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The role of Zirconium as thermal stabilizer of PDMS–TEOS hybrids

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Abstract Hybrid materials were prepared by sol–gel method using Tetraethylortosilicate and Polydimethylsiloxane silanol terminated with the addition of small contents of Zirconium Propoxide ≤ 5 wt%. The thermal stability of the prepared samples was studied by Infra-red spectroscopy, ^{29}Si Nuclear Magnetic Resonance, Thermal Analysis and Scanning Electron Microscopy. All samples were monolithic after drying at 120 °C. After heat treatment at 400 °C the samples prepared with 0 wt% in Zirconium Propoxide present high porosity. It was found that the content in Zirconium Propoxide is directly related with the thermal stability of the hybrid materials prepared in this study.

Keywords Ormosils · Sol–gel · Thermal stability

Introduction

The sol–gel process has been extensively used to prepare inorganic materials and to incorporate organics in gel derived silica materials commonly designated as ormosils (organically modified silicates) [1].

These hybrid materials have new and different properties (optical, electrical or mechanical) compared with the ones of conventional materials [2]. In this way the hybrid materials constitute a new class of potential high-performance and multifunctional materials intermediate between inorganic and polymeric materials [3].

Mackenzie et al. studied the mechanical properties, the gelation kinetics and the thermal stability of TEOS–PDMS hybrid materials [4–6].

The successful application of these materials is intimately related with its degradation temperature. So, the investigation of ways to increase the thermal stability of such materials is a relevant issue.

Several authors have so far presented different approaches to increase the thermal stability of hybrid TEOS–PDMS materials. Bescher et al. [7] succeed to increase the thermal stability by the addition of small contents of Fe^{3+} ions. The authors explained that the introduction of Fe^{3+} ions induced differences in the chemical structure formed in the liquid leading to PDMS chain cleavage and increased cross-linking to SiO_2 which is the cause for the enhanced thermal stabilization. Peña et al. [8] discussed the role of γ-aminopropyltrietoxysilane (γ-APS) on the thermal stability of TEOS–PDMS hybrids and attributed also the enhancement of the thermal stability of the hybrids to an increase in the cross-linking due to the addition of γ-APS.

Zaharescu et al. [9] studied the thermal stability behaviour of hybrid materials in the TEOS-MTEOS (tetraethoxysilan-methyltriethoxysilan) system and found that the thermal stability was related with the composition of the materials rather than with the conditions of the gelation process.

Previous work of the authors [10] showed that the structural stability of TEOS–PDMS hybrid materials prepared by gamma irradiation was dependent on the zirconium propoxide presence in the precursors mixture.

In this work it is proposed to study an alternative way of improving the thermal stability of TEOS–PDMS hybrid materials prepared by sol–gel by the addition of small percentages of zirconium.

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Experimental

Hybrid samples were prepared using Tetraethylortosilicate (TEOS) and Polydimethylsiloxane (PDMS) silanol terminated (DMS-S21) with average molecular weight equal to 4200 and Zirconium isopropoxide (Fluka). Ethylacetoacetate (Merck) was used to stabilize the zirconium alkoxide in a molar ratio equal to one. Six samples were prepared with the compositions given in Table 1.

The sample name Zx–y refers to sample with *x* wt% PrZr and *y* wt% PDMS. All samples were prepared with magnetic stirring at room temperature and then put at 60 °C until gelation occurred. In the following they were dried at 120 °C for 24 h and then heat treated at 400 °C (1 h) in air with a heating rate equal to 10 °C/min.

Several techniques were used to characterize the prepared samples. Namely, Thermal analysis (TA Instruments, TG-model 951 at the Polymer Characterisation Laboratory of ITN), X-ray diffraction (Rigaku Geigerflex), Infra-red spectroscopy (Mattson 7000) and ^{29}Si magic-angle spinning (MAS). NMR spectra were recorded at 79.49 MHz on a 9.4 T Bruker Avance 400 spectrometer, using 40° pulses, a recycle delay of 60 s and a spinning rate of 5 kHz. Chemical shifts are quoted in ppm from TMS. The morphology of samples was observed by Scanning electron microscopy (SEM-Hitachi SU-70).

Results and discussion

All prepared samples after drying at 120 °C are transparent and homogeneous. After heat treatment at 400 °C, for 1 h, the samples prepared with zirconium propoxide addition are dense samples, dark brown, whereas the samples prepared with no addition of zirconium propoxide are highly porous.

According to X-ray diffraction all samples were amorphous after heat treatment at 400 °C. A representative example of the XRD obtained diffractograms is shown in Fig. 1.

