



Organic/Inorganic Hybrid Materials Based on Silsesquioxanes Derived from (3-Methacryloxypropyl) Trimethoxysilane and Their Blends with Vinylester Resins

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Abstract. The crosslinking of blends of a silsesquioxane (SSO) derived from (3-methacryloxypropyl) trimethoxysilane, variable amounts of a vinylester resin (VE, dimethacrylate of bisphenol A), and benzoyl peroxide (BPO) or dicumyl peroxide (DCP) as initiators, was followed by differential scanning calorimetry (DSC). For the neat SSO a thermally-initiated polymerization was observed in the 150–250°C range, leading to a conversion close to 22% of the initial C=C groups. The final conversion could be increased to a maximum value close to 83%, by adding an initiator and using a thermal cycle attaining temperatures in the range of 200°C. The use of variable amounts of VE as a co-monomer produced a slight increase of the final conversion in SSO/VE/BPO blends. Neither the conversion of double-bonds nor the addition of the VE had any effect on the onset temperature of thermal degradation, which was associated to the presence of the methacryloxypropyl groups supplied by the SSO and the VE resin. However, a distinct two-step degradation process was observed in the presence of VE. Coatings based on SSO/VE/BPO blends exhibited more uniform thicknesses and lower values of the microhardness than those devoid of VE. However, the conversion of C=C groups did not show any significant effect on the values of microhardness.

Keywords: silsesquioxanes, (3-methacryloxypropyl) trimethoxysilane, vinyl ester resins, crosslinking, microhardness

1. Introduction

In recent years the interest in organic/inorganic hybrid materials has increased at a fast rate. There are many ways in which these materials may be synthesized, a typical one being the use of trialkoxysilanes. Their hydrolytic condensation leads to a silsesquioxane (SSO) that keeps one organic group bound to every silicon atom. Strictly speaking, the term refers to fully condensed structures of formula $(\text{RSiO}_{1.5})_n$ ($n = \text{even number}$). But the term is frequently extended to denote partially condensed products: $[\text{RSiO}_{1.5-x}(\text{OH})_{2x}]_n$. The organic group may be inert to further chemical

reactions (e.g., methyl, cyclohexyl, phenyl, etc.) or may be polymerizable by different mechanisms (e.g., 3-glycidioxypropyl, 3-methacryloxypropyl, vinyl, etc.). In the first case, the organic ligands serve to reduce the functionality of networks prepared from blends with tetraalkoxysilanes. This leads to a reduction in the mechanical stiffness of the network and makes the coating more hydrophobic [1–3]. But also the organic material may be removed by a convenient thermal treatment leading to the generation of tailor-made pore sizes and shapes that are particularly important in applications where molecular recognition is needed [4–7] or a low dielectric constant is required [8, 9].

In the second case, organic groups are usually copolymerized with organic monomers. This leads to

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hybrid materials, which may be used as coatings of glass surfaces [10] or of plastic substrates such as polycarbonate or polyethyleneterephthalate [11]. Coating of a glass surface may be required to increase the impact resistance or to change the surface polarity making it more hydrophobic or hydrophilic, or to introduce organic dyes for decorative purposes. In the case of plastics, good values of adhesion and of the scratch-resistance are usually the main required properties of the coating. Although a significant number of publications and patents dealing with this type of formulations is available in the literature, there are still some important questions that need to be answered. One of these questions is related to the way of controlling the conversion attained in the polymerization of the organic functional groups and the effect of this conversion on different properties of the hybrid materials.

The aim of this study is to provide an answer to this question for a particular system based on a silsesquioxane (SSO) derived from the hydrolytic condensation of (3-methacryloxypropyl) trimethoxysilane. The free-radical polymerization of C=C groups was followed by differential scanning calorimetry (DSC), either without adding initiators or using a low- or a high-temperature initiator and different thermal cycles. Blends with a vinyl ester resin (VE, dimethacrylate of bisphenol A), were also investigated. The influence of both the conversion of C=C double-bonds and the VE addition, on the thermal stability of the hybrid materials and the microhardness of coatings on glass substrates, was investigated.

