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Polymer 46 (2005) 6649–6656

polymer

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Synthesis of a soluble functionalized-silica by the hydrolysis and condensation of organotrialkoxysilanes bearing (β-hydroxy) tertiary amine groups with tetraethoxysilane

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Abstract

The hydrolytic condensation of organotrialkoxysilanes containing (β-hydroxy) tertiary amine groups generates a significant fraction of intramolecular cycles and leads to the formation of closed structures. The aim of this study was to investigate if their co-condensation with a tetraalkoxy silane would take place by predominant intramolecular cyclization steps, eventually leading to functionalized silicas that can be dissolved in appropriate solvents. Co-condensation of tetraethoxysilane (TEOS) with the organotrialkoxysilane derived from the reaction of *N*-(β-aminoethyl)-γ-aminopropyl trimethoxysilane with phenyl glycidyl ether, was performed in the presence of HCOOH using a thermal cycle attaining 150 °C. For TEOS molar fractions lower than 0.7, soluble functionalized-silicas containing up to about 25 wt% of inorganic silica chemically bonded to bulky organic groups, could be synthesized. The glass transition temperature of the organic part was close to 25 °C; it was inferred that the inorganic part was vitrified at the maximum temperature of the selected thermal cycle (150 °C). Most of the Si atoms supplied by the trialkoxysilane were present in fully condensed structures (T^3), while those supplied by TEOS were present mostly as Q^3 and Q^4 structures. These soluble functionalized-silicas may be used to introduce silica as a reinforcement of a polymer network. An example is shown, using an epoxy-diamine formulation. The equivalent of 10 wt% silica could be incorporated to the final network at the expense of a reduction of 26 °C in its glass transition temperature.

Keywords: Organic–inorganic hybrid polymers; Functionalized silica; Tetraethoxysilane

1. Introduction

The hydrolytic condensation of organotrialkoxysilanes, $RSi(OR')_3$, performed in the presence of water and an acid or base as catalysts, leads to products generically called poly(silsesquioxanes) or silsesquioxanes. These polymers have acquired increasing importance in the synthesis of functionalized organic–inorganic hybrid materials [1]. One significant characteristic of this family of polymers is the fact that multiple intramolecular cycles may be formed through Si–O–Si bonds. A generic *n*-mer may exhibit a distribution of species varying from linear or branched structures with no intramolecular cycles to cage structures with the maximum number of intramolecular cycles. Cage structures may be present for *n* (number of Si atoms) equal to or higher than 6, and are usually referred to as polyhedral oligomeric silsesquioxanes (POSS). A high variety of functionalized POSS are commercially available and their effect as modifiers of thermosetting polymers has been reported in many recent publications [2–12]. A major drawback of the use of commercial POSS is the fact that they are relatively expensive products either because they are synthesized from expensive monomers or due to the several steps required in their synthesis.

The possibility of conducting the hydrolytic condensation of organotrialkoxysilanes to generate exclusively cage structures in one step is very attractive. In principle it seems difficult to avoid the generation of a statistical distribution of structures for any *n*-mer. However, we found a striking result when starting from an organotrialkoxysilane derived from the reaction of *N*-(β-aminoethyl)-γ-aminopropyl trimethoxysilane with phenyl glycidyl ether (PGE) (Fig. 1, structure A) [13,14]. Its hydrolytic condensation carried out under both acid and basic conditions led to a sharp distribution of polyhedra with 8,

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doi:10.1016/j.polymer.2005.05.019