Table 1 Experimental conditions of preparation of PDMS–TEOS hybrid samples

Sample	PDMS (wt %)	TEOS (wt %)	PrZr (wt %)
Z1–20	20	79	1
Z5–20	20	75	5
Z1–50	50	49	1
Z5–50	50	45	5
Z0–20	20	80	–
Z0–50	50	50	–

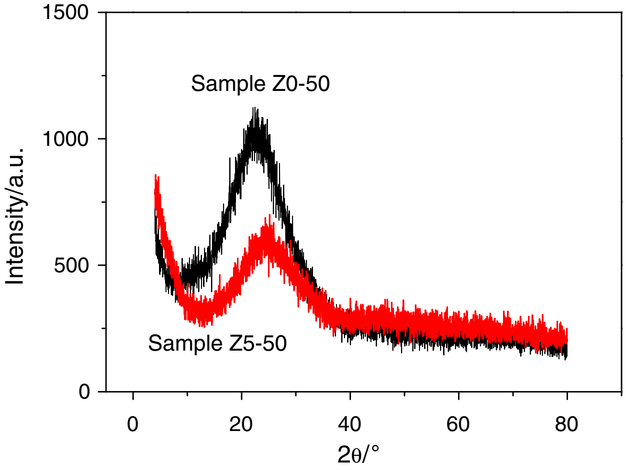

Fig. 1 XRD diffractograms of samples Z0–50 and Z5–50 heat-treated at 400 °C

A broad peak at small 2θ is observed for samples with and without PrZr. This peak reveals the short-range order characteristic of amorphous structure.

Figures 2 and 3 present the Infra-red spectra of samples dried at 120 °C and heat treated at 400 °C, with (a) and without (b) zirconium propoxide addition. All spectra show the characteristic bands of silica as well as the bands due to the presence of OH groups and the presence of molecular adsorbed water, respectively, at 1625 cm^{-1} and 3420 cm^{-1}. The characteristic bands of silica are observed at ~1263 cm^{-1} and ~1090 cm^{-1} (due to the assymetrical stretching modes of vibration of the O–Si–O bond). At ~447 cm^{-1} another characteristic band of silica (due to the bending modes of vibration of the Si–O–Si bond) is also observed [11, 12]. For samples dried at 120 °C a shoulder at 950 cm^{-1} attributed to stretching of Si–OH groups is present, decreasing in intensity with the heat-treatment at 400 °C due to the condensation of Si–OH groups to form Si–O–Si bonds. At 500–540 cm^{-1} a band is observed which is due to the formation of Si–O–Si bonds in four member rings [13].

The bands attributed to CH_3 symmetric bending of PDMS and to PDMS siloxane bond stretchings [14] are observed at ~780–800 cm^{-1} (due to the symmetrical stretching modes of vibration of the O–Si–O bond). This band is superposed with a band due to Si–C vibrations [8]. In samples heat-treated at 400 °C with Zr in their composition the intensity of this band, associated to the polymer, increases and it decreases clearly for the samples prepared without zirconium addition. The band at ~2976 cm^{-1} due to the presence of Si–CH_3 bonds in the spectra obtained for the four samples [9] heat treated at 120 °C disappears for the samples heat-treated at 400 °C prepared without zirconium propoxide.