2. Experimental

2.1. Materials

The silsesquioxane (SSO) was synthesized from (3-methacryloxypropyl) trimethoxysilane (MPMS, Dow Corning Z-6030). Its hydrolytic condensation was performed in bulk, using HCOOH 88%, in a molar ratio $\text{HCOOH/Si} = 3$ ($\text{H}_2\text{O/Si} = 1.05$), at 50°C during 5 days [12]. The mechanism by which concentrated formic acid produces the condensation of alkoxy-silanes has been described in the literature [13]. The characterization of the SSO with MALDI-TOF mass spectrometry showed the presence of a bimodal molar mass distribution with a first peak corresponding to species containing 6–11 Si atoms and a second peak associated to species with 12 to 30 Si atoms [12]. Al-

though a fraction of perfect polyhedra was present in the distribution, most of the species could be assigned to structures containing a fraction of SiOH groups. Within the experimental error of ^1H NMR it was shown that all methacryloxypropyl residues remained intact during the hydrolytic condensation process [12].

A vinyl ester resin (VE) was synthesized by reacting diglycidylether of bisphenol A (DGEBA MY790, Ciba; mass per epoxy equivalent = 176.2 g) with methacrylic acid, using triphenylphosphine as catalyst [14]. The main species was the dimethacrylated DGEBA (molar mass = 512 g/mol). To prevent polymerization during storage, 300 ppm of hydroquinone were added. Blends of the SSO and VE, containing 15, 30 and 45% VE, were prepared.

The initiators selected for the free radical polymerization were benzoyl peroxide (BPO, Lucidol 75%, Akzo Chemicals) and dicumyl peroxide (DCP, Akzo Chemicals). Reported temperatures at which half of the peroxide is decomposed in one hour are 91°C for BPO and 135°C for DCP. The amount of initiator added to different formulations ranged from 1.4 to 2.0 wt%.

2.2. Techniques

The C=C free-radical polymerization was studied using differential scanning calorimetry (DSC-50 Shimadzu), at 10°C/min under nitrogen, and Fourier-transformed infrared spectroscopy (FTIR, Mattson Genesis II), following the peaks at 1638 cm^{-1} and 943 cm^{-1} corresponding to the C=C double-bond of the methacryloxy group of both the SSO and the VE resin. The samples were mixed with spectroscopic-grade KBr and analyzed in transmission mode.

Small specimens for dynamic-mechanical thermal characterization were obtained in a brass mold coated with a mineral oil. After cure and demolding, samples were polished to final dimensions (20 mm × 3 mm × 2.5 mm). Dynamic mechanical spectra were obtained with a Perkin-Elmer DMA-7 system, operating at 1 Hz in the three-point-bending mode (span = 15 mm), at a heating rate of 2.5°C/min.

The thermal stability of the hybrid materials was analyzed using thermal gravimetric analysis (TGA-7 Perkin Elmer). Samples were heated in air, at 10°C/min up to 800°C.

The thickness and morphological characteristics of coatings were determined by scanning electron microscopy (SEM, Philips 505). The Knoop microhardness, H_K (GPa), was determined with a Tukon TU-300 device, using the following equation [15]:

$$H_K \text{ (GPa)} = 14229P/a^2$$

where P is the weight expressed in N and a is the length of the major diagonal in μm . A weight of $P = 0.049$ N was used for every measurement. About 25 determinations were performed for every type of coating.

2.3. Coatings on Glass Substrates

Coatings were prepared from a 15 wt% solution in tetrahydrofuran (THF) of: a) SSO, b) SSO/BPO with 1.5 wt% BPO and c) SSO/VE/BPO with 30 wt% VE and 1.5 wt% BPO.

