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Hybrid Organic-Inorganic Polymer Networks Based on the Copolymerization of Methacryloxypropyl-Silsesquioxanes and Styrene

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Summary: Silsesquioxanes synthesized by the condensation of (3-methacryloxypropyl)trimethoxysilane with concentrated formic acid, were copolymerized with styrene using benzoyl peroxide as initiator. When the ratio of styrene (S) to methacrylic (M) unsaturations was $S/M > 1$, the reaction attained an almost complete conversion as shown by the total reaction heat determined by differential scanning calorimetry. Several properties of the resulting hybrid organic-inorganic polymer networks were determined as a function of the silsesquioxane amount used in the formulation. Increasing the silsesquioxane fraction led to an increase of the glass transition temperature up to a point where devitrification was not observed prior to decomposition, an increase of the elastic modulus in the rubbery state, a decrease of the intensity of tan δ, and an increase of both Barcol hardness and thermal stability.

Introduction

Silsesquioxanes (SSO) are the products obtained by the polycondensation of monomers such as $RSiX_3$ (X = alkoxy, OH, Cl, etc., R = organic group), under appropriate acid or alkaline conditions. The resulting SSO consists of a distribution of species with a generic structure: $[RSiO_{1.5-x}(OH)_{2x}]_n$, where n may vary in a broad range. Multimodal distributions of molar masses are frequently observed, with relative maxima at n close to 8, 16, and higher values.[1,2] Depending on the selected reaction conditions, unhydrolyzed X groups (e.g., methoxy groups) may replace hydroxyls in the generic

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structure.[3] Figure 1 shows typical structures of silsesquioxanes.

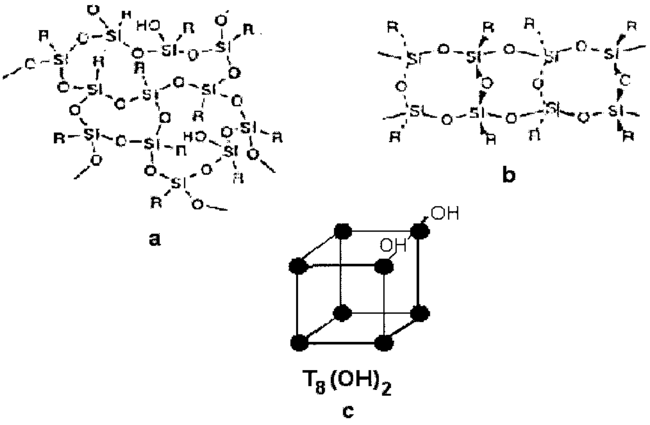

Figure 1. Typical structures of silsesquioxanes; a) random structure, b) ladder structure, c) incompletely condensed polyhedron (black circles represent Si atoms).

When the organic group R bears a reactive functionality (e.g., epoxy, vinyl, etc.), hybrid organic-inorganic polymer networks may be obtained by the addition of appropriate initiators, comonomers and catalysts.[4-9] Materials with a broad range of thermal and mechanical properties may be obtained by varying the relative proportions of the organic and inorganic parts.

The aim of this paper is to analyze thermal and mechanical properties of organic-inorganic hybrid materials obtained by the copolymerization of a methacryloxypropyl-functionalized SSO with variable amounts of styrene.

Experimental Part

Synthesis of the Silsesquioxane (SSO)

The SSO was obtained by polycondensation of (3-methacryloxypropyl)trimethoxysilane (Z-6030 Dow Corning), in bulk, with concentrated formic acid (Merck, 98 wt%). The reaction was carried out at 50 °C during about 14 days, leading to a homogeneous viscous liquid that could be completely dissolved in different solvents like tetrahydrofuran (THF), chloroform and styrene.

