Neat and Silica-Enriched Polysilsesquioxanes in Dispersed Media

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SUMMARY: The synthesis and characterization of organic-inorganic hybrid materials derived from 3-glycidoxypropyl trimethoxy silane (GPMS) is described. The hydrolytic condensation of GPMS was performed in two steps. The first one was carried out using tetrahydrofuran (THF) as solvent and diluted formic acid as catalyst (24 h at 50 °C). The reaction product was then dissolved in diglycidylether of bisphenol A (DGEBA) and the formation of the inorganic polymer was continued using different thermal cycles. A polysilsesquioxane (SSQO) dispersed in a reactive solvent was obtained. Its characterization by size exclusion chromatography (SEC) showed the presence of a broad distribution of clusters where the fundamental units were associated with cube-like cages. The organic polymer network was formed by adding methyltetrahydrophthalic anhydride (MTHPA) as hardener and benzyl dimethylamine (BDMA) as initiator of the chainwise polymerization (involving the epoxy groups of the SSQO and those of DGEBA). A SSQO-modified epoxy network was obtained. A significant increase in the abrasion resistance of the hybrid material with respect to the neat epoxy was observed. Silica-enriched SSQO were obtained by adding tetraorthosilicate (TEOS) together with GPMS in the initial hydrolytic condensation step.

Introduction

Organic-inorganic hybrid materials have attracted an increasing level of attention in recent years because of their wide and often unusual combination of physical and chemical properties[1,2]. They may be synthesized using different strategies related to the sequence of reactions taking place and the possibility of producing covalent bonds between the organic and inorganic parts. Here we will discuss the synthesis and characterization of hybrid materials derived from 3-glycidoxypropyl trimethoxy silane (GPMS) (Fig.1).

Functionalized trialkoxysilanes as GPMS were used as the starting point of hybrid materials using the following procedure: a) the hydrolytic condensation of the trialkoxysilane dissolved

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in a reactive solvent was carried out first, leading to a polysilsesquioxane bearing unreacted functional groups (epoxides in the case of GPMS), covalently bound to the inorganic structure; b) the polymerization of the organic functional group was then performed by adding an appropriate comonomer and a catalyst or initiator. This led to a polysilsesquioxane-modified organic polymer network. Step a) may be considered as the formation of an inorganic polymer in a dispersed medium. The structure of the inorganic part may be modified by making the hydrolytic condensation of a mixture of tri- and tetraalkoxysilanes like TEOS (tetraethoxysilane)(Fig.1). This leads to silica-enriched polysilsesquioxanes, bearing organic functional groups that are polymerized in a subsequent step.

The aim of this paper is to discuss the synthesis and characterization of epoxy networks modified by polysilsesquioxanes or silica-enriched polysilsesquioxanes, using GPMS as the starting monomer.

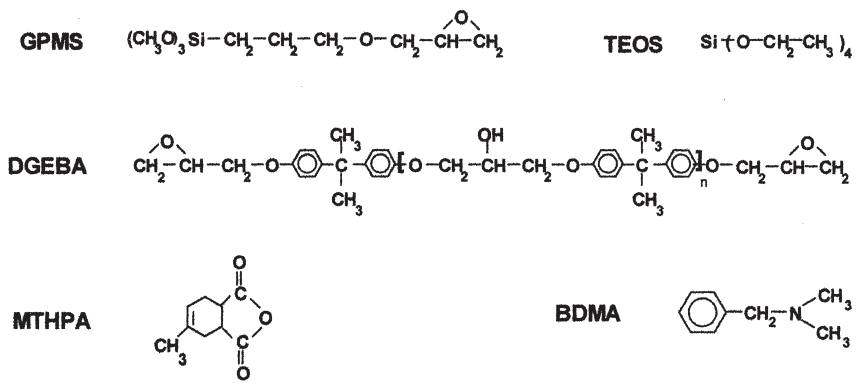

Figura 1.Structures of chemical reagents.