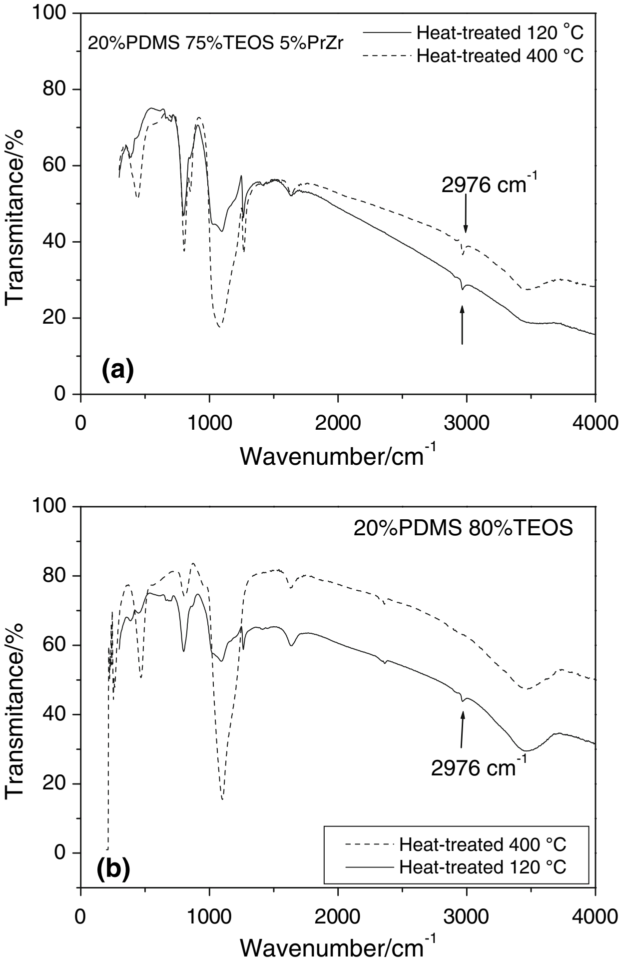

Fig. 2 Infra-red spectra of samples prepared with 20 wt% PDMS, dried at 120 °C and heat treated at 400 °C (**a**) (Z5–20) with and (**b**) (Z0–20) without zirconium propoxide

Zaharescu et al. [9] had found that the presence of the band at 2976 cm^{-1} was indicative of higher thermal stability of silica based hybrid materials. Similarly, in this work the decrease in intensity or the disappearance of the bands due to PDMS with the heat treatment in the spectra obtained for samples prepared without zirconium propoxide showed that the addition of zirconium leads to higher thermal stability of the hybrid material.

Figure 4 shows ^{29}Si MAS NMR results for sample Z5–20 (with zirconium addition) and sample Z0–20 (without zirconium addition) heat treated at 400 °C.

For the sample prepared with zirconium (Z5–20) a minor resonance at −19,5 ppm attributed to cyclic PDMS molecules is observed together with a strong resonance at −22,7 ppm due to D^2 units (Si(CH$_3$)$_2$O$_2$) of long PDMS chains. Resonances around −103 ppm and −110 ppm attributed respectively to Q^3 (Si(–O–Si$\equiv$)$_3$OH units and Q^4 (Si(OSi$\equiv$)$_4$ units are present for this sample [8]. A resonance at −68 ppm is assigned to T^3 units [15].

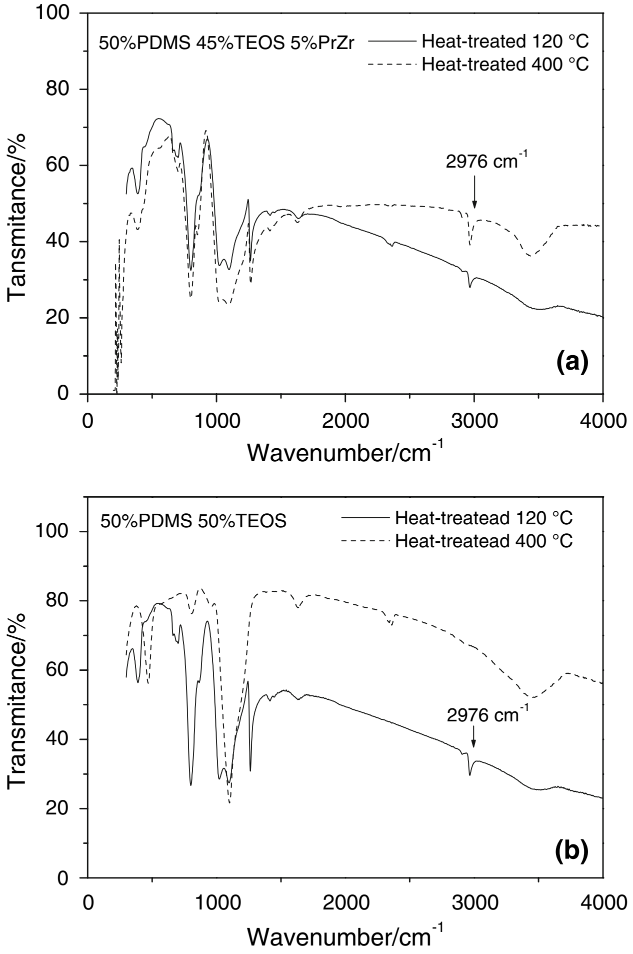

Fig. 3 Infra-red spectra of samples prepared with 50 wt% PDMS, dried at 120 °C and heat treated at 400 °C (**a**) (Z5–50) with and (**b**) (Z0–50) without zirconium propoxide