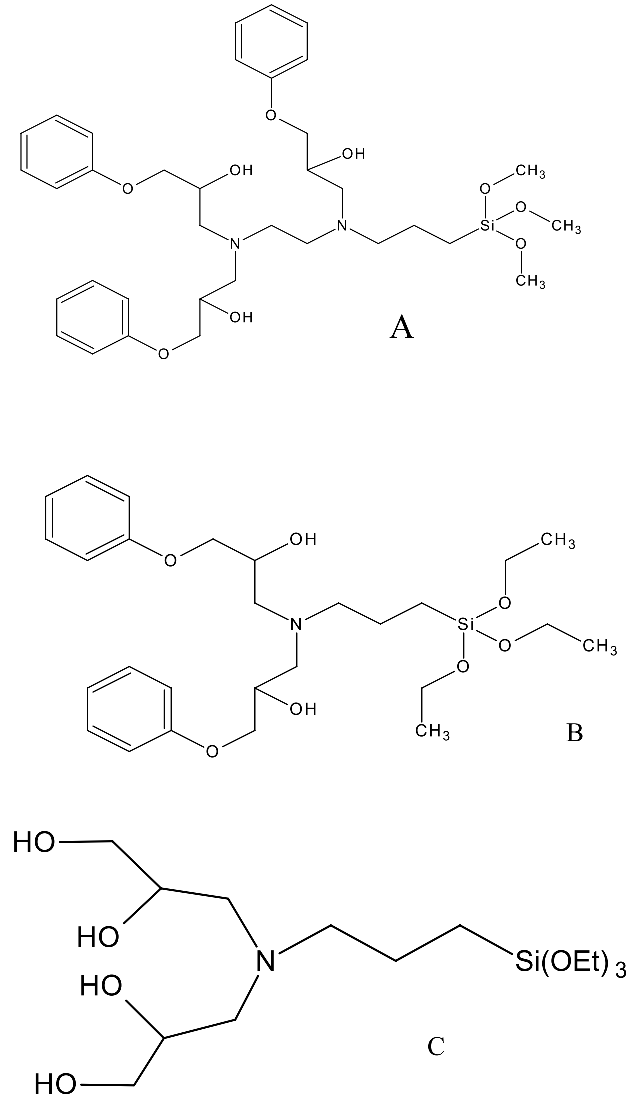

Fig. 1. Chemical structures of organotrialkoxysilanes bearing (β-hydroxy)tertiary amine groups. (A) Product derived from the reaction of *N*-(β-aminoethyl)-γ-aminopropyl trimethoxysilane with phenyl glycidyl ether (PGE); (B) product derived from the reaction of γ-aminopropyl triethoxysilane with PGE; (C) product derived from the reaction of γ-aminopropyl triethoxysilane with glycidol.

9 and 10 Si atoms, with a small tail of polyhedra with 7 and 11 Si atoms (polyhedra derived from an odd number of Si atoms are imperfect and contain one free Si–OH group). These polyhedra are usually identified as T_8, T_9OH and T_{10}. The exclusive formation of cages was ascribed to the bulkiness of the organic group attached to the Si atom [13,14]. Although this might be one reason, the analysis of the hydrolytic condensation of other silanes bearing less bulky organic substituents but still containing (β-hydroxy) tertiary amine groups (Fig. 1, structures B and C), revealed also the formation of closed structures [15–17]. However, the structure of these cages depended on the nature of the starting silane and on the selected conditions of the hydrolytic condensation. Under acid conditions, the silane derived from the reaction of γ-aminopropyl triethoxysilane with PGE (Fig. 1, structure B), led to a distribution of polyhedral species containing 8–11 Si atoms, but exhibiting also some stable Si–O–C bonds [15]. Under basic conditions the same silane led to a distribution of closed structures produced by intramolecular cyclization through a high fraction of Si–O–C bonds [15,16]. A similar set of reaction products was observed by performing the hydrolytic condensation of the silane derived from the reaction of γ-aminopropyl triethoxysilane with glycidol (Fig. 1, structure C), under acid conditions [17].

Hence, the formation of closed structures either through Si–O–Si bonds or through Si–O–C bonds, seems to be originated by the presence of (β-hydroxy) tertiary amine groups in the structure of the starting organotrialkoxysilane. By optimal geometrical structure calculations it was shown that the rotation of a β-hydroxy group places it at a distance of 2.5 Å from the neighboring N atom, leading to the formation of a 5-member ring through a hydrogen-bond [16]. This activates the C–OH group for reaction with Si–OH or Si–OR′ groups leading to Si–O–C bonds that may be stable or can act as intermediate structures to generate silsesquioxane cages.

Many commercial formulations used for organic–inorganic hybrid coatings are derived from the hydrolytic condensation of tri- and tetra-alkoxysilanes (a usual one is TEOS: tetraethoxysilane). When coatings prepared from these solutions are submitted to a thermal cycle at appropriate temperatures they are transformed into gels (this is usually referred to as a sol–gel process). It may be asked if it is possible to use the high driving force of organotrialkoxysilanes bearing (β-hydroxy) tertiary amine groups, to generate closed structures and avoid gelation during the hydrolytic condensation of their mixtures with tetraalkoxysilanes, even after a prolonged heating at relatively high temperatures. If the use of particular organotrialkoxysilanes is effective to avoid gelation, the result will be the generation of a kind of stable functionalized-silica, that might be stored as a glassy product but that should exhibit solubility in appropriate solvents (the term solubility is used to indicate that the product can be dispersed at the molecular level). The aim of this study is to show that using the silane derived from the reaction of *N*-(β-aminoethyl)-γ-aminopropyl trimethoxysilane with phenyl glycidyl ether (Fig. 1, structure A), this is in fact possible. Some preliminary results of the incorporation of the resulting soluble functionalized-silica to epoxy formulations, will be presented.

