

SILSESQUIOXANE SYNTHESIS AND INCORPORATION INTO ORGANIC/INORGANIC HYBRIDS BASED ON EPOXY RESIN

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Key words: Organic-inorganic hybrid, Silsesquioxane, Epoxy resin, Free volume, Glass transition, Cross-link density.

Summary: *Silsesquioxane structures have been incorporated into polymeric matrices in order to improve certain properties, such as mechanical and thermal resistance. Nonetheless, the rules which govern the behavior of such organic/inorganic hybrids are not always clear. In this study, a silsesquioxane containing epoxy functionality (SSQO-E) was incorporated into DGEBA (diglycidyl ether of bisphenol A) in different concentrations, up to 20 wt%. In this epoxy system, DETA (diethylenetriamine) was used as the curing agent. The SSQO-E was synthesized from GPTMS (3-glycidoxypropyl trimethoxysilane) through a hydrolytic condensation reaction, using tetramethylammonium hydroxide as a catalyst. The molar mass of the SSQO-E was estimated by SEC to have a value close to the cubic cage silsesquioxane structure (SSQO-T₈). ²⁹Si NMR and ¹H NMR spectra of SSQO-E were also similar to the SSQO-T₈, presenting predominately completely condensed silsesquioxane molecules. In addition, DGEBA/SSQO-E/DETA hybrids were prepared in a tetrahydrofuran/DGEBA medium to ensure the homogeneous dispersion of SSQO-E into the epoxy resin, which was verified by the single glass transition temperature (T_g) values (determined by differential scanning calorimetry, DSC) shown by the organic/inorganic hybrids. It was observed that T_g decreased with SSQO-E content, with a lowering of approximately 20 °C for the 20 wt% SSQO-E content hybrid in relation to the T_g of epoxy resin, whilst the free volume (investigated by comparing the heat capacity change, Δ_{cp}, measured during the material glass transition) of the organic/inorganic hybrids showed no significant variation in relation to the epoxy resin. The cross-link density (evaluated by the swelling of the systems in THF solvent) was observed to increase with SSQO-E content despite the increase in bulkier SSQO-E molecules. The opposite effects of increasing in cross-link density and decreasing in T_g for higher SSQO-E content observed in the organic/inorganic hybrids may be attributed to: the presence of the more flexible 2-hydroxypropyl-n-propylether ((CH₂)₃-O-CH₂-CH(OH)-CH₂-) groups in DGEBA/SSQO-E/DETA hybrids in contrast to the less flexible hydroxypropyl ether (-O-CH₂-CH(OH)-CH₂-) groups present in epoxy resin; and to the higher number of flexible groups in hybrids (eight flexible groups per SSQO-E molecule) compared to the number in epoxy resin (two flexible groups per DGEBA molecule).*

1 INTRODUCTION

Organic/inorganic hybrids are generally formed by mixing organic polymer chains and inorganic silicon compounds. These phases are mixed at a molecular level, usually at the nanoscale, which ensures the macroscopic homogeneity of the material [1-4]. The inorganic phase is generally obtained from a silicon precursor, such as a trialkoxysilane, whose hydrolytic condensation may give rise to a hybrid silsesquioxane (SSQO) structure [5-7]. A variety of SSQO structures may be prepared, including open structures (random or ladder polymers) and partially or fully condensed structures, with the general formula given by $(\text{RSiO}_{3/2})_n$, where n is commonly 6, 8 or 10. These structures are denoted as T_n or as polyhedral silsesquioxane [4, 8]. Polyhedral silsesquioxanes have been used as molecular building blocks in several polymeric matrices to improve certain specific properties. For example, epoxy resins have been reinforced with SSQO, which may be incorporated as a junction epoxy network or as a pendant group bounded to the epoxy network, depending on the chemical functionality of the organic groups bonded to the silicon polyhedral [9-18].