Experimental

The chemical structures of different reagents are shown in Fig.1. The synthesis was based on 3-glycidoxyy propyl trimethoxysilane (GPMS, Sigma). It was hydrolytically condensed either alone, leading to polysilsesquioxanes (SSQO), or together with tetraorthosilicate (TEOS, Aldrich), leading to silica-enriched SSQO. The reactive solvent was diglycidylether of bisphenol A (DGEBA, MY790 Ciba-Geigy with an average n value equal to 0.03, Fig.1). It

was carefully dehydrated before use. The final hybrid material was produced by adding a stoichiometric amount of methyltetrahydrophthalic anhydride (MTHPA, HY 918 Ciba-Geigy) and 0.04 moles of benzyldimethylamine (BDMA, Sigma), per mol of epoxy groups, as intiator of the epoxy-anhydride polymerization.

The distribution of products arising from the hydrolytic condensation was followed by size exclusion chromatography (SEC, Shimadzu GPC 80, using columns 801,802 and 803 covering the range of molar masses comprised between 10^2 to 10^5, a refractive index detector, THF at 1 ml/min as carrier and butylated hydroxytoluene, BHT, as internal standard). Thermal Analysis was performed using a Mettler TA 3000 equipment provided with a DSC (differential scanning calorimeter) and a TMA (thermal mechanical analyzer), both operated at 10 °C/min. The DSC was used to determine the heat evolved in the epoxy-anhydride reaction while the TMA was used to determine the glass transition temperature (Tg) of the hybrid materials (2nd scan using a static force of 0.02 N).

Hybrid materials were also characterized by determining the following physical properties at room temperature: density (ASTM D 792), elastic modulus (three-point bending at 5 mm/min using an Instron 4467 universal testing machine), microhardness (using a Wilson Tukon 300 device with a Vickers indenter and applying a 5 Kg force during 15 s), and the abrasion resistance using a dry sand/ rubber wheel apparatus (ASTM G65-91, Procedure D). Thermal gravimetry analysis (TGA, Mettler TG50), was carried out at 10°C/min up to 800°C, under nitrogen flow.

Hydrolytic Condensation

One of the most typical characteristics of the hydrolytic condensation of trialkoxysilanes is the formation of cyclic structures as intermediates of perfect or incompletely condensed polyhedra[3-5] (Fig.2). Rigorously speaking, SSQO are perfect polyhedra of generic formula $(RSiO_{1.5})_n$. However, the term is usually applied to the distribution of products arising from the hydrolytic condensation of trialkoxysilanes, of generic formula $(RSiO_{1.5-x}(OH)_{2x})_n$. Silsesquioxane cages with n = 8, 10 or 12 Si atoms are particularly stable[6]. In most systems incompletely condensed polyhedra act as cagelike intermediates for the generation of an

inorganic polymer network. Gelation takes place at high conversions in the condensation reaction.

