, increases the molar mass from 4105 Da to 7425 Da). The glass transition temperature of OH–SSO was 40 °C while that of COOH–SSO was 50 °C (Fig. 5).

Therefore, main species present in COOH–SSO were perfect and imperfect polyhedra with 8–11 Si atoms, containing 2 (β-carboxyl)ester groups per organic branch (from 16 to 22 carboxyl groups per molecule). The COOH–SSO was a stable glassy product at room temperature and could be dissolved in a variety of organic solvents (i.e., THF

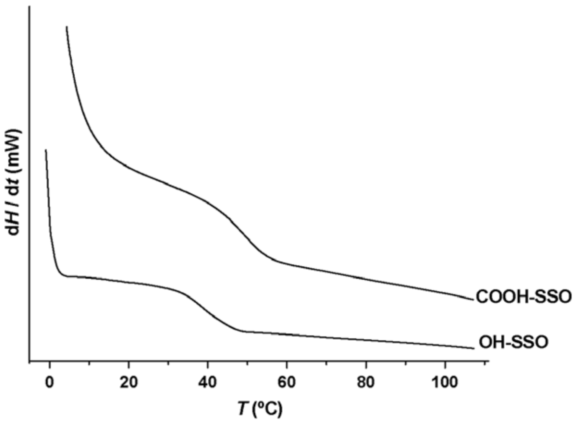

Fig. 5. DSC scans of OH–SSO and COOH–SSO.

and aromatic solvents). This functionalized SSO may be used for a variety of applications. As an illustration, in the next section we will analyze the use of COOH–SSO as a co-monomer to generate a polymer network by reaction with DGEBA in the presence of a tertiary amine (DMAP).

3.2. Reaction of COOH–SSO with DGEBA in the presence of DMAP

The epoxy-acid chemistry is complex involving different possible reactions [10–12]. In the presence of a tertiary amine main reactions are the epoxy-acid addition to give an hydroxyester (Eq. (1) in Fig. 6), and transesterification reactions involving the generated ester groups (Eq. (2) in Fig. 6), and those initially present in the (β-carboxyl)ester groups of the silsesquioxane (Eqs. (3a) and (3b) in Fig. 6). Intramolecular transesterification reactions may also take place producing a complex crosslinked structure.

In the presence of an epoxy excess alkoxide anions are generated by reaction of the epoxy group with the tertiary amine (Eqs. (4) and (5) in Fig. 6). These alkoxide anions produce a catalytic effect on the transesterification reactions [13,14], and they initiate the epoxy homopolymerization (Eq. (6) in Fig. 6). In the latter reaction an epoxy group is bifunctional so that a diepoxide behaves as a tetrafunctional monomer leading to a network. Chain transfer and chain termination reactions do also take place leading to short polyether chains [15]. In particular, hydroxyls are very effective chain transfer agents. Therefore the previous epoxy-acid reaction that generates hydroxyl groups should produce a decrease in the average length of polyether chains and, consequently, a decrease in the concentration of crosslink points associated with these