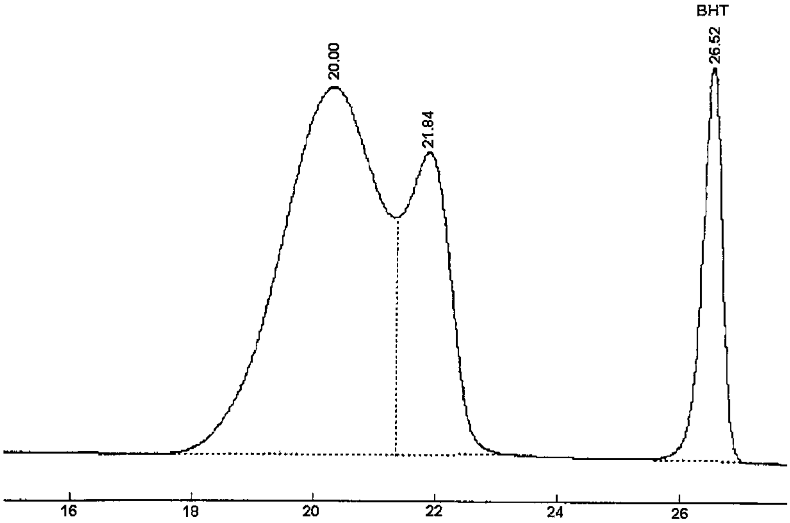

Figure 2. Size exclusion chromatogram of the silsesquioxane (butylated hydroxytoluene, BHT, was used as internal standard).

Size exclusion chromatograms (Shimadzu GPC 80, with sim-pack Shimadzu columns 801, 802 and 803, refractive index detector and THF as carrier at 1 ml/min), showed the presence of a bimodal molar-mass distribution (Figure 2). From a calibration with polystyrene standards (Shodex, range of molar masses from 10^3 to 6×10^6), the peak at 21.84 min was assigned to species with n = 6-11, while predominant species in the peak at 20.0 min corresponded to n values comprised between 17-20. Mass spectrometry confirmed the assignment and showed that these oligomers exhibited a high fraction of intramolecular cycles.[10] The average structural formula of the SSO could be represented by $(RSiO_{1.42}(OH)_{0.16})_n$, where R: $CH_2{=}C(CH_3)COO(CH_2)_3$. This gives a mass of 180.4 g/mol of C=C double bonds.

Copolymerization with Styrene

Benzoyl peroxide (BPO) was dissolved in styrene, in an amount equal to 1.9 wt % of total organic mass (including the mass of the R group of the SSO, added in a subsequent step). The SSO was then dissolved, giving a solution characterized by a particular value of the wt % styrene. The free-radical polymerization was performed under two different conditions: a) at 10 °C/min up to 180 °C, under N_2, in a differential scanning calorimeter (Mettler TA 3000 DSC-20); b) casting the solution into a mold consisting of two glass plates coated with siliconized paper, spaced by rubber cords 2 mm in diameter, and heating in an oven at 80 °C during 17 h, with a postcure step at 160 °C during 3h. The resulting hybrid organic-inorganic materials were transparent. Hybrids containing less than about 30-40 wt % styrene were very brittle, making it very difficult to demold the part without breaking it. Cured samples containing different amounts of styrene, were kept in THF during 4 days at room temperature, plus another 2 hours in an ultrasonic bath. No loss of mass was observed after this period, meaning that the copolymerization of the SSO and styrene had been effective.

Characterization Techniques

The total reaction heat was obtained using differential scanning calorimetry (Mettler TA 3000 DSC-20). Dynamic scans were performed at 10 °C/min up to 180 °C, under N_2.

Specimens, about 10x10x2 mm in size, were machined from the molded plaques and subjected to single cantilever bending in a DMTA IV Rheometrics, under the following conditions: scanning rate = 3 °C/min, frequency = 1 Hz, maximum strain = 0.1%.