2. Experimental

2.1. Materials

Reagents used in the different synthesis were: *N*-(β-aminoethyl)-γ-aminopropyl trimethoxysilane (Aldrich,

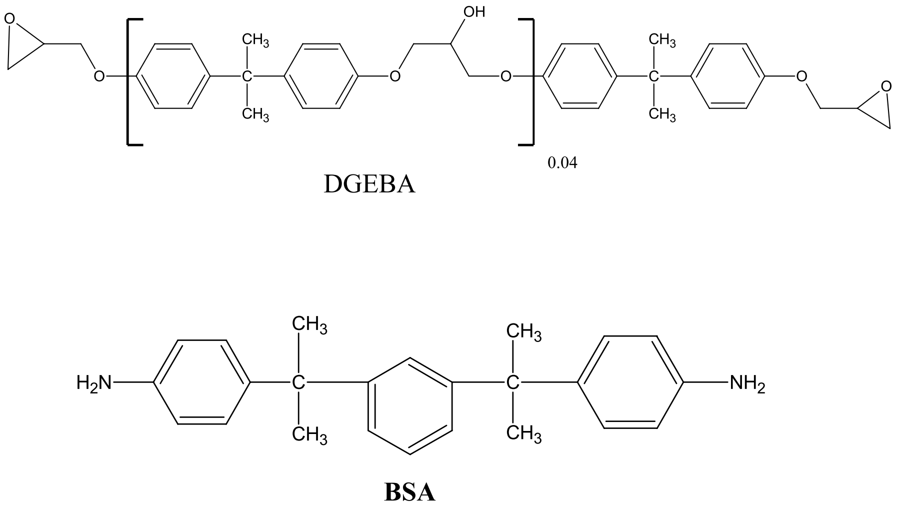

Fig. 2. Chemical structures of the epoxy monomer (DGEBA) and the diamine (BSA).

97% purity), phenyl glycidyl ether (PGE, Aldrich, 99% purity), tetraethoxysilane (TEOS, Aldrich, 98% purity), diglycidyl ether of bisphenol A (DGEBA, MY790 Ciba, mass per mol of epoxy equal to 176.2 g mol^{-1}), 4,4′-[1,3 phenylene-bis-(1-methylethylidene)-bis(aniline)] (BSA, Ken Seika, 99% purity, melting temperature = 116 °C). Chemical structures of DGEBA and BSA are shown in Fig. 2.

2.2. *Synthesis of functionalized-silica*

The organic trialkoxysilane (Fig. 1, structure A) was synthesized by reaction of stoichiometric amounts of *N*-(β-aminoethyl)-γ-aminopropyl trimethoxysilane with phenyl glycidyl ether at 50 °C for 24 h [13,14]. A typical synthesis was performed using 5 g of the silane and 10.13 g of PGE. The modified silane was dissolved in tetrahydrofuran (THF), in a concentration of 0.7 g ml^{-1}. Tetraethoxysilane was added to this solution to give a molar fraction, x_{TEOS}, in the range of 0.2–0.8 (moles of TEOS divided by the sum of moles of TEOS and moles of the trialkoxysilane). Solutions of diluted HCOOH (molar ratios: HCOOH/Si = 0.1, H_2O/Si = 2.2), and concentrated HCOOH (molar ratios: HCOOH/Si = 3.65, H_2O/Si = 1.65), were added as catalysts of the hydrolytic condensation. For example, the synthesis of the product with $x_{\mathrm{TEOS}} = 0.65$ using concentrated formic acid, was performed with 5 ml of the THF solution containing 3.5 g of the modified silane, adding 2.01 g of TEOS and 1.03 g of an 85 wt% solution of HCOOH. The reaction was carried out using the same thermal cycle for every formulation. Temperature was first kept at 50 °C for 24 h, and then increased in steps: 1 h at 75 °C, 3 h at 100 °C, 3 h at 120 °C and 1 h at 150 °C. Volatiles were eliminated during this thermal cycle leading to the final product.

2.3. *Characterization of functionalized-silica*

The critical molar fraction of TEOS that led to gelation was obtained by solubility tests of reaction products in THF at room temperature. The persistence of an insoluble fraction after prolonged (several days) contact times was an indication that gelation took place.

The glass transition temperature (onset of the change in the specific heat), was determined using differential scanning calorimetry (DSC Pyris 1, Perkin–Elmer). Dynamic runs were performed at 10 °C min^{-1} under nitrogen, during a second scan, following a first scan up to 150 °C.