Glass substrates were washed and kept immersed in isopropanol. Dip coating was performed using a rate of 27 cm/min, at room temperature. After drying in air for about 30 s, the coated glasses were kept in an oven, at $T_0 = 80^\circ\text{C}$ for 24 h. Then, they were heated to a temperature T_1 and kept at this value for 1 h to obtain the final coated glass. T_1 was varied in the range 150, 200, 300 and 400°C , for different samples.

3. Results and Discussion

3.1. Conversion of C=C Groups of the Neat SSO

Figure 1 shows a DSC scan of the neat SSO, revealing that in the absence of initiators an exothermic reaction in the temperature range comprised between 150 and 250°C takes place. This may be ascribed to the thermally-initiated free radical polymerization of the methacryloxypropyl double-bonds. The experimental value of the reaction heat was 70 J/g or 12.6 kJ/mol of double-bonds. This may be compared to the heat

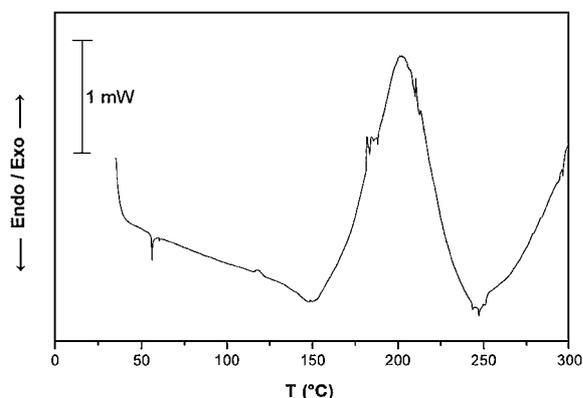


Figure 1. DSC scan of the neat SSO.

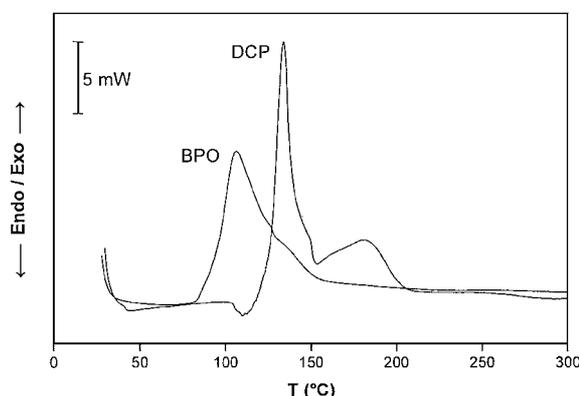


Figure 2. DSC scans of SSO/BPO and SSO/DCP samples.

of polymerization of propyl methacrylate, equal to 57.4 kJ/mol [16]. This means that about 22% of methacryloxypropyl double-bonds were polymerized by the thermally-initiated process. The effect of this reaction may be of importance when coatings based on this silane are used to prepare microporous silica by organic templating. The presence of a polymerization reaction may invalidate the assumption of a random dispersion of organic templates in the hybrid material before their pyrolytic removal [7].

Figure 2 shows DSC scans of SSO/BPO and SSO/DCP samples. With BPO as initiator, a single exothermic peak at 108°C is present. The use of DCP as initiator led to the appearance of two exothermic peaks at 133°C and 180°C . While the former lies in the temperature range where DCP is decomposed at a significant rate, the latter may be associated to the thermally-initiated polymerization. The total reaction heat was the same for both initiators (260 J/g or 47.9 kJ/mol of C=C groups), revealing that the maximum extent of the organic polymerization was independent of the thermal cycle when a final temperature close to 200°C was attained. The value of the total reaction heat was 83% of the maximum value expected on the basis of the heat of polymerization of propyl methacrylate. This is consistent with results reported for the formation of vinyl/dimethacrylate networks where NIR results showed that the total double-bond conversion never reached the value of 100%, even at high cure temperatures [17]. For example, for a system based on styrene and a dimethacrylate of tetraethoxylated bisphenol A, a maximum conversion of 80% of the theoretical value was reported. A significant fraction of pendant double-bonds remained trapped in the highly crosslinked network [17].