According to the literature, the addition of SSQO to epoxy matrices can increase, decrease, or not affect the glass transition temperature (T_g) of the nanocomposites. A. Lee and J. D. Lichtenhan [9], among others [15, 19], reported an increase in the T_g of SSQO/epoxy compounds with an increase in SSQO content, which was attributed to the epoxy molecular motion hindrance caused by the SSQO molecules bounded to the epoxy network. A. Strachota et al. [12] reported different T_g behavior for SSQO/epoxy compounds depending on the SSQO functionality. They showed that T_g was not significantly affected by the presence of SSQO when bounded to the epoxy network as a monofunctional pendant group. In contrast, a remarkable increase in T_g of ~ 50 °C was reported in an epoxy network containing SSQO monofunctional oligomer previously reacted with DGEBA, which was attributed to the severely restricted mobility of the resulting epoxy network. These authors also investigated the T_g behavior of an octafunctional SSQO/epoxy network, observing a decrease in T_g relative to the epoxy network, due to the flexible hexyl substituents present in the SSQO units, which acted as a “soft” junction in the network.

In the present study a silsesquioxane was synthesized from GPTMS (3-glycidoxypropyl trimethoxysilane) through a hydrolytic condensation reaction. After its characterization, it was incorporated into an epoxy network up to 20 wt% content. The influence of the synthesized silsesquioxane on the epoxy matrix was investigated through heat capacity change during glass transition, measured using DSC, which was related to the free volume and the cross-link density of the resulting epoxy networks.

2-EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA, Araldite GY 1109 BR, Vantico), with an epoxide equivalent weight of 213 g/equiv; diethylenetriamine (DETA, Aradur HY 950 BR, Huntsman); 3-glycidoxypropyl trimethoxysilane (GPTMS, Sigma Aldrich); tetramethylammonium hydroxide (25 wt% Me_4NOH in methanol solution, Acros Organics) and tetrahydrofuran (THF, Merck) were used as received.

SSQO-E synthesis and characterization

SSQO-E was synthesized in basic medium in two steps. Initially, GTPMS was

solubilized in THF (1.0 mol/L) and an aqueous solution of Me₄NOH catalyst (0.02 mol/L) was added until H₂O/Si = 3 molar ratio. This solution was maintained at 50°C for 24 hours, stirred continuously. The SSQO-E prepared in this stage was characterized by SEC, ¹H and ²⁹Si NMR. Next, DGEBA was added to this solution in order to maintain a DGEBA:GPTMS molar ratio of 1:1. This mixture was placed in a rotary evaporator at 40°C for 43 hours to remove the THF, resulting in a DGEBA/SSQO-E mixture.

Size Exclusion Chromatography (SEC)

Molar mass distribution of SSQO-E was determined in a PerkinElmer SEC Series 200, using a polystyrene column (HPLC Column VA 300/7.7 NUCLEOGEL GPC 500-5), a refractive index detector and THF (0.5 mL/min) as a carrier.

NMR spectroscopy

¹H NMR and ²⁹Si NMR spectra were performed in a Bruker Avance III 500 at 500MHz and 11.75 Tesla for ¹H, and at 99 MHz for ²⁹Si. The SSQO-E was dissolved in deuterated chloroform (CDCl₃). Tetramethylsilane (TMS) solution (0.05% v/v) in CDCl₃ was used as internal standard.

Organic/inorganic hybrids

Hybrids with different SSQO-E contents (1, 3, 5, 10 and 20 wt%) were prepared by first diluting the DGEBA/SSQO-E mixture with DGEBA. DETA was then added as a curing agent, in stoichiometric proportion to the glycidoxo groups (considering only the presence of cubic T₈ structures in the mixture). The DGEBA curing process was conducted initially in a desiccator at 25 °C for 24 h, followed by 2h at 120 °C to complete curing.

Differential Scanning Calorimetry (DSC)

After the cure cycle, the DGEBA resin and organic/inorganic hybrids were analyzed using the Modulated DSC Q 100, TA Instruments, with modulation conditions: ±0.5 °C and a 60 s. Samples were heated at 5 °C/min, from -20 °C to 140 °C, and analyses were performed in two scans. Heat capacity change (ΔC_p) during polymer glass transition (Figure 1) was used to estimate the free volume variation of DGEBA resin and organic/inorganic hybrids.