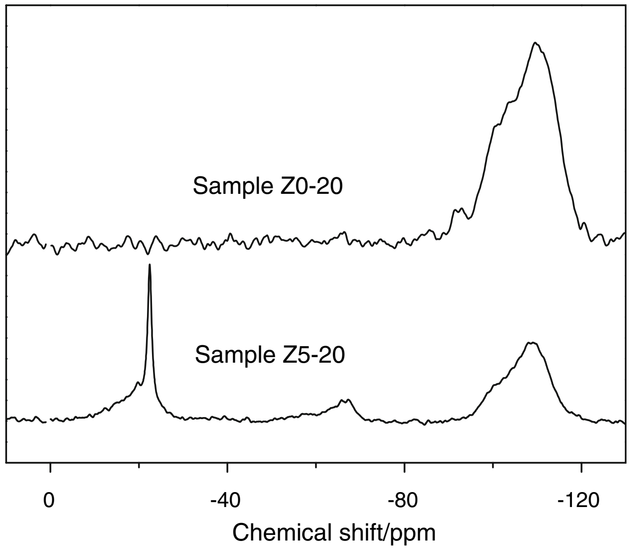

Fig. 4 ^{29}Si MAS NMR results for two samples, heat treated at 400 °C, one with zirconium addition (Z5–20) and another without zirconium addition (Z0–20)

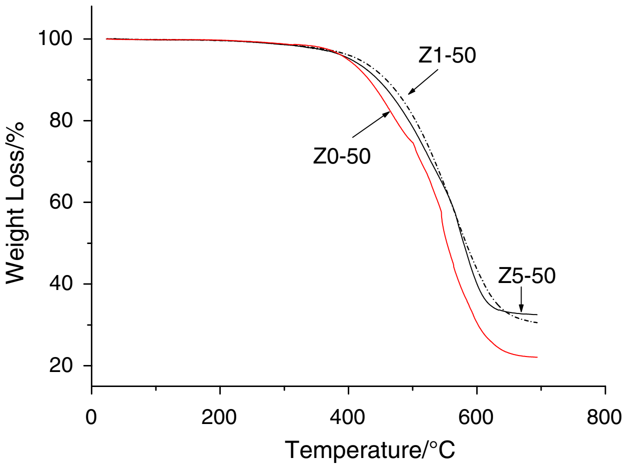

Fig. 5 Curves obtained for the prepared samples dried at 120 °C

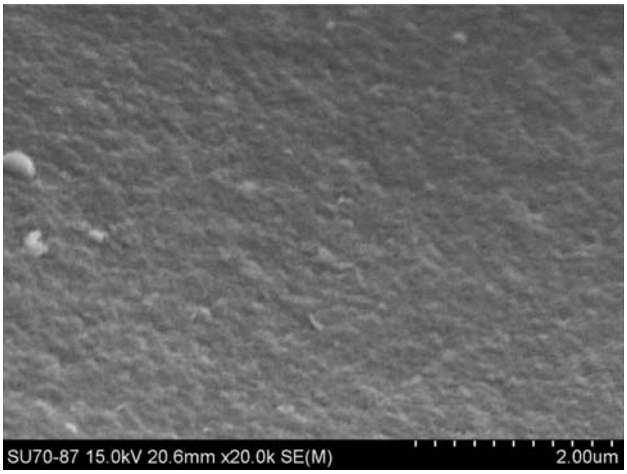

Fig. 6 SEM micrograph of Z5–20

In the case of the sample prepared without zirconium (Z0–20) no resonances due to units related with PDMS are observed. This is indicative that the polymer degradation occurs in samples prepared without zirconium during the heat treatment at 400 °C. This result is in agreement with the IR studies on these samples where the decrease in intensity or the disappearance of the bands due to PDMS is in accordance to the conclusion that small additions of zirconium enhance significantly the thermal stability of the hybrids materials prepared in this study.

In Fig. 5, TG results obtained for all 50 wt% of PDMS samples dried at 120 °C are presented. These confirm that the materials prepared with addition of zirconium propoxide show a tendency for a shift of the thermal degradation temperature to higher values before the accelerated weight loss as compared to the sample without Zr.

These results are indicative of the enhancement of the thermal stability of the materials with small additions of zirconium. Similar tendency was referred by Bescher et al. [7] with small additions of iron to TEOS–PDMS hybrids. Figure 5 also shows that the enhancement of the thermal stability does not increase linearly with Zr content, for all contents, indicating that there must be an optimal value for that content. In a previous study [16] the authors found that small amounts of Zr in PDMS–TEOS system prepared by gamma irradiation were fundamental to obtain a stable hybrid material but the further increase in its content was found to have the opposite effect.