The molar mass distribution of soluble functionalized-silicas dissolved in THF was determined using size exclusion chromatography (SEC). Two different devices were used: a Waters 510 and a Knauer K-501, both provided with refractive index detectors and various sets of columns. THF was used as carrier at 1 ml min^{-1} and the calibration was performed with polystyrene standards.

Solid-state ^{29}Si CP/MAS NMR spectra were obtained at room temperature with a Bruker A400 device at 9.4 T and a resonant frequency of 79.49 MHz. Chemical shifts values (δ) are given in ppm referred to tetramethylsilane (TMS). Magic angle spinning (MAS) was performed at 10 kHz spinning frequency. The proton 90° pulse was of 6 μs, the delay between pulses was of 30 s, the contact time was fixed at 2 ms and the number of accumulated spectra was 400.

2.4. *Synthesis and characterization of epoxy networks modified by soluble functionalized-silica*

The product synthesized with $x_{\mathrm{TEOS}} = 0.65$ was used as a modifier of epoxy-amine networks. A solution of the functionalized silica in THF (about 0.7 g ml^{-1}) was added to DGEBA and the solvent evaporated at room temperature.

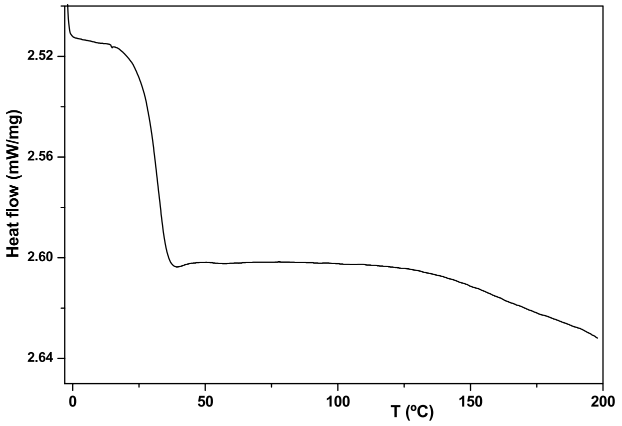

Fig. 3. DSC thermogram of a soluble functionalized-silica containing 60% moles of TEOS, synthesized using diluted HCOOH.

Then, temperature was increased to 125 °C and a stochiometric amount of BSA was added while stirring (some advance in the epoxy-amine reaction occurred during this step). For example, to synthesize an epoxy-amine network modified by 40 wt% of the soluble functionalized silica, the following amounts were used: 7 ml of the THF solution containing 4.96 g of soluble silica were mixed with 5 g of DGEBA, and after solvent evaporation and temperature increase to 125 °C, 2.444 g of BSA were added.

Cure was performed in a differential scanning calorimeter (DSC-50 Shimadzu), at 10 °C min^{-1}, up to 250 °C under nitrogen. The glass transition temperature, defined at the onset of the change in specific heat, was determined during a second scan at 10 °C min^{-1}.

To analyze the possibility of a chemical reaction between the functionalized silica and DGEBA, their solutions devoid of BSA were heated during 3 h at 150 °C. SEC chromatograms of reactants and products were compared.

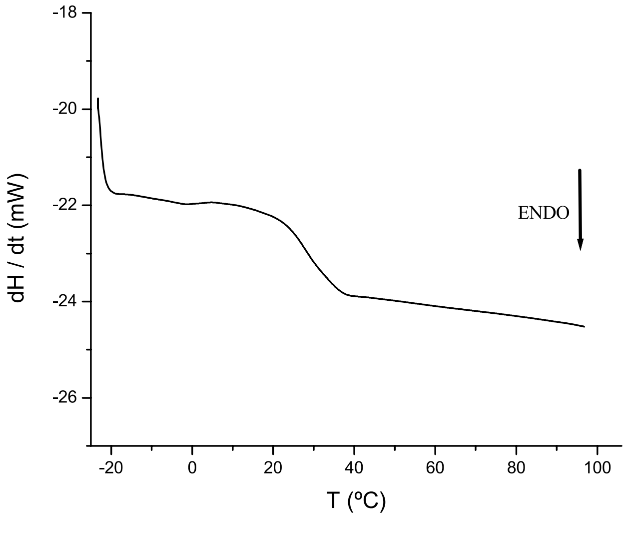

Fig. 4. DSC thermogram of the silsesquioxane obtained by the hydrolysis and condensation of the organotrialkoxysilane shown in Fig. 1(A).