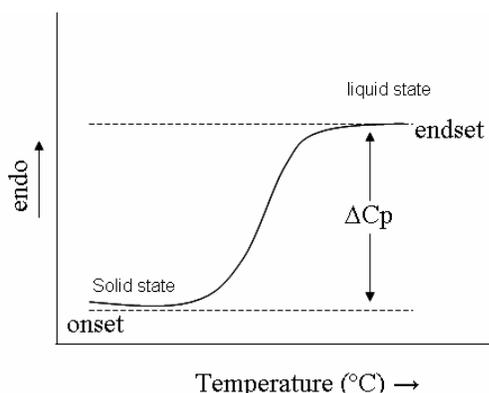


Figure 1: Schematic illustration of the heat capacity change determination during polymer glass transition.

Soxhlet Extraction

The DGEBA/DETA resin and organic/inorganic hybrid containing 20 wt% SSQO-E

were submitted to THF extraction in a soxhlet apparatus for 15 h to ensure the extraction of any DGEBA monomer or free SSQO-E. The soluble THF fraction was evaluated by Fourier transform infrared spectroscopy (FT-IR) spectroscopy in a PerkinElmer Spectrum One spectrometer, operating at a resolution of 4 cm^{-1} , 20 scans over the wavenumber range 4000 to 500 cm^{-1} in transmission mode. Samples were analyzed using the liquid film technique.

Swelling test

Swelling tests were conducted by immersing the DGEBA resin and organic/inorganic hybrids in THF, until the epoxy compounds attained equilibrium. The weight of the samples was monitored for 5 days, up to a constant weight value. Gel fraction (F_g) was calculated by

$$F_g(\%) = [(w_f / w_i)].100 \quad (1)$$

where w_f is the sample dry weight after THF swelling and w_i is the sample dry weight before THF swelling.

3-RESULTS AND DISCUSSION

SSQO-E Characterization

The SSQO-E average molar mass determined by SEC (1365 g/mol) was close to the nominal molar mass calculated for SSQO-E cubic cage T_8 (1338 g/mol). Moreover, the polydispersity was close to 1, indicating the predominant presence of T_8 structures, with a low concentration of T_{10} and T_{12} , detected as a shoulder in the molar mass distribution curve (Figure 2). The SSQO-E was characterized by ^1H and ^{29}Si NMR spectra. ^{29}Si NMR spectrum of SSQO-E showed chemical shifts at -64.10 , -66.12 , -67.91 and -70.26 ppm, which correspond to the cubic cage molecular structure [20]. ^1H NMR spectrum of SSQO-E showed chemical shifts at 2.6; 2.8 and 3.2 ppm related to the hydrogen in epoxy ring CHOCH_2 [13] and hydrogen from the $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2$ aliphatic chain ($\alpha\text{-CH}_2$ at 0.7 ppm, $\beta\text{-CH}_2$ at 1.7 ppm and $\gamma\text{-CH}_2$ at 3.4 ppm) [8, 13]. It is worth emphasizing that chemical shifts related to silanol groups were not observed, which confirms the completely condensed SSQO-E structure.

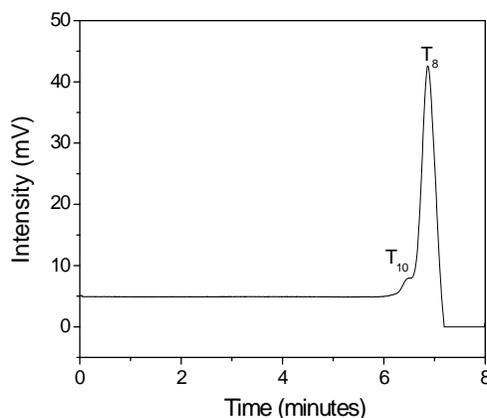


Figure 2: SEC Chromatogram of the SSQO-E.

Organic/Inorganic Hybrids

The DGEBA/SSQO-E/DETA hybrids were transparent, which points to the homogeneous dispersion of the epoxy and SSQO-E phases in dimensions smaller than the visible light wavelength in all the SSQO-E contents studied.