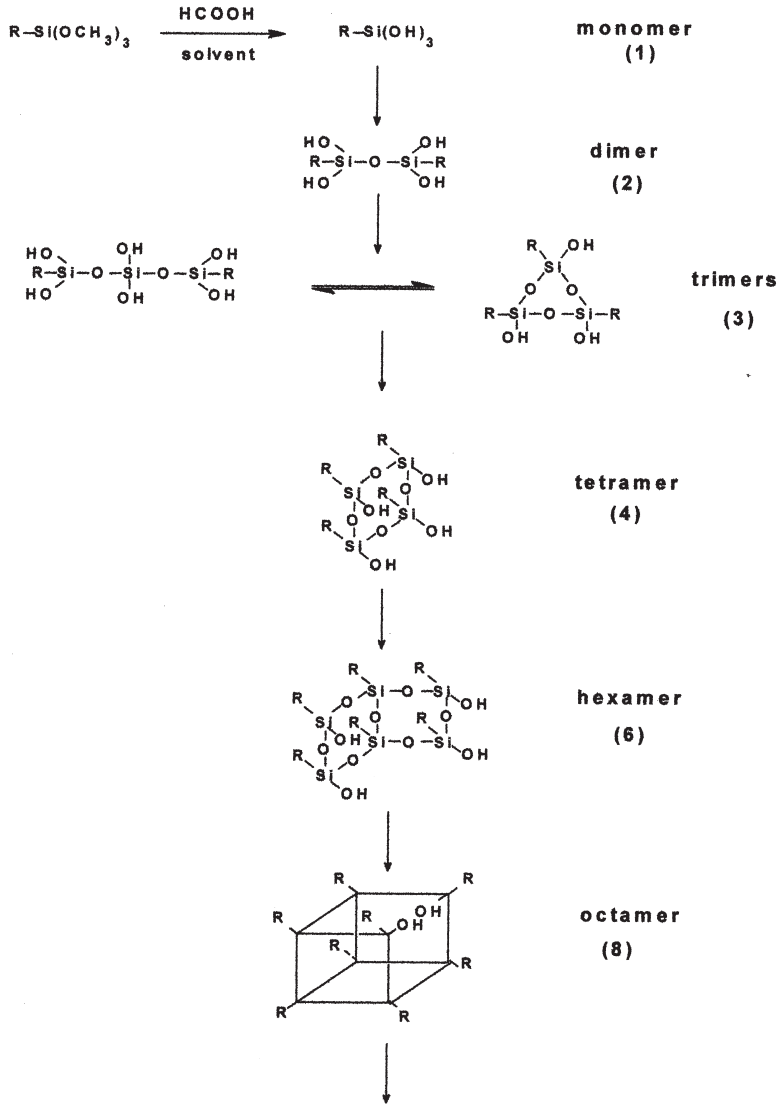

Fig. 2. Steps of the hydrolitic condensation.

The hydrolytic condensation of GPMS was performed in two steps. The first one was carried

out using tetrahydrofuran (THF) as solvent, at a concentration of 1.5 g/ml, and HCOOH 0.1 N as catalyst, keeping the ratio H_2O / Si = 3. The reaction was performed during 24 h at 50 °C. Figure 3 shows a SEC chromatogram of the reaction products after the hydrolytic condensation in THF. Peaks were assigned to the hydrolyzed monomer, dimer, trimer and (cyclic) tetramer. These are the first species that appear in SEC chromatograms during the uncatalyzed hydrolytic condensation of GPMS [7].

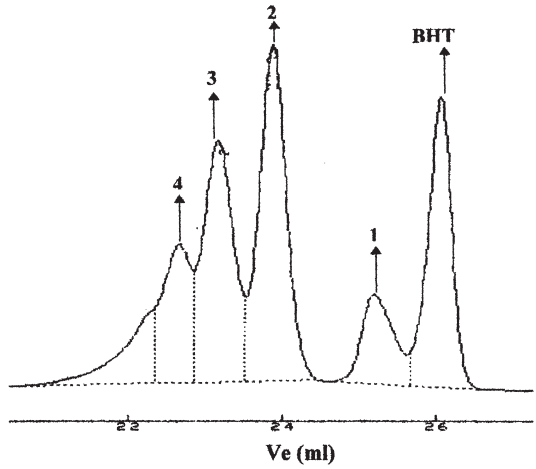

Fig. 3. SEC after 24 h in THF.

The second step of the hydrolytic condensation was performed by adding DGEBA as reactive solvent. The amount of DGEBA was such that the fraction of epoxy groups contributed by the SSQO was either 25% or 50%. This leads to mass fractions of SSQO equal to 12.3% and 24.6% in the final hybrid materials. The hydrolytic condensation was continued for 24 h at 70 °C. THF was removed during this second step leading to a solution of the epoxy-functionalized SSQO in DGEBA. Fig.4 shows a SEC chromatogram of the reaction products for a sample with 50% of the epoxides contributed by the SSQO. Peaks of the two main components of DGEBA (n=0 and n=1) remained unchanged. The dimer, trimer and tetramer were still present although in very small fractions. The significant peak appearing next to the tetramer was assigned to an octamer (n=8) because the elution volume was close to the one expected for this species using a calibration curve with polystyrene (PS) standards. The octamer was present in significant amounts during the hydrolytic condensation of GPMS catalyzed by 1-methylimidazol [7]. Its structure is possibly that of a partially condensed cube

(Fig. 2). The next peak (B) has a maximum at a mass that is about three times the mass of the octamer, based on PS standards. It is then assigned to an oligomer with n=24. The location expected for the species with n=16 is also indicated. These species may be regarded as clusters containing 2 or 3 cubes. Peak A includes a broad distribution of larger clusters.