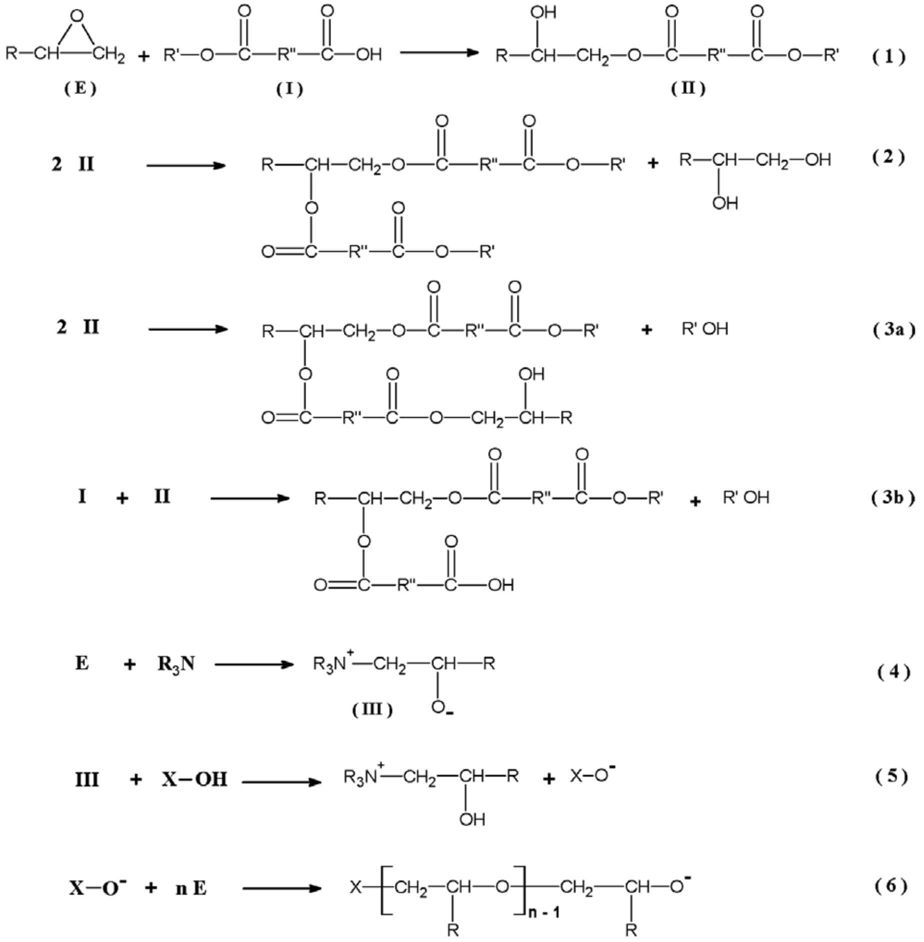

Fig. 6. Reactions taking place in the epoxy + (β-carboxyl)ester reaction in the presence of a tertiary amine, using an epoxy excess.

chains. Other chain transfer reactions generate hydroxyl and vinyl groups by intramolecular proton abstraction [15].

A first insight of the behavior of the system was obtained from DSC scans (Fig. 7). In the presence of DMAP pure DGEBA reacts at a very fast rate leading to a complete conversion of epoxy groups [9]. The total reaction heat was 91.4 kJ/mol, in close agreement with the value of 92 kJ/mol reported for the epoxy homopolymerization [16]. The addition of COOH–SSO produces a significant change of the DSC scans (curves b and c of Fig. 7). In the temperature range comprised between 100 °C and about 130 °C the conversion of epoxy groups is significantly lower than in the case of the neat epoxy. At higher temperatures cure reactions takes place at a fast rate.

A possible explanation of this effect is the complexation of the tertiary amine by (β-carboxyl)ester groups as depicted in Fig. 8. In this scheme, the conformation of both fragments was first optimized using Chem Sketch software; then, they were approached forming an H-bond between the hydroxyl group and the nitrogen atom of DMAP with a $\delta(-)$ charge, and another secondary bond between the carbonyl group and the nitrogen atom of DMAP with a $\delta(+)$ charge. As the formation of these secondary bonds must be exothermic [17], at low temperatures the equilibrium is shifted towards complex formation reducing the concentration of free tertiary amine that is available to catalyze/initiate cure reactions. At high temperatures the complex concentration decreases liberating the free tertiary amine and activating cure reactions. Therefore, in the presence of (β-carboxyl)ester groups the tertiary amine acts as a latent catalyst/initiator of the cure reactions.

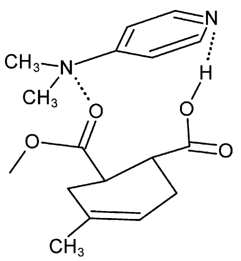

Fig. 8. Complex formed by the tertiary amine and (β-carboxyl)ester groups.