The glass transition temperature of the epoxy compounds was investigated using DSC (Figure 3-a). All organic/inorganic hybrids presented a single T_g, with values decreasing smoothly as the SSQO-E content increased up to 5 wt%, followed by a more intense reduction of approximately 20 °C for the hybrid containing 20 wt% SSQO-E. As the transparency observed for the organic/inorganic hybrids, the presence of a single T_g indicates the homogeneity of distribution of the organic and inorganic phases into the hybrid materials.

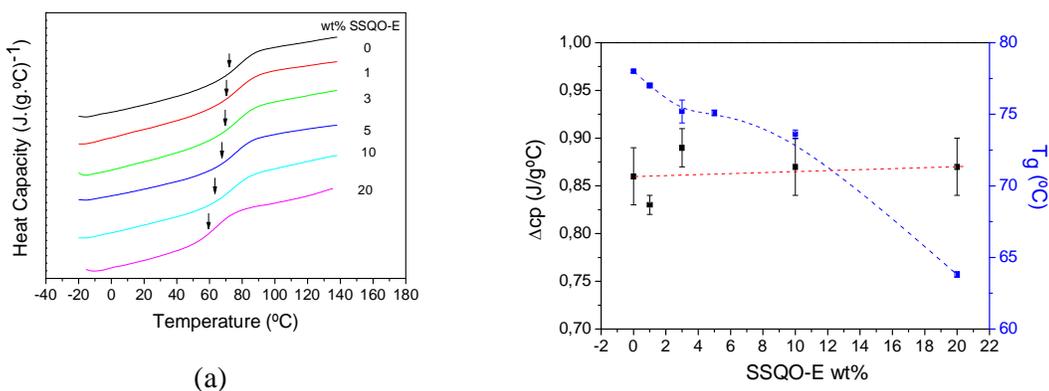


Figure 3: (a) DSC curves of organic/inorganic hybrids containing different concentrations of SSQO-E; (b) Heat capacity changing (Δc_p) and glass transition temperature (T_g) as a function of SSQO-E content in organic/inorganic hybrids. (-□-) experimental T_g (DSC) and (-Δ-) estimated T_g considering the 1 wt% SSQO-E as a reference.

A reduction in T_g in organic/inorganic hybrids containing SSQO bounded to flexible groups has been reported previously [12, 21]. In these cases, the SSQO flexible groups provide more mobility to the epoxy network and consequently cause the reduction in T_g.

In the present study, the incorporation of SSQO-E into an epoxy network resulted in partial substitution of the less flexible hydroxypropyl ether (-O-CH₂-CH(OH)-CH₂-) groups present in epoxy resin for the more flexible 2-hydroxypropyl-n-propylether ((CH₂)₃-O-CH₂-CH(OH)-CH₂-) groups bound to SSQO-E. Moreover, the larger number of flexible groups in the organic/inorganic hybrids (eight flexible groups per SSQO-E molecule) compared to that in epoxy resin (two flexible groups per DGEBA molecule) should also have contributed to the decrease in T_g with the increase in SSQO-E content.

Nonetheless, other causes have been associated with a reduction in T_g observed in organic/inorganic hybrids containing SSQO, such as the increase of free volume attributed to the presence of SSQO groups in an epoxy network [19, 22] and the incomplete network cross link due to the steric hindrance caused by bulky SSQO [10, 23]. These possible causes were investigated as follows.

The first was the increase in free volume. In polymer systems, free volume can be estimated by the heat capacity change (Δc_p) measured using the DSC technique, which reflects the degree of freedom before (solid state) and after (liquid state) material glass

transition. An increase in Δc_p is expected whenever there is an enhancement in polymer free volume. The Δc_p of the organic/inorganic hybrids was calculated as schematized in Figure 1.

In Figure 3-b the Δc_p calculated during glass transition are shown along with the T_g of the organic/inorganic hybrids, both as a function of the SSQO-E content. Both the organic/inorganic hybrids and the epoxy resin presented similar Δc_p values, regardless of SSQO-E content, showing that the free volume of these materials practically did not vary with the increase in SSQO-E content.