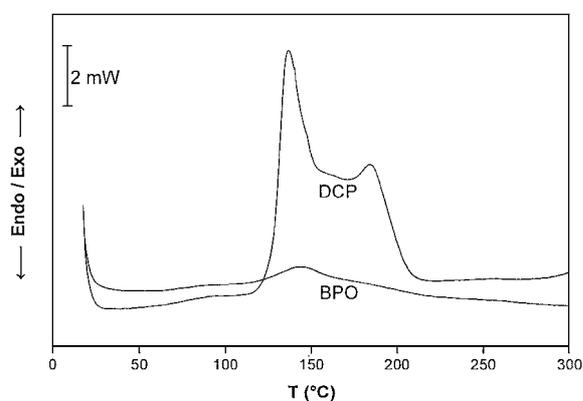


Figure 3. DSC scans of SSO/BPO and SSO/DCP samples showing the residual reaction heat after a preheating period at 80°C during 10 h.

Another way of analyzing the possible influence of thermal cycles is through the use of a two-step cure process. Samples of SSO/BPO and SSO/DCP were heated during 10 h at 80°C, cooled and scanned in the DSC up to 300°C. Residual reaction heats obtained during the DSC scans, are shown in Fig. 3.

The BPO-initiated polymerization did not attain the maximum possible conversion during the heating at 80°C. This was ascribed to the fact that the material vitrified in the course of polymerization (the glass transition temperature, T_g , became equal to the cure temperature). An experimental verification of this hypothesis will be provided in the next section. In the glassy state the polymerization rate decreases several orders of magnitude due to diffusional restrictions, until it may be considered arrested for practical purposes [18]. When the material devitrifies in the course of the DSC scan, the reaction is completed. For the SSO/BPO system the residual reaction heat was about 13% of the value obtained when the DSC scan was performed without an intermediate heating step.

A small advance of the polymerization process took place at 80°C for the SSO/DCP samples, as revealed by the decrease in the contribution of the first exothermic peak to the overall heat of reaction (compare DSC thermograms shown in Figs. 2 and 3). In this case the residual reaction heat was about 81% of the value obtained from a fresh sample during a DSC scan.

Results presented in this section indicate that the free-radical homopolymerization of C=C groups of the SSO may be carried out to a conversion close to 83% by selecting an adequate initiator and a thermal cycle

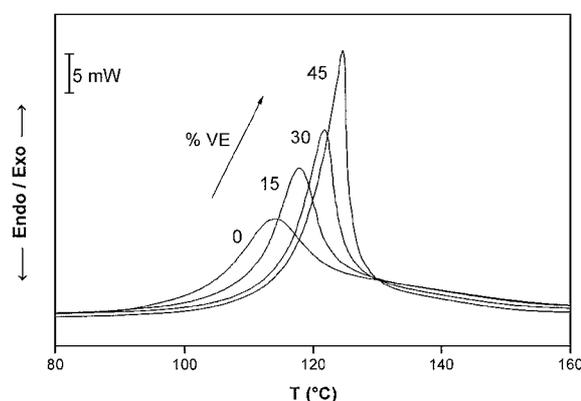


Figure 4. DSC scans of SSO/VE/BPO blends containing different mass fractions of the VE resin.

attaining a final temperature of about 200°C. In the absence of initiators, a thermally-initiated polymerization takes place, leading to a 22% conversion of C=C groups when temperature attains values in the range of 250°C.

3.2. Conversion of C=C Groups in SSO/VE Blends

Figure 4 shows DSC scans of SSO/VE blends containing different mass fractions of the VE resin and using BPO as initiator. By increasing the VE concentration there is a shift of the curves to higher temperatures. This is originated by the presence of the small amount of hydroquinone added to the VE resin to prevent the initiation of a free-radical polymerization during storage. After the inhibitor is depleted by reaction with the free radicals generated by the peroxide decomposition, the chainwise polymerization is initiated.