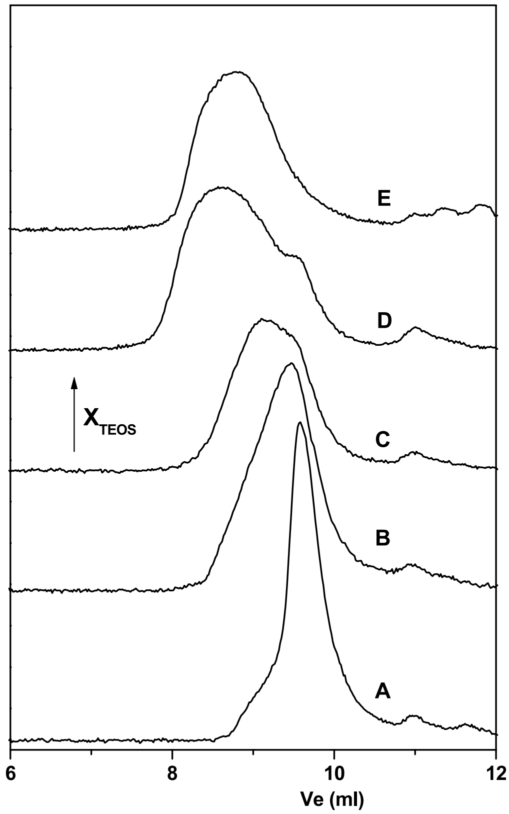

Fig. 5. Set of SEC chromatograms for products synthesized using different molar fractions of TEOS: 0 (A), 0.2 (B), 0.4 (C), 0.6 (D), 0.65 (E). Products A–D were synthesized using diluted HCOOH and product E was synthesized using concentrated formic acid.

3. Results and discussion

3.1. Critical TEOS concentration to obtain soluble functionalized-silicas

The critical molar fraction of TEOS that led to gelation was first established. The resulting experimental value was $x_{\mathrm{TEOS}}(\mathrm{crit})=0.7$. Formulations containing $x_{\mathrm{TEOS}}=0.65$ led to a functionalized silica that could be dissolved in THF and in aromatic solvents. It has to be emphasized, however, that this critical value has to be considered only valid for the selected experimental conditions (concentrations of reagents and catalyst, order and time of addition of every component, temperature vs. time history).

In order to determine if the critical TEOS fraction leading to gelation depended on the selected thermal cycle, the product with $x_{\mathrm{TEOS}}=0.65$ was heated during another 3 h at 150 °C without altering its solubility in THF. However, if a second heating step was performed during 2.5 h at 180 °C, the resulting product was not completely soluble in THF, meaning that the critical molar fraction of TEOS depended on the maximum temperature of the thermal cycle.

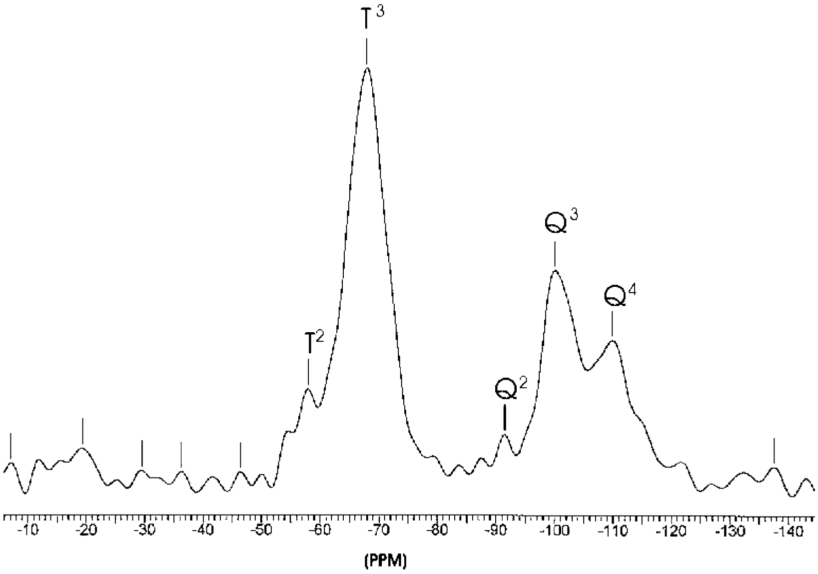

Fig. 6. ^{29}Si NMR spectrum of the soluble functionalized-silica containing 65% moles of TEOS, synthesized using concentrated HCOOH.

3.2. Characterization of soluble functionalized-silicas

The glass transition temperature (T_g) of soluble functionalized-silicas was close to 25 °C (Fig. 3). This value is similar to the one of the condensation product of the neat trialkoxysilane (Fig. 4), and is therefore ascribed to the mobility of the organic branches.