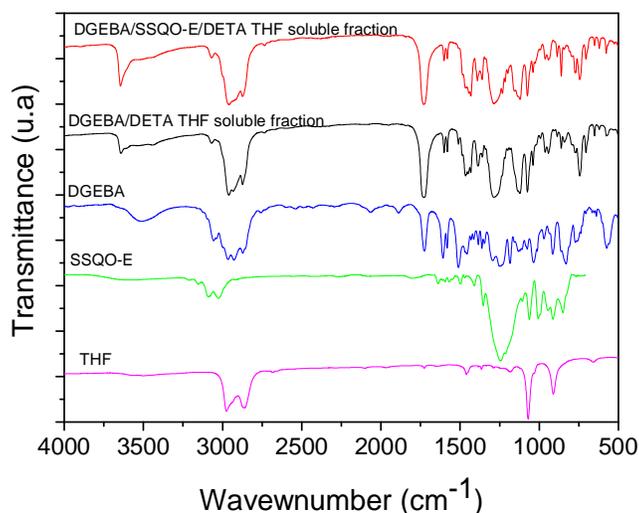


Figure 4: FT-IR spectra of THF soluble fractions of DGEBA/SSQO-E/DETA containing 20 wt% of SSQO-E and DGEBA/DETA; DGEBA resin, pure SSQO-E and THF solvent.

Another possible cause for the T_g reduction observed in thermosets containing SSQO could be the incomplete network cross link due to the steric hindrance because of the presence of bulky SSQO [10, 23]. The organic/inorganic hybrid containing 20 wt % SSQO-E was submitted to soxhlet extraction in a THF solvent to ensure the extraction of any DGEBA monomer or free SSQO-E. After extraction, the THF soluble fraction was analyzed by FT-IR spectroscopy and compared to that extracted from a DGEBA/DETA resin, used as a control. The spectra of both extracted fractions were similar (Figure 4), and showed characteristic absorptions related to dibutyl phthalate and aliphatic glycidyl ether, which are additives used in DGEBA. The most characteristic absorption of dibutyl phthalate was observed at 1725 cm^{-1} , which was attributed to the RCOR group. In Figure 4 the infrared spectra of individual components, DGEBA monomer (3504 cm^{-1} , attributed to OH, 1247 cm^{-1} assigned to C-O aromatic; 915 cm^{-1} and 831 cm^{-1} , related to epoxy ring CH₂-O-CR) and SSQO-E (1090 cm^{-1} , Si-O-Si) [20, 24] are also shown. The characteristic absorptions of DGEBA monomer and SSQO-E were not observed in the THF soluble fraction FT-IR spectra, indicating that both species were chemically incorporated into the epoxy network.

The presence of partially bound SSQO-E in the epoxy network causing the reduction in its cross link density and the consequent T_g reduction was investigated using the swelling test in THF solvent. Organic/inorganic hybrids were exposed to the THF solvent up to constant mass. The gel fractions calculated for 5, 10 and 20wt% SSQO-E were 86, 94 and

99%, respectively, showing that, in the studied system, the cross link density actually increased with the increase in SSQO-E content.

These results indicate that the T_g reduction observed for organic/inorganic hybrids was probably caused by the introduction of more flexible 2-hydroxypropyl-n-propylether groups bound to SSQO-E, which increase the mobility of the epoxy network in comparison to that observed in DGEBA/DETA resin.

4-CONCLUSIONS

SSQO-E was successfully synthesized by basic catalysis, yielding predominantly a cubic cage silsesquioxane structure. Its incorporation into an epoxy network using DGEBA as a solvent during the SSQO-E synthesis system resulted in transparent and homogeneous organic/inorganic hybrids, which presented a single T_g value, determined through DSC analysis. A reduction in T_g values was observed with the increase in SSQO-E content, which was mainly attributed to the presence of the more flexible 2-hydroxypropyl-n-propyl ether groups in DGEBA/SSQO-E/DETA hybrids in contrast to the less flexible hydroxypropyl ether groups present in epoxy resin; and to the larger number of flexible groups in the organic/inorganic hybrids (eight flexible groups per SSQO-E molecule) compared to that in epoxy resin (two flexible groups per DGEBA molecule).

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