The reaction heat was close to 50 kJ/mol for every SSO/VE blend, meaning that the addition of VE as co-monomer led to a slight increase in the overall conversion of C=C groups. This modest increase in conversion is possibly associated to the fact that the maximum conversion of the neat VE resin is also limited by sterical factors [17]. The situation may be different in blends of the SSO with small vinyl monomers. For example, quantitative analysis of the photochemical polymerization of C=C groups in a hybrid material resulting from the hydrolytic condensation of MPMS and tetraethoxysilane (TEOS), revealed that about 20% of the initial double-bonds remain unreacted. However, the addition of a convenient amount of methyl methacrylate (MMA) led to the complete

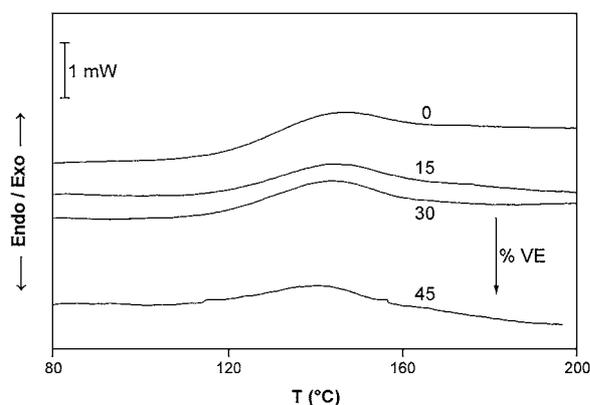


Figure 5. DSC scans of SSO/VE/BPO blends showing the residual reaction heat after a preheating period at 80°C for 10 h.

polymerization of the methacrylate groups from both sources (MPMS and MMA) upon UV irradiation [19].

SSO/VE/BPO blends were polymerized during 10 h at 80°C, cooled and scanned in the DSC (Fig. 5). Residual reaction heats for SSO/VE blends were about 6–7% of the value obtained when the DSC scan was performed without an intermediate heating step. Again, the reaction could not be completed at 80°C due to the onset of vitrification during polymerization. But the conversion attained during the polymerization at 80°C was higher for SSO/VE blends than for the neat SSO, indicating that networks derived from these blends are more flexible (higher conversion for the same T_g), than those derived from the SSO alone.

In order to verify that the maximum attained conversion was limited by vitrification during the isothermal cure, the T_g of the resulting materials was determined by dynamic mechanical analysis (DSC did not have enough sensitivity for this determination; this is a usual restriction for highly crosslinked networks). But the problem was that specimens were so brittle that fracture occurred during the mechanical test. Figure 6 shows a dynamic mechanical spectrum for a SSO/VE/BPO blend containing 15 wt% VE, previously polymerized at 90°C during 14 h. Although this specimen was fractured when T was close to 106°C, it was possible to obtain the desired information. The elastic modulus in the glassy state exhibited a value of 2 GPa. Devitrification is associated to a decrease in E' and a corresponding increase in $\tan \delta$. The onset of this increase was observed at $T = 95^\circ\text{C}$, which is a few degrees above the polymerization temperature, as expected [18]. At 106°C the material was still in the devitri-

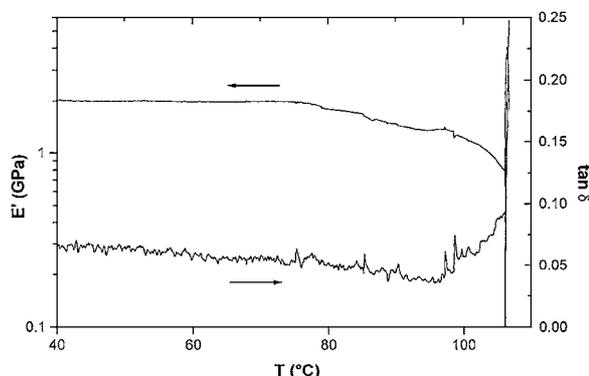


Figure 6. Dynamic mechanical spectrum for a SSO/VE/BPO blend with 15 wt% VE, previously polymerized at 90°C during 14 h.

fication range, with $E' = 800$ MPa and $\tan \delta$ close to 0.09.