The Barcol hardness of plaques (ASTM D 2583), was measured with a Portable Hardness Tester (Barber-Colman, Model 934-1).[11]

Thermal gravimetric analysis (TGA, Mettler TG 50) was carried out under nitrogen flow at 10 °C/min up to 800 °C. At this temperature, nitrogen was replaced by oxygen and heating was continued up to 900 °C, attaining a constant residual mass. This enabled the ceramic yield to SiO_2 to be determined.[5]

Results and Discussion

Total Reaction Heat

Figure 3 shows experimental values (circles) of the total reaction heat obtained by differential scanning calorimetry, as a function of the wt% of styrene in the initial formulation. Squares represent theoretical values expected for complete conversion of vinyl groups of both styrene and the silsesquioxane.

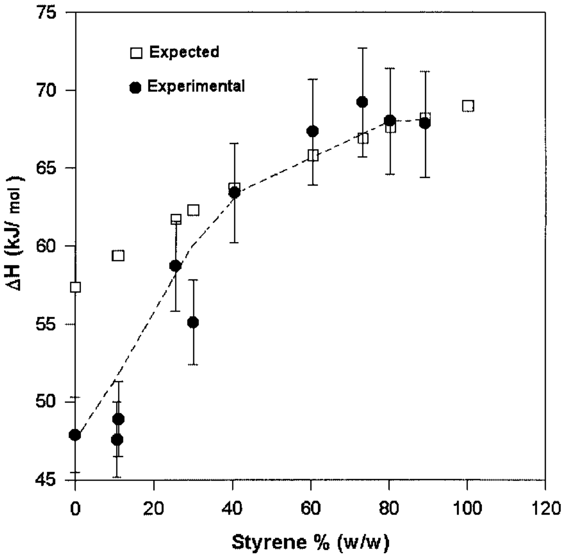

Figure 3. Experimental values (circles) of the total reaction heat obtained by differential scanning calorimetry, as a function of the wt % styrene in the initial formulation. Squares represent theoretical values expected for complete conversion of vinyl groups of both styrene and the silsesquioxane.

A value of 69 kJ/mol was taken for styrene (S) and 57.4 kJ/mol for the vinyl groups of the SSO, considered equal to the value reported for the polymerization of n-propyl methacrylate.[12]

For a wt % S higher than about 30-40, experimental values of reaction heats were close to expected values within experimental error. For a wt % S = 36.5 both monomers were present in equimolar amounts. This means that the necessary condition to get a complete conversion, is to add one mol of styrene per mol of methacryloxy groups of the SSO. For a smaller amounts of styrene, the reaction could not attain complete conversion, probably due to steric reasons. For the pure SSO, the maximum conversion of vinyl groups was 83% of the expected value.

Trends found for this particular system agree with experimental results reported for other hybrid polymers. For example, quantitative analysis of the photochemical polymerization reaction of an hybrid polymer obtained by the hydrolytic condensation of a 1:1 mixture of (3-methacryloxypropyl)trimethoxysilane and $Si(OEt)_4$, revealed that about 20% of the initial double bonds remain unreacted. However, addition of 2 moles of methyl methacrylate per mol of methacryloxy groups of the hybrid polymer, led to a complete conversion of double bonds upon UV irradiation.[13]

Dynamic Mechanical Characterization

Figure 4 shows the storage modulus of cured hybrids formulated with different SSO amounts, as a function of temperature. The curve for an injection-grade polystyrene is also included for comparison purposes. Increasing the amount of SSO up to 30 wt % led to an increase of the glass transition temperature and the rubbery modulus, due to the increase in crosslink density. For higher amounts of SSO, hybrids were very brittle. This led to the generation of microcracks that eventually produced the material's fracture in the course of the test. One of these runs is shown in Figure 4, for a hybrid containing 90 wt % SSO. Although a small decrease of the glassy modulus with temperature, was observed, devitrification did not take place in the temperature range preceding thermal degradation (small step-decreases of the storage modulus were assigned to the presence of microcracks).

