Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 1, 99–103

THERMAL ANALYSIS OF HYBRID MATERIALS PREPARED BY γ-IRRADIATION

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Hybrid materials were prepared by γ-irradiation of a mixture of polydimethylsiloxane (PDMS), with tetraethylorthosilicate (TEOS) and zirconium propoxide (PrZr), using a ^{60}Co γ source, without any addition of solvents. Thermogravimetry, differential scanning calorimetry and X-ray diffraction measurements showed that the obtained hybrids are amorphous materials of the nanocomposite type. The results highlighted the different influence of each of the metallic alkoxides on the hybrid structure. The material rupture temperature, associated with the degradation of the organic component, depends mainly on the TEOS content, whereas the inorganic component structural stability depends on the relative PrZr content in the alkoxides mixture.

Keywords: *hybrid materials, γ-irradiation, PDMS-based materials, thermal properties*

Introduction

Hybrid materials consist of both organic and inorganic components, assembled for the purpose of designing new materials with enhanced or unusual properties.

These materials are currently processed by using conventional sol–gel chemistry which involves the mixture of a polymer with a metal alkoxide or a mixture of metal alkoxides that undergo hydrolysis and condensation reactions followed by gelification [1–3]. Final hybrid properties may be controlled by the sol–gel processing conditions [4]. Sol–gel prepared PDMS networks containing precipitated silica have been thoroughly characterized as concerns the preparation, mechanical, thermal and optical properties. These materials have many applications such as sensors, water repellent coatings, corrosion resistant films, waveguides, pressure-sensitive adhesives, cosmetics, etc. The hybrid material can be either a homogeneous system derived from monomers and miscible organic and inorganic components or a heterogeneous system (nanocomposite) where at least one of the components domains has a dimension ranging from some Å to some nanometres. The properties of these materials are strongly dependent on the role of the inner interfaces. The nature of the interface has been used to grossly divide these materials into two distinct classes. In class I, organic and inorganic components are embedded and only week bonds (Van der Walls, hydrogen or electrostatic interactions) give the cohesion to the whole structure. In class II materials, the two components are linked together through strong chemical bonds (covalent or iono-covalent). The frontier between both classes is not always simple and materials can eventually present class I and class II characteristics [1].

In a previous work the authors used a new preparation method to obtain hybrid materials prepared with PDMS, silanol terminated, TEOS and PrZr. This new preparation process is based on the fact that the crosslinking of polymer chains can be promoted by γ-ray irradiation [5], without the addition of solvents being required. The influence of several parameters in the γ-irradiation method for the preparation of hybrid materials has been already studied [6]. It was observed that to obtain hybrids by γ-irradiation, the presence of a small content of PrZr was mandatory since in its absence most of TEOS evaporated during the drying stage of the irradiated sample. In samples prepared without the Zr alkoxide, although no hybrid was obtained, the presence of TEOS during the irradiation process was found to affect significantly the final PDMS cross-linked network [7]. The elemental analysis of irradiation prepared hybrids showed that the initial carbon (and H) mass loss, before any heat-treatment, originates from the reactions between the two alkoxides [8]. The role of both, needed further investigation.

In the present work, the thermal behaviour of the hybrids prepared by γ-irradiation is studied by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetry (TG). These techniques have been used to analyse samples prepared with various PDMS/alkoxide ratios and different

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1388–6150/$20.00

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compositions of the alkoxide mixture. In this way it is intended to clarify the role of TEOS and PrZr in the irradiation prepared hybrids. This study is part of the systematic work that has been pursued to fully characterize the hybrid materials prepared by γ-irradiation. Since the final properties of the hybrids strongly depend on the processing conditions, the investigation of the thermal, mechanical, optical and other properties of these materials is necessary before proceeding to their proper applications.

Experimental

Sample preparation

Tetraethylorthosilicate (TEOS), purity 99%, from Riedel-de Haën, zirconium(IV) propoxide, 70 mass% solution in 1-propanol, (PrZr), p.a. reagent, from Aldrich and polydimethylsiloxane (PDMS), silanol terminated, p.a. reagent, from ABCR, with average molecular mass M_w=43 500 g mol^{-1}, referred as S33, were used as raw materials to prepare samples with compositions xPDMS(100–x)ALK with ALK=yPDMS+zPrZr where 25 mass%≤ y ≤75 mass% and 7 mass%≤ z ≤25 mass%. In summary, samples with PDMS contents of 20, 33, 50, 67 and 80% have been prepared using different contents of PrZr.