With the aim of analyzing the effect of the cure cycle on the final attained conversion, a SSO/VE/BPO blend containing 30 wt% VE was polymerized with two different thermal cycles: i) with a heating rate of 10°C/min up to 200°C; ii) isothermal polymerization at 80°C during 10 h followed by a scan to 200°C, at a heating rate of 10°C/min. Figure 7 shows the FTIR absorption spectra of both samples together with the one of the initial sample. The reaction of C=C groups is related to the significant decrease of the absorption peaks at 943 and 1638 cm^{-1} . However, there is no evident distinction between the spectra of the resulting materials meaning

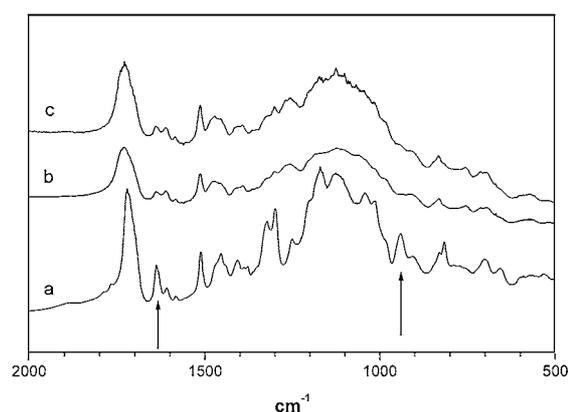


Figure 7. FTIR absorbance spectra for a SSO/VE/BPO blend with 30 wt% VE, showing the decrease of the peaks associated to C=C groups at 943 and 1638 cm^{-1} , in the course of polymerization (a: initial sample; b: sample after conducting the polymerization at 10°C/min in the DSC; c: sample resulting from an isothermal heating at 80°C during 10 h followed by a DSC scan up to 200°C).

that there is no influence of the selected thermal cycles on the maximum attained conversions.

Therefore, different types of networks may be generated on the basis of the starting SSO: a) SSO networks after a thermal treatment at temperatures below 150°C, with no conversion of C=C groups; b) SSO networks after a thermal cycle attaining temperatures in the range of 250°C, characterized by a conversion of C=C groups close to 22%; c) SSO/BPO networks with a high conversion of C=C groups after a polymerization at 80°C, and a maximum conversion close to 83% after thermal cycles attaining 200°C; d) SSO/VE/BPO blends with similar conversions than SSO/BPO blends but with a different (more flexible) chemical structure. The effects of different conversions of C=C bonds and the chemical modification with a VE resin on: i) the thermal stability, ii) the microhardness of coatings on glass substrates, will be reported in the following sections.

3.3. Thermal Stability of the Hybrid Materials

Samples of SSO, SSO/BPO and SSO/VE/BPO with 30 wt% VE, were kept at 80°C during 24 h and subjected to thermal gravimetric analysis. Results are shown in Fig. 8. Thermal degradation occurred at a fast rate when temperature attained 400°C and it was completed at about 800°C, leaving SiO₂ as residue. The experimental fraction of residual masses was 33.6% for the SSO sample (expected value = 33.3%), 31.9% for the SSO/BPO sample (expected value = 32.8%), and 23.3% for the SSO/VE/BPO sample (expected value = 22.9%).

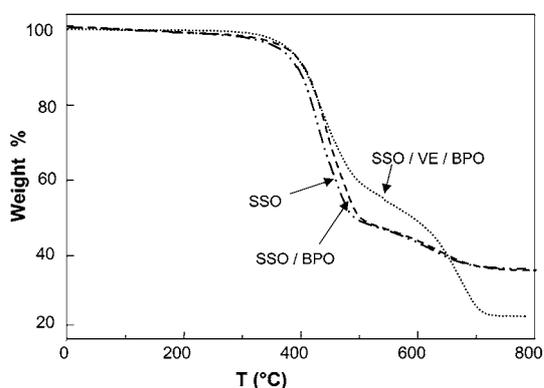


Figure 8. TGA scans during the heating in air of different samples up to 800°C; for the samples devoid of VE the dashed-dotted line represents the neat SSO and the dashed line the SSO/BPO material.