FTIR spectra gave evidence of the formation of H-bonds in the initial reaction mixture. Fig. 9 shows a comparison of FTIR spectra in the carbonyl stretching region for pure COOH–SSO and for the COOH–SSO present in the initial reaction mixture (with DGEBA and DMAP). When mixing COOH–SSO with DGEBA and DMAP, the carboxyl band at 1712 cm^{-1} emerges from the initial band at 1729 cm^{-1}. Taking into account the significant decrease observed in the reaction rate when adding COOH–SSO to the formulation, we assigned the band at 1712 cm^{-1} to the carbonyl stretching of carboxyl groups H-bonded to DMAP (Fig. 8). At the end of the thermal cycle this band disappeared from the spectrum because of the consumption of the

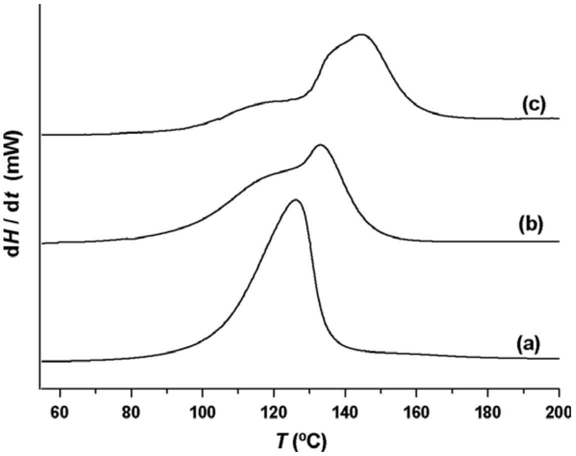

Fig. 7. DSC scans for the cure of: (a) DGEBA, (b) DGEBA + COOH–SSO (molar ratio COOH/epoxy groups = 0.15) and (c) DGEBA + COOH–SSO (molar ratio COOH/epoxy groups = 0.25). For every system the same molar ratio of tertiary amine was used (DMAP/epoxy groups = 0.08).

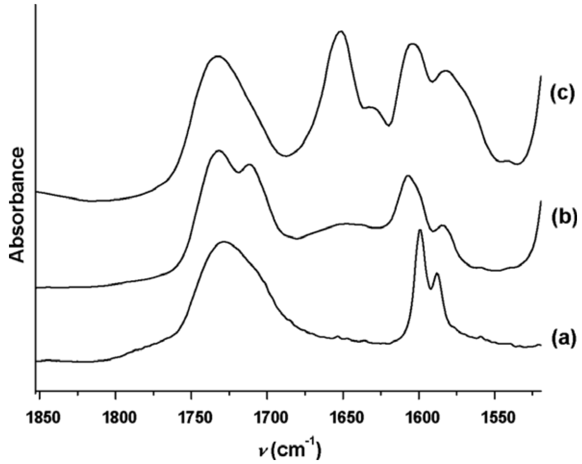

Fig. 9. FTIR spectra of COOH–SSO (a), and a blend with DGEBA and DMAP (molar ratios: COOH/epoxy groups = 0.25, DMAP/epoxy groups = 0.08), after mixing (b) and at the end of reaction (c).

carboxyl groups by reaction with epoxy groups. Characteristic bands of epoxy groups at 863 cm^{-1} and 914 cm^{-1} also disappeared from the FTIR spectra at the end of the thermal cycle. A significant increase in the band at 1651 cm^{-1} was observed at the end of reaction. This band is characteristic of vinyl groups produced by intramolecular chain transfer reactions during the homopolymerization of epoxy groups [9,15].

Therefore, the addition of COOH–SSO to the DGEBA/DMAP formulation produced a shift of the cure reactions to higher temperatures but a complete conversion of epoxy groups could be attained in every case. In the following section we will analyze some thermal and mechanical properties of the resulting networks.