Fig. 5 shows a set of SEC chromatograms obtained for products synthesized with different amounts of TEOS: 0 (A), 0.2 (B), 0.4 (C), 0.6 (D), 0.65 (E). Products A–D were synthesized using diluted HCOOH and product E was synthesized using concentrated formic acid. As the TEOS amount was increased, the peak was shifted to lower elution volumes or, equivalently, to higher molar masses. Except for the product containing 65% moles of TEOS, the distribution exhibits a shoulder at the same elution volume of the product resulting from the condensation of the neat trimethoxysilane (POSS). This arises by the faster hydrolysis of methoxy groups with respect to ethoxy groups [18], and the fact that the hydrolysis and condensation rates of alkyl- and aryl-trialkoxysilanes are significantly faster than those of tetraalkoxysilanes [19,20]. Pre-hydrolysis of TEOS before addition to the trialkoxysilane solution, is a conventional procedure to produce a more random condensation product. It might change both the critical TEOS concentration and the molar mass distributions of condensation products. The shoulder assigned to POSS has practically disappeared for $x_{TEOS}=0.65$, meaning that a more random condensation between both co-monomers took place for this composition.

The product devoid of TEOS is mainly a distribution of polyhedral oligomeric silsesquioxanes with molar masses equal to 4830 Da (T_8), 5443 Da (T_9OH) and 6038 Da (T_{10}) [14]. The elution volume at the peak of this product may be assigned to the molar mass of T_9OH. Based on this value and on the derivative of the logarithm of the molar mass with respect to the elution volume obtained by calibration with polystyrene standards, the molar mass at the peak of the product with $x_{TEOS}=0.65$ was estimated as a value close to 12,000 Da.

The ^{29}Si NMR spectrum of the soluble functionalized-silica with $x_{TEOS}=0.65$, synthesized using concentrated HCOOH, is shown in Fig. 6. Peaks in the T region are contributed by Si atoms of the trialkoxysilane while those in the Q region arise from Si atoms of TEOS. Although the spectrum is not quantitative (the area of peaks in the Q region should be 65% of the total area), it still provides significant information about the structure of the functionalized silica. T^3 represents Si atoms joined to the organic group and forming three Si–O–Si bonds; T^2 indicates Si atoms joined to the organic group, bearing one uncondensed SiOH group and forming two Si–O–Si bonds (although T^3 structures present in strained cycles might be also present in this range of chemical shifts). The high intensity of the T^3 peak reveals the high degree of condensation of the original trialkoxysilane. Q^n represents a Si atom of TEOS forming n Si–O–Si bonds and bearing $(4-n)$ OH groups. While the fraction of Q^2 structures is negligible, both Q^3 and Q^4 are present in significant concentrations.

Therefore, the functionalized silica exhibits a significant fraction of SiOH groups contributed by the original TEOS monomer. Both intra and intermolecular condensation of SiOH groups occurred during the whole thermal cycle but conversion was no complete. When this product was heated at 180 °C for 2.5 h, gelation was observed meaning that condensation reactions were re-activated at temperatures higher than the maximum one used in the synthesis. A possible explanation is related to the incompatibility of the inorganic framework and pendant organic chains, leading to microphase separation and spontaneous self-organization of

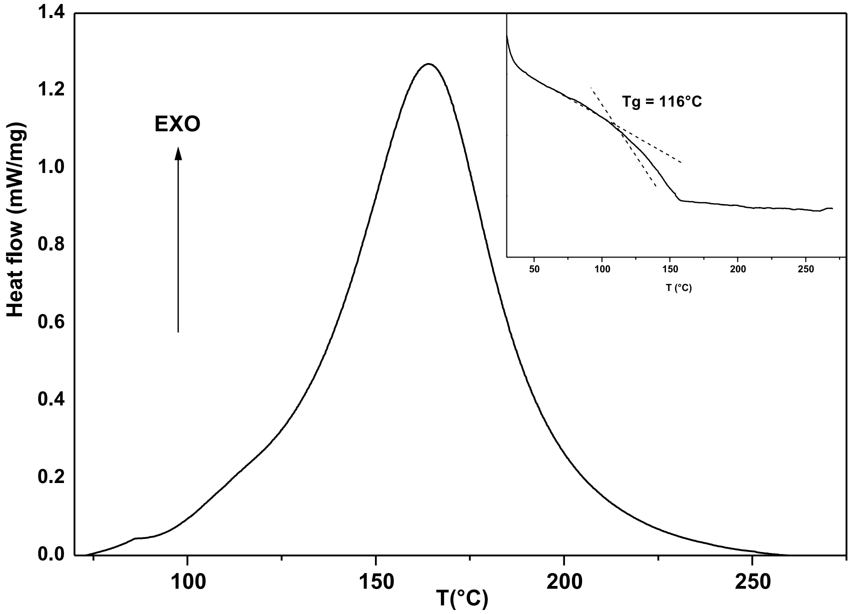

Fig. 7. DSC thermogram of a stoichiometric DGEBA-BSA solution, at 10 °C/min; the inset shows the glass transition temperature of the completely reacted product, obtained in a second scan.