The onset of thermal degradation was independent of the conversion of C=C bonds or the addition of the VE resin and may be exclusively related to the presence of the methacryloxypropyl chemical structure in every system. For the SSO/VE/BPO blend, thermal degradation occurred in two well-defined stages separated by a plateau in the 500–650°C range. This is possibly associated to degradation products involving the aromatic rings incorporated with the VE resin. Residual masses were 62.6% at 500°C and 50.6% at 600°C.

3.4. Microhardness of Coatings on Glass Substrates

Coatings on glass substrates with thickness varying in the range of 0.5–1 μm, were prepared with SSO, SSO/BPO and SSO/VE/BPO (30 wt% VE) blends. Figure 9 shows a SEM micrograph of a coating obtained with SSO/VE/BPO after heating 1 h at 200°C. The view was taken from a side of the glass substrate (bars represent a 10 μm length). The coating looks homogeneous with an apparent good adhesion to the glass surface. Its thickness was about 1 μm. The heating to 400°C produced a reduction in thickness, associated to the densification produced by the partial thermal degradation of the organic constituents and the condensation of the inorganic structure. But it did not affect the integrity of the coatings except in regions where a defect (bubble, inclusion) was originally present. Cracks propagating from these regions were observed, possibly due to the generation of thermal stresses.

Figure 10 shows the Knoop microhardnesses, H_K (GPa), of different coatings after thermal treatments between 80 and 400°C ($H_K = 6$ GPa for the glass substrate). In spite of the use of very small loads, the absolute values of the microhardness could be influenced by the glass substrate due to the small thickness of the coatings. However, the test was able to discriminate the values of the different materials and can be used for comparison purposes.

Two main conclusions may be obtained from Fig. 10. The first one is that the conversion of C=C groups does not affect the hardness of the coatings as revealed by the similar values of coatings based on SSO and SSO/BPO, heated to different temperatures. The second one is that the incorporation of VE leads to a decrease of the hardness, associated to the higher flexibility of the resulting network. Also interesting is the fact that coatings based on SSO/VE/BPO formulations exhibited a significant decrease in the dispersion of



Figure 9. SEM micrograph of a coating obtained with a SSO/VE/BPO material after a thermal heating at 200°C. The view was taken from a side of the glass substrate (bars represent a 10 μm length).

experimental values obtained from different regions of the material. This was ascribed to the more uniform thickness obtained when adding the VE resin to the initial formulation.

The heating to 300 and 400°C produced a significant degradation of the coatings, revealed by the increase in the values of hardness and the fact that they become very close one to each other, independently of the initial addition of the VE resin.

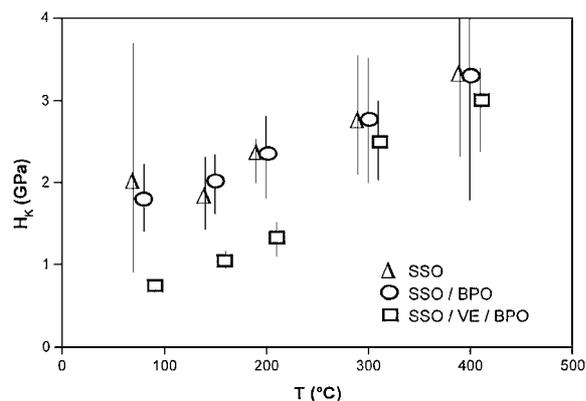


Figure 10. Knoop microhardness, H_K (GPa), of different coatings after thermal treatments between 80 and 400°C (bars represent the dispersion range of experimental results).