3.3. Thermal and mechanical properties of the resulting networks

It is a priori difficult to estimate the effect of the addition of COOH–SSO to the DGEBA/DMAP formulation on the crosslink density of the resulting network. The addition of a multifunctional comonomer should in principle increase the concentration of crosslink points in the network. However, there are at least two other effects that should act in the opposite sense. First, it is conceivably that a fraction of DGEBA molecules is involved in intramolecular reactions with carboxyl groups of organic branches pertaining to the same silsesquioxane species. Second, hydroxyl groups generated in the carboxyl-epoxy reaction are very effective chain transfer agents in the homopolymerization of epoxy groups. This reduces the average length of polyether chains and produces a decrease in the concentration of crosslink points. To elucidate which is the prevailing trend, the elastic modulus in the rubbery state was measured by DMTA. Resulting values taken at 50 °C above the glass transition temperature, were 100 MPa for pure DGEBA, 32 MPa for the network synthesized with a molar ratio COOH/epoxy = 0.1, and 22 MPa for the material produced with a molar ratio COOH/epoxy = 0.15. As the rubbery modulus is proportional to the concentration of elastic chains, the prevailing trend is a decrease in the crosslink density when increasing the fraction of COOH–SSO in the formulation.

Fig. 10 shows the glass transition temperature of the networks as a function of the molar ratio of COOH/epoxy groups in the initial formulation. In order to predict the plasticization effect produced by the presence of COOH–SSO ($T_{g,SSO} = 323$ K) in the cured epoxy network ($T_{g,EP} = 433$ K), Fox equation may be used [18]:

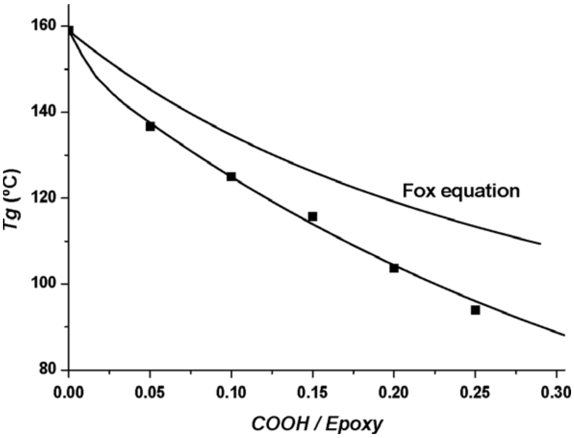

Fig. 10. Glass transition temperature as a function of the molar ratio COOH/epoxy groups. The prediction of Fox equation is also shown.

$$1/T_g = w_{SSO}/T_{g,SSO} + (1 - w_{SSO})/T_{g,EP}$$

where w_{SSO} is the mass fraction of COOH–SSO in the epoxy formulation. As shown in Fig. 10, Fox equation predicts higher glass transition temperatures than those experimentally observed. Although the experimental trend can be fitted using equations providing an extra adjustable parameter like the one proposed by Gordon and Taylor [19], the decrease in crosslink density when increasing the amount of COOH–SSO should also have a bearing on the observed trend.

Fig. 11 shows the variation of the elastic modulus in the glassy state with the molar ratio of COOH/epoxy groups, measured in uniaxial compression tests. A maximum is observed for COOH/epoxy = 0.05. 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 [20]. The presence of these relaxations was monitored by DMA, starting at −150 °C. Fig. 12 shows the variation of tan δ with temperature for the neat epoxy and for cured materials containing various COOH/epoxy molar ratios. The α-relaxation is shifted to lower temperatures when increasing the COOH/epoxy ratio, consistently with the decrease observed in the glass transition temperature (Fig. 10). A β-relaxation is present for the different materials at about −80 °C.

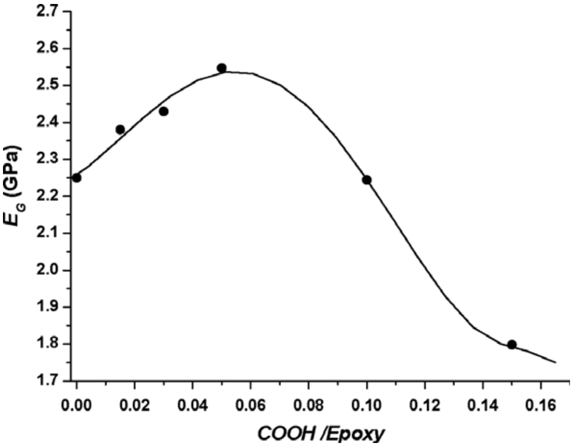

Fig. 11. Elastic modulus in the glassy state determined in uniaxial compression tests, as a function of the COOH/epoxy molar ratio.