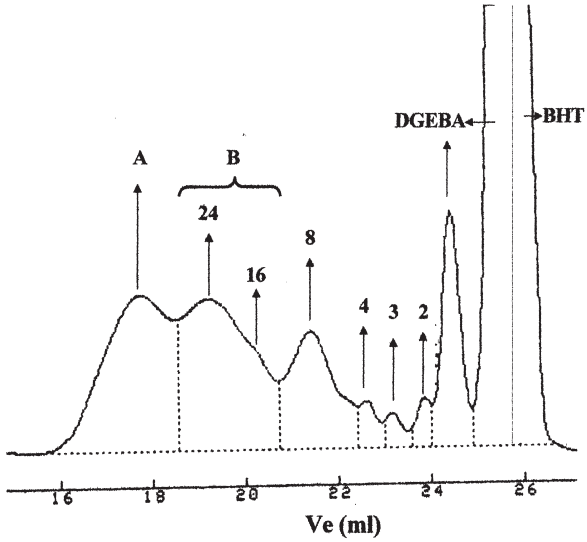

Fig. 4. SEC after 24 h in DGEBA

A third step of the hydrolytic condensation was alternatively carried out for some of the samples. In this step, the following heating schedule was used: 3h at 75 °C, 6h at 105 °C and 6h at 140°C. Fig.5 shows a SEC chromatogram of the reaction products for a sample with 50% of the epoxy groups contributed by the SSQO. While the DGEBA peaks remained unchanged, the SSQO clusters evolved to higher molar masses but still showing the presence of single cube-cagelike intermediates (n = 8) and shoulders corresponding to species containing two (n = 16) and three cubes (n = 24). The fraction of clusters with larger molar masses has now considerably increased.

In what follows, the SSQO distribution will be referred to as: "after the 2nd step" (meaning the heating in DGEBA at 70°C) or "after the 3rd step" (meaning post-heating to 140°C).

Silica-enriched SSQO were synthesized by introducing TEOS together with GPMS in the initial formulation. In this case, both the first and second step of the hydrolytic condensation

were performed using DGEBA as reactive solvent (24h at 50 °C and 24h at 70 °C, using HCOOH 0.1 N as catalyst with H_2O/alkoxy(OR) = 1). The total amount of TEOS + GPMS was 25 wt% with OR (TEOS) / OR (GPMS) = 1. This led to 7.8 wt% of the silica-enriched SSQO in the final hybrid material (assuming complete condensation).

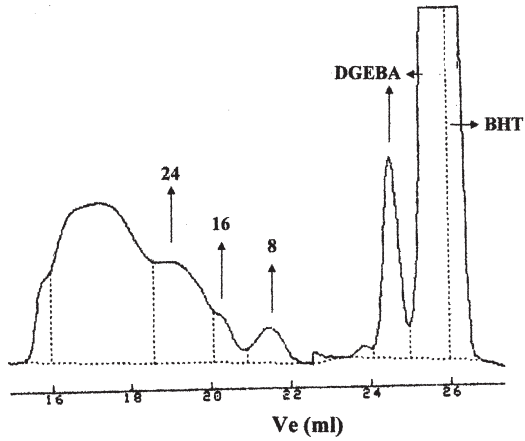

Fig. 5. SEC after the heating to 140°C.

Hybrid Materials

The hybrid materials were obtained by polymerizing the epoxy groups, present in both the SSQO and DGEBA, by adding a stoichiometric amount of MTHPA and BDMA as initiator. The formation of the epoxy-anhydride polymer network was followed by DSC. The reaction heat for the different formulations was comprised between 50 and 55 kJ/eq, e.g., lying in the same range of values reported in the literature[8,9]. This means that the epoxy-anhydride reaction gets full conversion within experimental error. The following cure cycle was selected for the obtention of plaques: 24h at 70 °C, 2h at 75 °C, 3h at 100 °C, 3h at 110 °C, 3h at 120 °C and 2h at 140 °C. The resulting materials were transparent. Physical properties of SSQO-modified epoxy-anhydride networks are shown in Table 1.