4. Conclusions

Hybrid materials based on a SSO containing methacryloxypropyl groups, were synthesized using different initial formulations and thermal cycles. For the neat SSO a thermally-initiated polymerization was observed in the 150–250°C range, leading to a conversion close to 22% of the initial C=C groups. The final conversion could be increased to a maximum value close to 83%, by adding an initiator and using a thermal cycle attaining temperatures in the range of 200°C. The use of variable amounts of VE as a co-monomer produced a slight increase of the final conversion in SSO/VE/BPO blends.

The influence of both the conversion of C=C groups and the presence of the VE resin on the thermal stability of the materials and the microhardness of coatings on glass substrates, was investigated. Neither the conversion of double-bonds nor the addition of the VE had any effect on the onset temperature of thermal degradation, which was associated to the presence of the methacryloxypropyl groups supplied by the SSO and the VE resin. However, a distinct two-step degradation process was observed in the presence of VE. Coatings based on SSO/VE/BPO blends exhibited more uniform thicknesses and lower values of the microhardness than those devoid of VE. However, the conversion of C=C

groups did not show any significant effect on the values of microhardness.

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References

1. N.K. Raman, M.T. Anderson, and C.J. Brinker, *Chem. Mater.* **8**, 1682 (1996).
2. N.K. Raman and C.J. Brinker, *J. Membr. Sci.* **105**, 273 (1995).
3. M.J. Vanbommel, T. Wolde, and T.N.M. Bernards, *J. Sol-Gel Sci. Technol.* **2**, 167 (1994).
4. Y. Lu, L. Hang, C.J. Brinker, T.M. Niemczyk, and G.P. López, *Sensors Actuators B* **35**, 1 (1996).
5. G. Cao, Y. Lu, G.P. López, and C.J. Brinker, *Adv. Mater.* **8**, 588 (1996).
6. R.A. Peterson, M.A. Anderson, and C.G. Hill, Jr. *J. Membr. Sci.* **94**, 103 (1994).
7. Y. Lu, G. Cao, R.P. Kale, S. Prabakar, G.P. López, and C.J. Brinker, *Chem. Mater.* **11**, 1223 (1999).
8. S.M. Kim, D.Y. Yoon, C.V. Nguyen, J. Han, and R.L. Jaffe, *Mat. Res. Soc. Symp. Proc.* **511**, 39 (1998).
9. J.L. Hedrick, R.D. Miller, C.J. Hawker, K.R. Carter, V. Volksen, D.Y. Yoon, and M. Trollsás, *Adv. Mater.* **10**, 1049 (1998).
10. J. Kron, S. Amberg-Schwab, and G. Schottner, *J. Sol-Gel Sci. Technol.* **2**, 189 (1994).
11. R. Nass, E. Arpac, W. Glaubitt, and H. Schmidt, *J. Non-Cryst. Solids* **121**, 370 (1990).
12. P. Eisenberg, R. Erra-Balsells, Y. Ishikawa, J.C. Lucas, A.N. Mauri, H. Nonami, C.C. Riccardi, and R.J.J. Williams, *Macromolecules* **33**, 1940 (2000).
13. K. Sharp, *J. Sol-Gel Sci. Technol.* **2**, 35 (1994).
14. M.L. Auad, M.I. Aranguren, and J. Borrajo, *J. Appl. Polym. Sci.* **66**, 1059 (1997).
15. R.F. Cook and G.M. Pharr, *J. Am. Ceram. Soc.* **73**, 787 (1990).
16. R.M. Joshi, *Makromol. Chem.* **66**, 114 (1963).
17. L. Rey, J. Galy, and H. Sautereau, *Macromolecules* **33**, 6780 (2000).
18. R.J.J. Williams, in *Polymer Networks: Principles of their Formation, Structure and Properties*, edited by R. F. T. Stepto (Blackie Academic & Professional, London, 1998), p. 93.
19. L. Delattre, C. Dupuy, and F. Babonneau, *J. Sol-Gel Sci. Technol.* **2**, 185 (1994).