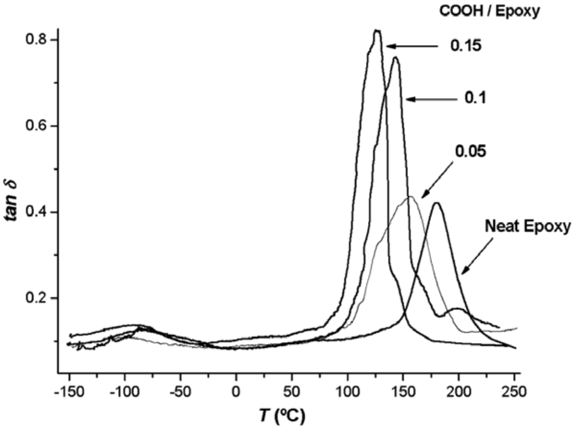

Fig. 12. Variation of tan δ with temperature for the neat epoxy and for cured materials containing various COOH/epoxy molar ratios.

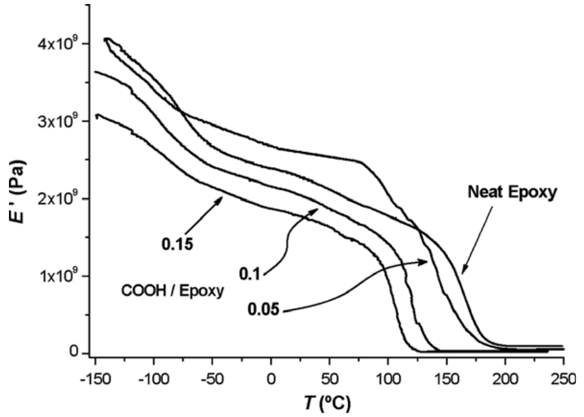

Fig. 13. Variation of the elastic modulus (E') with temperature for the neat epoxy and for cured materials containing various COOH/epoxy molar ratios.

Fig. 13 shows the variation of the elastic modulus (E') with temperature for the neat epoxy and for cured materials containing various COOH/epoxy molar ratios. Although the absolute value of the elastic modulus is determined with a higher precision in uniaxial compression tests (Fig. 11), values arising from Fig. 13 at room temperature exhibit a similar trend (a maximum value for COOH/epoxy = 0.05 and a decreasing trend for higher COOH–SSO amounts).

The presence of a maximum in the elastic modulus can be explained using Fig. 13. The unrelaxed moduli measured below T_β (e.g., at -130 °C) show a maximum for the neat epoxy and a decreasing trend when increasing the COOH/epoxy molar ratio. This means that the cohesive energy density of the networks decreases when increasing the COOH/epoxy molar ratio. However, the magnitude of the β-relaxation is higher for the neat epoxy than for the material with COOH/epoxy = 0.05. This leads to a higher elastic modulus at room temperature for the modified material with respect to the neat epoxy, and explains the presence of a maximum in Fig. 11.

4. Conclusions

A carboxyl-functionalized silsesquioxane consisting on perfect and imperfect polyhedra with 8–11 Si atoms, and containing two (β-carboxyl)ester groups per organic branch (from 16 to 22 carboxyl groups per molecule), was derived from a hydroxyl-functionalized silsesquioxane by reaction with an acid anhydride. The COOH–SSO was a stable glassy product at room temperature and could be dissolved in a variety of organic solvents. Carboxyl-functionalized SSO can be used for a variety of applications including the scavenging of metal ions and organic amines from solutions. Its use as a modifier of an epoxy-tertiary amine formulation showed a shift of the maximum polymerization rate to higher temperatures, explained by an increase in the latency of the tertiary amine by its complexation with (β-carboxyl)ester groups. The glass transition temperature decreased when increasing the amount of COOH–SSO in the formulation, a fact ascribed to the combination of a plasticization effect and a decrease in crosslink density (decrease in rubbery modulus). The glassy modulus measured at room temperature exhibited a maximum for the material synthesized with a molar ratio COOH/epoxy = 0.05. This was explained by a combination of variations of cohesive energy density and the magnitude of β-relaxations.

Acknowledgements

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