An explanation of the significant dependence of the dynamic-mechanical behavior of the synthesized hybrids with their composition, may be postulated on the basis of recent results reported by Matejka et al.[14] By analyzing the structure of several silsesquioxanes using small-angle X-ray scattering, they found that because of the incompatibility of the polyhedral SSO framework and organic chains, microphase separation took place and spontaneous self-organization occurred. A micellar arrangement of compact SSO domains with a correlation distance corresponding to the size of the substituent, was observed. In our case, it may be postulated that a self-organization was present before polymerization and it was frozen after formation of the polymer network. For hybrids with low SSO mass fractions, the organic microphase may be considered as the continuous one, and the materials exhibited a characteristic T_g that increased with crosslink density.

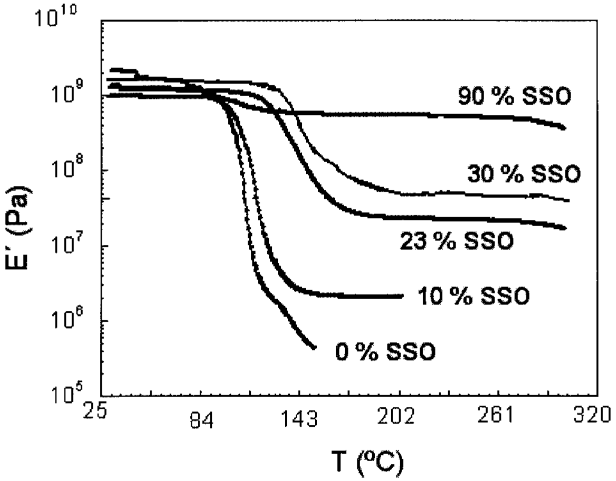

Figure 4. Storage modulus of cured hybrids formulated with different wt % SSO, as a function of temperature.

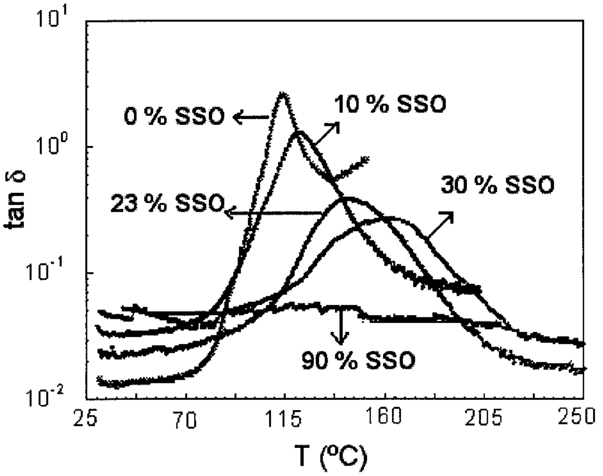

Figure 5. Evolution of tan δ for the same hybrids of Figure 4.