inorganic and organic domains [21]. By DSC only the glass transition temperature of the organic domains could be recorded (Fig. 3). The arrest of SiOH condensation reactions in the inorganic phase at 150 °C, but its continuation at 180 °C, might be ascribed to the formation of an inorganic glass with a T_g close to the maximum temperature of the thermal cycle (although no indication of this second T_g could be obtained in the DSC thermogram shown in Fig. 3). If this explanation is correct, when heating to 180 °C devitrification of inorganic domains should take place and the condensation reaction proceed to a higher conversion leading to gelation. As the condensation increases so does the glass transition temperature of the inorganic domains. When it reaches 180 °C, the condensation is again arrested by vitrification. Both the critical molar fraction of TEOS leading to gelation and the residual fraction of SiOH groups in the final product must be dependent on the maximum temperature of the selected thermal cycle.

The chemical structure of the functionalized silica with $x_{\mathrm{TEOS}}=0.65$ may be described as: $(\mathrm{SiO}_{2-x}(\mathrm{OH})_{2x})_{0.65}$–$(\mathrm{RSiO}_{1.5})_{0.35}$, where the small contribution of T^2 structures has been neglected and the value of the subscript x is less than 0.5, accounting for the fact that most of the structures derived from the TEOS condensation are either Q^3 ($x=0.5$) or Q^4 ($x=0$). The mass per repeating unit is close to 253.3 g/mol of Si atoms (it varies from 250.4 g for $x=0$–256.2 g for $x=0.5$). For a molar mass equal to 12,000 Da this leads to an average of 47.4 moles of Si, 16.6 of which are attached to organic groups. The mass fraction of organic groups lies between 75.3% for $x=0.5$, and 77.1% for $x=0$. Therefore, due to the bulky organic substituent, these functionalized silicas contain about 1/4 of inorganic phase and 3/4 of organic phase that enables its dissolution in different solvents. DSC revealed only the glass transition temperature of the organic phase (Fig. 3).

3.3. Synthesis and characterization of epoxy networks modified by the soluble functionalized-silica

DGEBA and BSA were selected as monomer and co-monomer due to their aromatic structure that makes them compatible with the functionalized silica. The polymerization of stoichiometric amounts of DGEBA and BSA was first studied. In order to prevent a significant advance in the reaction during the mixing stage, BSA was dissolved in DGEBA at temperatures lower than 100 °C. A dynamic DSC run of this solution is shown in Fig. 7. The total reaction heat was 102 kJ/mol, that lies in the range of values reported for several epoxy-amine systems [22]. The glass transition temperature of the final polymer network was determined during a second heating scan. Its value was 116 °C as shown in the inset of Fig. 7.

In order to incorporate about 10 wt% silica as a reinforcement of the epoxy-amine network, it is necessary to add 40 wt% of the functionalized silica with $x_{\mathrm{TEOS}}=0.65$, to the initial formulation. The price to be paid is a lowering of the glass transition temperature due to the plasticizing effect of the organic branches bonded to Si atoms ($T_g=$ 25 °C). These organic branches contain hydroxy groups that are catalysts of the epoxy-amine reaction and tertiary amine groups that can initiate the homopolymerization of epoxy groups as a parallel reaction.

In order to analyze if the homopolymerization of DGEBA could be initiated by the functionalized silica, solutions containing 30 wt% of functionalized silica (obtained with 65% moles of TEOS), in DGEBA, were

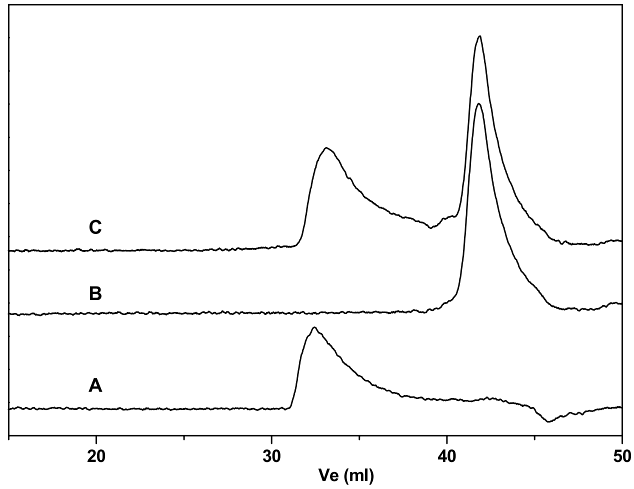

Fig. 8. SEC chromatograms of: (A) functionalized silica (obtained with 65% moles of TEOS), (B) DGEBA, and (C) 30 wt% solution of functionalized silica in DGEBA, after the heating period at 150 °C.