The use of the SSQO obtained after the 2nd step of the hydrolytic condensation led to a significant decrease of the glass transition temperature of the hybrid material with respect to the neat epoxy. The reason may be the presence of a relatively large concentration of small oligomers (Fig.4), that act as flexible elements of the polymer network. Higher Tg values

were observed when using the high molar mass SSQO resulting from the 3rd step of the hydrolytic condensation. The high-molar-mass SSQO clusters must be more rigid than the low-molar-mass species. But flexible structures led to denser networks than rigid structures. The elastic modulus and the microhardness were not influenced by the presence of the SSQO but the abrasion resistance exhibited a significant increase (even for the hybrid material whose Tg was equal to the one of the neat epoxy). This seems to be the most important consequence of the incorporation of SSQO to this particular epoxy formulation.

Table 1. Physical Properties of Hybrid Materials

Properties	wt % SSQO				
	0 (neat matrix)	12.3% (after 2nd step)	12.3% (after 3rd step)	24.6% (after 2nd step)	24.6% (after 3rd step)
Tg (°C)	108.9	75.3	108.8	34.8	68.5
ρ (g/ml)	1.2096	1.2605	1.2259	1.2519	1.2227
E (GPa)	3.4	3.3	3.3	3.5	3.4
Microhardeness (GPa)	5.54	5.10	5.64	5.47	5.29
Abrasion Resistance	1	1.13	1.22	1.40	1.23

Several hybrid materials were prepared using TEOS in the initial formulation. The most important change was the increase in the final Tg when compared with a similar material without TEOS. For the hybrid material containing 7.8 wt% of silica-enriched SSQO the Tg was 98.3 °C, compared to 88.6 °C obtained when using pure GPMS in a similar proportion. Fig. 6 shows TGA scans for the neat matrix and the hybrid material containing 7.8 wt % of silica-enriched SSQO. A significant increase in the residue at 800°C is observed for the modified matrix.

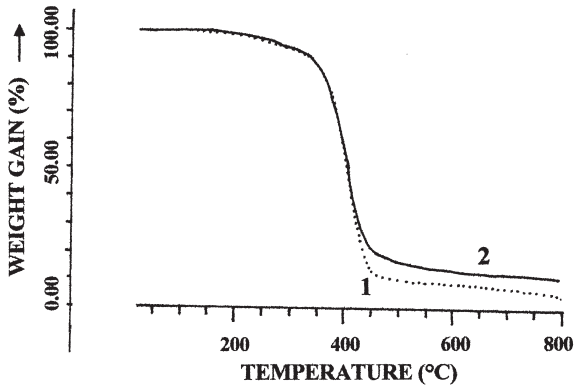

Fig. 6. TGA scans for the neat matrix (1) and the hybrid material conteining 7.8 wt % of silica enriched SSQO (2).

Conclusions

A SEC analysis of the hydrolytic condensation of GPMS catalyzed by formic acid, showed the generation of relatively stable oligomers as the cyclic tetramer and a cagelike octamer (one of the possible isomers is shown in Fig.2), and the further condensation of the cagelike structures through free SiOH groups. The resulting polysilsesquioxane exhibited a distribution of clusters of different sizes (n = 8,16,24,...). This is an untypical step polymerization characterized by the fact that the monomers react to generate a fundamental building block that produces the final structure by its self-condensation.

Organic-inorganic hybrid materials were obtained by performing the hydrolytic condensation of GPMS in a reactive solvent (DGEBA), and then polymerizing the epoxy groups through the addition of a hardener (MTHPA) and an initiator (BDMA). The resulting SSQO-modified epoxies were transparent materials showing a significant increase of the abrasion resistance when compared to the neat epoxy matrix.

Acknowledgements

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