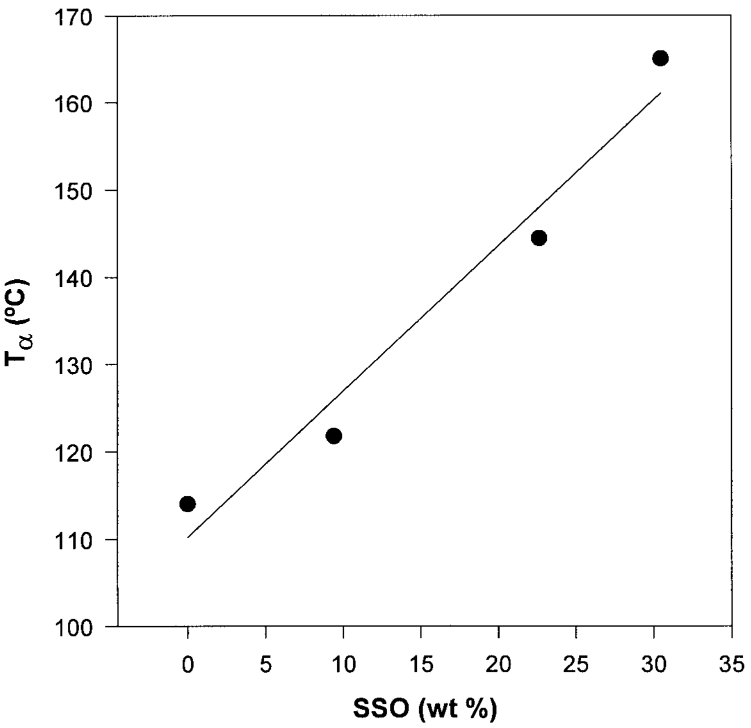

Figure 6. T_α relaxation, defined at the maximum of tan δ, as a function of the wt % of SSO in the hybrid material.

When the SSO mass fraction is high, the rigid inorganic microphase percolates through the structure, leading to the appearance of a glassy behavior up to the degradation temperature. Hybrids with a high SSO content might be used as coatings with a thickness small enough to avoid manifestation of the brittle behavior.

Figure 5 shows the evolution of tan δ for the same hybrids of Figure 4 (including the neat polystyrene for comparison purposes). Increasing the amount of SSO led to a significant decrease in the intensity of tan δ, associated with an increase in the rigidity of the network structure. For the hybrid with 90 wt % SSO, no neat network relaxation could be observed in the whole temperature range.

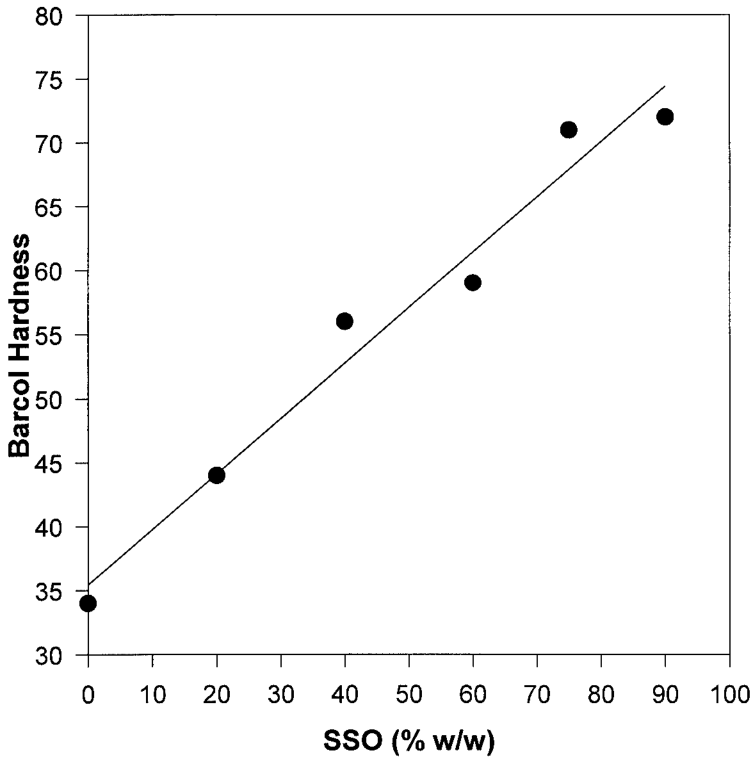

Figure 7. Barcol hardness of the hybrids as a function of the wt % SSO.

The T_α relaxation, defined at the maximum of tan δ, is plotted in Figure 6 as a function of the wt % of SSO in the hybrid material. For a 30 wt % SSO, T_α (associated with the glass transition temperature), increased by about 50 °C with respect to pure polystyrene.

Hardness

The Barcol hardness of the hybrids increased linearly with the wt % SSO, as shown in Figure 7. This resulted from the relative contribution of the individual hardnesses of both microphases, present in the glassy state at room temperature. For comparison purposes, the hardness of a typical crosslinked unsaturated polyester was measured with the same test and found to be close to that of the hybrid with 40 wt % SSO.