Figures 6, 7, 8 and 9 show the scanning electron micrographs of samples prepared with and without zirconium and heat treated at 400 °C. The effect of zirconium in the increase of the thermal stability of the hybrid samples is clearly visible: the samples prepared with addition of zirconium, Z5–20 and Z5–50, are homogeneous and exhibit no pores after heat-treated at 400 °C, whereas those of similar composition and heat-treatment but prepared

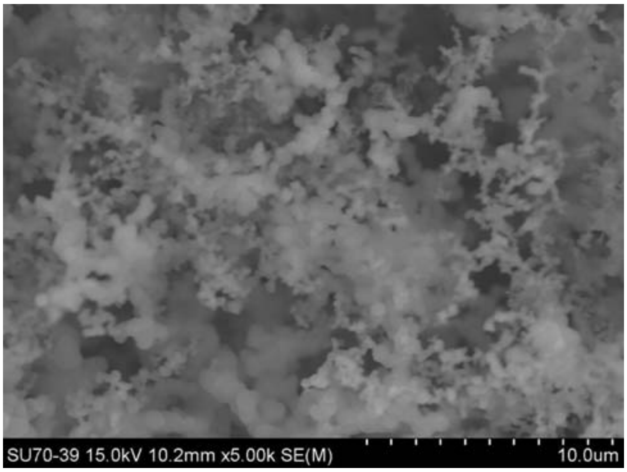

Fig. 7 SEM micrograph of Z0–20

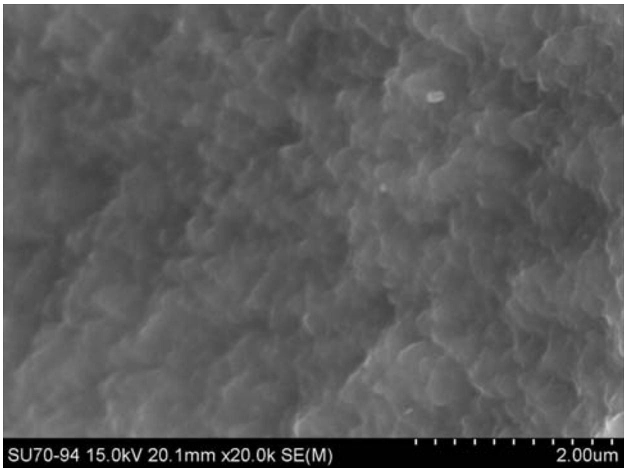

Fig. 8 SEM micrograph of Z5–50

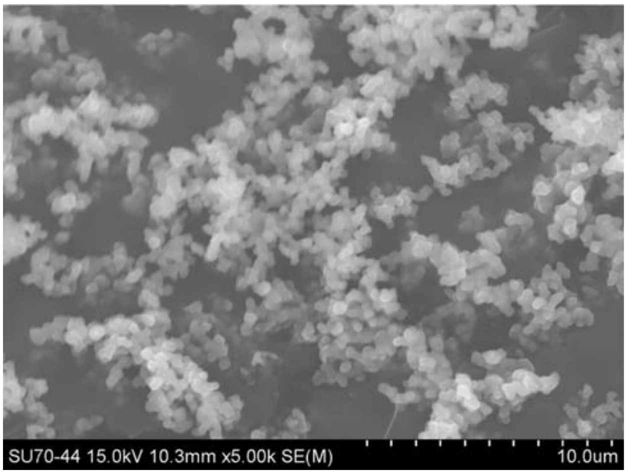

Fig. 9 SEM micrograph of Z0–50

without addition of zirconium, Z0–20 and Z0–50, are highly porous resulting from the degradation of the polymer.

Conclusions

Monolithic samples of PDMS–TEOS hybrids were obtained after drying at 120 °C. Upon heat treatment at 400 °C the samples prepared without zirconium propoxide addition were highly porous whereas the addition of zirconium propoxide allows retaining the dense monolithic character of the hybrid samples.

The characteristic IR bands associated to PDMS decrease in intensity or disappear with the heat treatment at 400 °C for samples prepared without zirconium propoxide while these bands are still observed in samples prepared with zirconium propoxide heat-treated at the same temperature. The fact that no IR resonances due to units related with PDMS are observed for samples prepared without zirconium propoxide is indicative that the polymer degradation occurred during the heat treatment until 400 °C. These IR results were further confirmed by ^{29}Si NMR and thermal analysis.

In brief it was shown that the thermal stability of TEOS–PDMS hybrid materials can be increased by small additions of zirconium.

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