kept at 150 °C for 3 h. SEC chromatograms of: (A) functionalized silica (obtained with 65% moles of TEOS), (B) DGEBA, and (C) 30 wt% solution of functionalized silica in DGEBA, after the heating period at 150 °C, are shown in Fig. 8. No significant reaction took place under these conditions.

Stoichiometric epoxy-amine formulations containing different amounts of the functionalized silica synthesized with $x_{\mathrm{TEOS}}=0.65$, were polymerized in the course of a DSC scan. Apart from the epoxy-amine reaction, it cannot be discarded that SiOH–SiOH condensation reactions took also place during the DSC scan. Glass transition temperatures of cured networks, determined in a second scan, are shown in Fig. 9. The incorporation of the equivalent of 10 wt% of silica (40 wt% of functionalized silica), led to a decrease of 26 °C in the final T_g due to the plasticizing effect of the organic branches present in the functionalized silica.

4. Conclusions

Soluble functionalized-silicas containing up to about 25 wt% of inorganic silica chemically bonded to bulky organic groups, could be synthesized from solutions of TEOS and a trialkoxysilane bearing (β-hydroxy) tertiary amine groups. The glass transition temperature of the organic part was close to 25 °C; it was inferred that the inorganic part was vitrified at the maximum temperature of the selected thermal cycle (150 °C). Most of the Si atoms supplied by the trialkoxysilane were present in fully condensed structures (T^3), while those supplied by TEOS were present mostly as Q^3 and Q^4 structures.

These soluble functionalized-silicas may be used to introduce SiO_2 as a reinforcement of a polymer network. The presence of OH groups in the organic branches can generate covalent bonds in different types of polymer networks (e.g. polyurethanes). Alternatively, these functionalized silicas can be dissolved in the system without participating in the chemical reaction. An example of this last case was shown, using a DGEBA-BSA stoichiometric formulation. The equivalent of 10 wt% silica could be incorporated in the final network at the expense of a reduction of 26 °C in its glass transition temperature.

There are multiple possibilities of varying the critical TEOS concentration necessary to avoid gelation as well as the structure of the resulting products. Other trialkoxysilanes may be used like those shown in Fig. 1(B) and (C), TEOS may be pre-hydrolyzed and partially condensed before performing the co-condensation with the trialkoxysilane, different thermal cycles may be employed, etc. Some of these possibilities are currently being investigated.

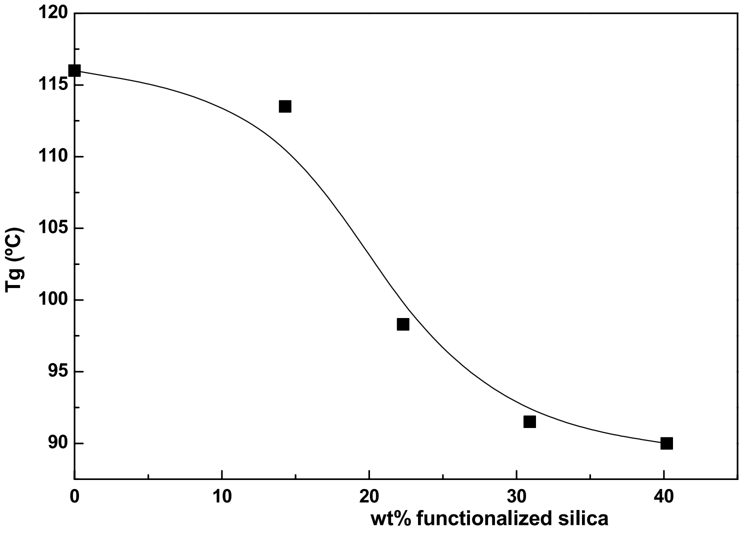

Fig. 9. Glass transition temperature as a function of the wt% of functionalized silica (obtained with 65% moles of TEOS), used as modifier of the DGEBA-BSA network.

Acknowledgements

The financial support of University of Mar del Plata, CONICET and ANPCyT (Argentina), is gratefully acknowledged.

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