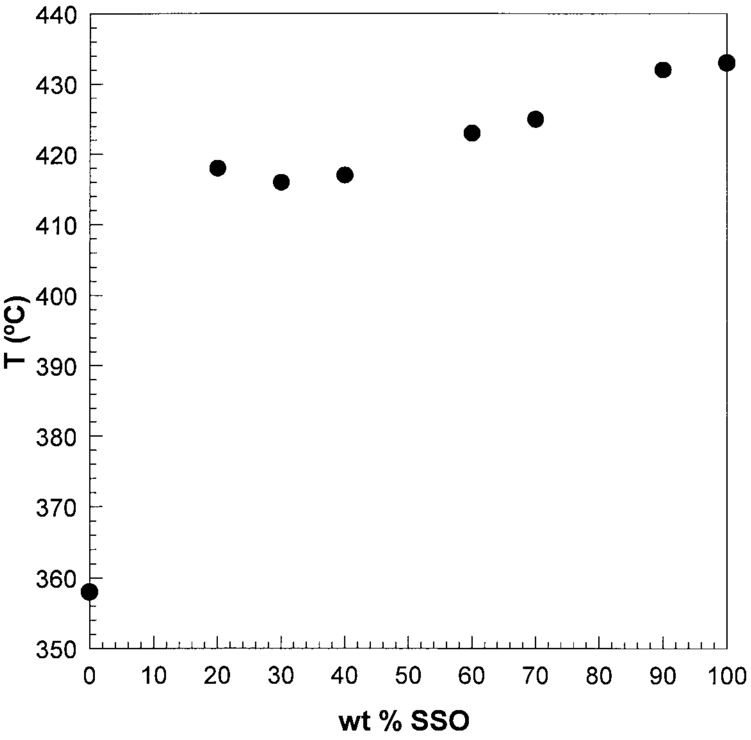

Figure 8. Temperature at the maximum rate of thermal degradation as a function of the wt % SSO in the hybrid material.

Thermal Stability

It has been reported that thermoplastics modified with polyhedral silsesquioxanes exhibit an increase in their decomposition temperature and are very resistant to combustion. This property has been associated with the preceramic nature of the silsesquioxane component, which forms a glassy layer of SiO_xC_y during pyrolysis, retarding the diffusion of gases through the surface char.[15] For example, the decomposition temperature of poly(4-methylstyrene), defined as the temperature at which 10 % weight loss was observed when heating a powdered sample under nitrogen at 10 °C/min, was 388 °C.[16] The copolymerization of 4-methylstyrene with an octahedral silsesquioxane bearing one polymerizable styryl group, led to hybrid organic-

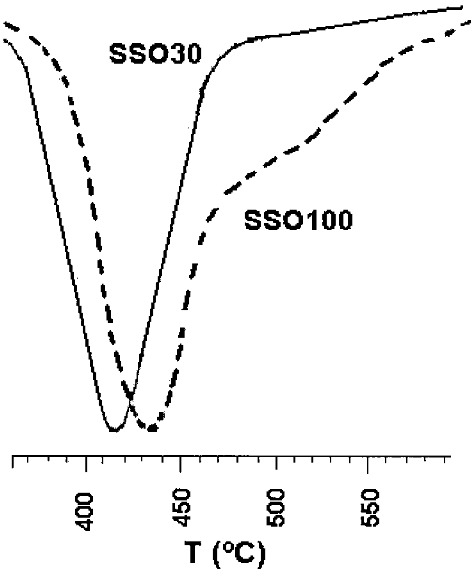

Figure 9. Rate of mass variation by thermal degradation, dm/dT, as a function of temperature for a hybrid with 30 wt % SSO and for the neat SSO.

inorganic thermoplastics. Their decomposition temperature increased with the SSO amount, attaining values as high as 445 °C for the pure poly(silsesquioxane) (the particular value depended on its molar mass).[16]

In our case, a polymer network was generated by copolymerization of the multifunctional SSO species with styrene. Figure 8 shows the temperature corresponding to the maximum rate of thermal degradation under nitrogen, as a function of the wt % SSO in the hybrid material. The degradation temperature increased from 358 °C for pure PS, to about 417 °C for hybrids with 20-40 wt % SSO, and to about 435 °C for the pure SSO. A significant increase in the thermal stability of resulted from the incorporation of only 20 wt % SSO. Possibly, network formation produced an extra increase of thermal stability when compared with SSO-modified thermoplastics.