The sample irradiation was carried out at the ^{60}Co irradiation facility, UTR [9]. The description of the preparation method is given elsewhere [6]. All samples have been irradiated until they reached the state of non-flowing gel. This state is obtained at different doses depending on the polymer content.

The state of non-flowing gel can be originated from chain entanglement and/or from chain cross-linking, depending on the molecular mass of the polymer used and on its relative content [10–12]. In this work, the PDMS used in all cases was S33, with the aim to obtain a gel matrix made of cross-linked polymer chains. To check the nature of the polymer matrix, the gel fraction was determined for hybrid samples prepared with different PDMS contents by irradiation until reaching the non-flowing state in the following way. The prepared samples were put into a good solvent (tetrahydrofuran, purity 99.5%) of the polymer in order to remove any material that was not incorporated into the macroscopic network. Afterwards, they were taken out of the solvent, dried and weighed. The gel fraction was determined as the ratio between the masses of the sample dried after withdrawal from the solvent and its initial mass.

Instrumental methods

A Sartorius electronic analytical balance, with error ±0.01 g, was used to determine the mass of precursors in the preparation of samples and the mass of the obtained materials.

The thermal analysis has been performed by TG and DSC techniques. The measurements were carried out in a nitrogen atmosphere, ranging from 25 to 700°C, at a rate of 10°C min^{-1}, using equipment from TA Instruments (TG-model 951; DSC-model 910), at the Polymer Characterisation Laboratory of ITN. The inert atmosphere was used in order to avoid oxidation reactions that tend to accelerate any degradation process.

The TG curves obtained for some of the hybrid samples were quite complex, therefore a graphic procedure was established in order to determine the main features of the curves. Figure 1 shows a schematic view of the referred procedure. The relevant temperatures are those related to the beginning of mass loss, T_{wl} and to the thermal rupture, T_{tr}, associated to the crossover that shows the beginning of the accelerated mass loss. These temperatures are related to different phenomena and were determined as shown in Fig. 1. The former marks the beginning of mass loss that originates from the liberation of the products of alkoxides radiolysis naturally followed by condensation reactions whereas the latter is associated to the breaking of the chains into volatile fragments and reveals the rupture of the structure. When the mass loss stops, the remaining mass% is called the residue or residual mass. Furthermore, for each sample, several DSC and TG measurements were performed and the average value for each of the relevant temperatures and residues has been taken. This was done to take into account that the samples might have non-uniform distribution of homogeneity. The error was ΔT= ±10°C and Δ residual mass=±4%.

XRD was also performed in the prepared materials using the CuK$_\alpha$=1.5418 Å in a Rigaku, Geigerflex instrument at the University of Aveiro.

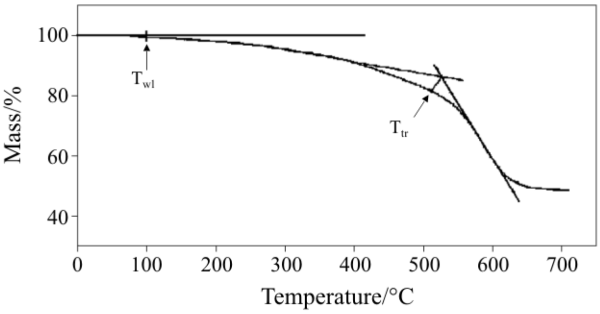

Fig. 1 Schematic view of the graphic procedure followed to determine the relevant TG temperatures

Results and discussion

The gel fraction was determined and found to be >0.90 for all hybrid samples prepared with S33 by irradiation until reaching the stage of non-flowing gel. Thus it was confirmed that the gel matrix is made of cross-linked polymer chains.

XRD was performed in all prepared samples. An example of the obtained diffractograms is shown in Fig. 2. All materials are amorphous, presenting a broad peak characteristic of the amorphous silica, both in samples as prepared and after heat treatment.

TG and DSC measurements revealed that in the large amount of different samples, those with the same PDMS content showed a similar general behaviour. In fact, the curves fell into two distinct patterns depending whether the PDMS mass is smaller or larger than the ALK mass. To illustrate the former case, 33% PDMS samples have been chosen, whereas samples with 67% PDMS will represent the latter. The curves obtained for the hybrid samples are shown together with that obtained for pure PDMS irradiated sample for comparison. TG plots are shown in Fig. 3.

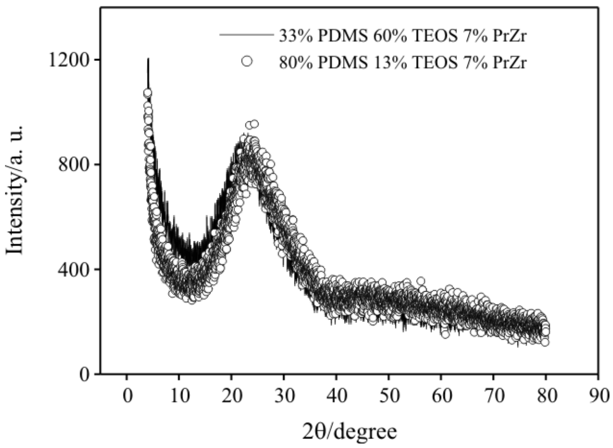

Fig. 2 X–ray diffractograms of hybrid samples prepared with different composition

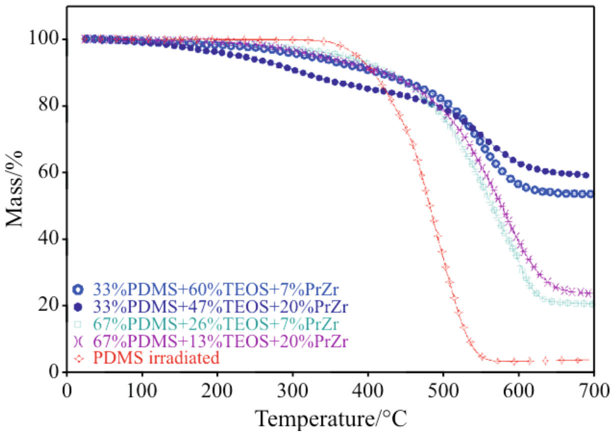

Fig. 3 Thermogravimetry results of hybrid samples with varying compositions

Figure 3 shows that the rupture temperature for pure irradiated PDMS is significantly lower than that of hybrid samples and that the PDMS sample presents a negligible residual mass. TG results obtained from the hybrid materials show that a small mass loss begins at a relatively low temperature, T_{wl}<150°C, and proceeds until the rupture temperature is attained. This lower temperature degradation of the material will be discussed later. The curves for the hybrids also show that their residual mass increases with the alkoxide content, and for each alkoxide value, they increase slightly with the PrZr content. This can be explained by the fact that the alkoxide mixture is the main source for the inorganic mass and on the other hand because the Zr mass is larger than that of Si. The higher rupture temperature of the hybrid material can be due to a protective shielding effect of the inorganic component on the polymer. The variation of the rupture temperature is shown in Fig. 4, for PDMS and for hybrids prepared with 7 and 20% PrZr, as a function of the TEOS content used in the precursors mixture.

It is found that the rupture temperature of the hybrid materials prepared with PrZr increases linearly with the TEOS content, this temperature being lower for PDMS, with an actual value of ca. 400°C. Thus, when PDMS is part of the hybrid material, it seems to be under some protective shield, degrading at a higher temperature. This indicates that the inorganic component should be distributed in the vicinity of the polymer rather than away from it. The results also show that for the same alkoxide content, that with more TEOS produces a more effective shielding. A similar shielding behaviour was observed between two polymeric networks [13]. In a previous work by the authors [6] it was shown that Zr plays a very important role in the preparation of hybrid materials by γ-irradiation. Yet, these results show