Examples of the derivatives of the mass loss, dm/dT, as a function of temperature are shown in Figure 9 for a hybrid with 30 wt % SSO and for the neat SSO. The shoulder observed in the high-temperature range for the neat SSO, may be ascribed to the formation of a SiO_xC_y glassy layer that retards further decomposition.[15]

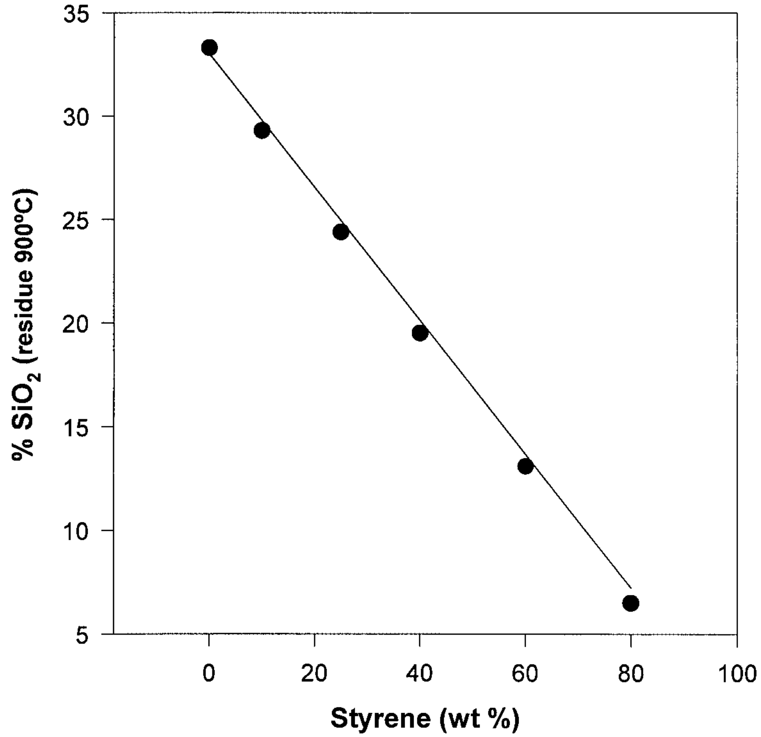

Figure 10. Residual SiO_2 wt % at 900 °C in an oxygen atmosphere, compared with the expected value (full line), for hybrids containing different styrene amounts.

The ceramic yield to SiO_2 was obtained by heating the hybrids to 900 °C in an oxygen atmosphere. Figure 9 shows the residual SiO_2 wt % obtained for the different hybrids, compared with the expected values (full line). A very good agreement was observed.

Conclusions

Hybrid organic-inorganic materials based on a silsesquioxane functionalized with methacryloxy groups, copolymerized with styrene, exhibited a broad range of thermal and mechanical properties, depending on the weight fraction of SSO in the formulation. Increasing the SSO amount led to an increase of the glass transition temperature (T_α

relaxation), the elastic modulus in the rubbery state, hardness and thermal stability. Dynamic-mechanical properties were explained by assuming a self-organization of the structure in organic and inorganic domains, as found for several silsesquioxanes.[14] Percolation of the inorganic domains occurs at large SSO fractions and provokes the disappearance of the glass transition temperature. In these conditions, the hybrid behaves as a brittle glass up to the degradation temperature. The thermal stability of the hybrid materials increased significantly with the SSO content. This was ascribed to the formation of a SiO_xC_y glassy layer that retarded the degradation process.

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