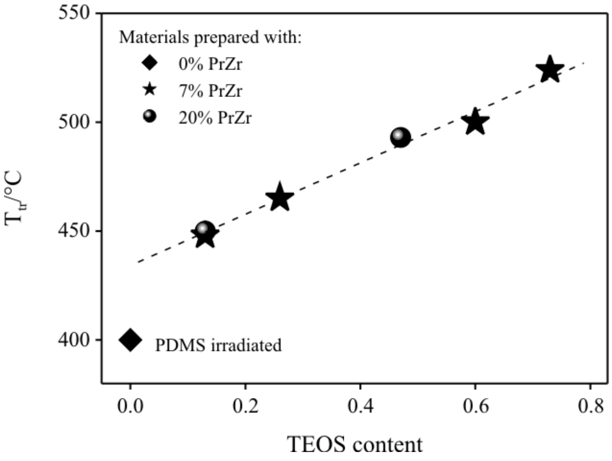

Fig. 4 Rupture temperature as a function of TEOS for different PrZr content

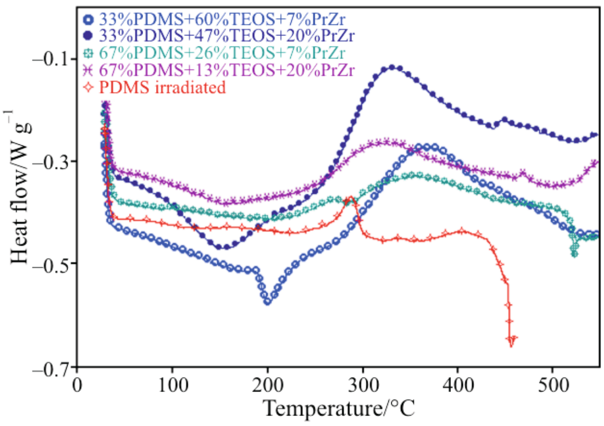

Fig. 5 DSC plots of hybrids with varying compositions

that, provided Zr is present, its content in the range used in this work, has no significant impact in the rupture temperature of the material.

Figure 5 shows the DSC plots obtained for the same samples.

The pure PDMS sample exhibits a relatively narrow exothermic peak just below 300°C. This is attributed to the physical ordering of the chains as it is associated with no mass loss in the TG curve at the corresponding temperature. The DSC plots for hybrid samples prepared with PDMS mass larger than that of the ALK also show a broad exothermic peak at around the same temperature. However, this peak is now associated with some mass loss as observed in the corresponding TG curve. Thus such an exothermic peak is related to some sort of restructuring of the material. Hybrid materials prepared with PDMS mass smaller than that of ALK, present two peaks: a similar broad exothermic peak, even more intense, plus an endothermic peak at a lower temperature, ca. 200°C. Since the exothermic peak is more pronounced for samples prepared with smaller PDMS content, the restructuring process should involve mainly the inorganic component. To investigate the origin of the endothermic peak, samples obtained from the same metal alkoxides, but without any polymer, have been studied. Inorganic samples, one of composition 90% SiO_2+10% ZrO_2 and the other of SiO_2, prepared by sol–gel following the procedure described elsewhere [14, 15] were also investigated by DSC for comparison. The results for these inorganic samples are shown in Fig. 6.

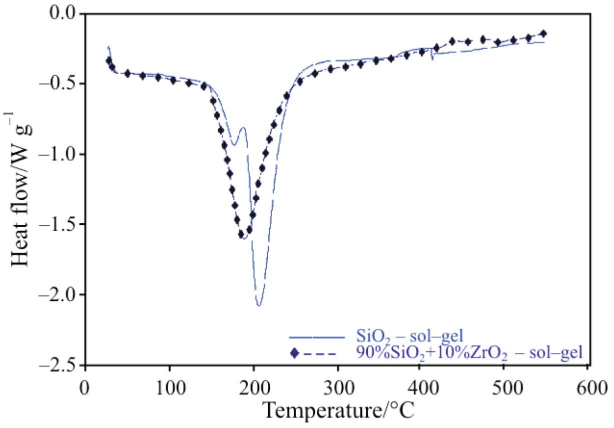

Fig. 6 DSC plot from TEOS and 90% TEOS+10% PrZr materials prepared by sol–gel

The inorganic xerogels present only an endothermic peak whose peak position is at approximately 200°C. This is a broad peak, extending from ca. 150 to 250°C that has been associated to the release of OH groups from the amorphous inorganic oxide network [14].

Hybrid materials prepared with smaller PDMS mass than that of ALK show a similar endothermic peak, at roughly the same temperature, in their respective DSC plots which confirms the presence of inorganic oxide regions made of mixed SiO_2 and ZrO_2 as previously assumed [6]. Those hybrids thus seem to be materials of the nanocomposite type. As referred before, TG plots for these samples show a slight mass loss to begin at ca. 150°C. This should therefore be related to the same processes that originate the endothermic peak, that is, the release of OH groups occurring in the inorganic component of the material. Other authors have interpreted the mass loss around this same temperature as due to dehydroxylation [16] or sample dehydration [17, 18]. Above 300°C these materials present a broad and intense exothermic peak, associated with a significant mass loss in the corresponding TG plots. This peak can be explained by the restructuring of the inorganic oxide domains that are distributed in close vicinity of the cross-linked polymer. The significant mass loss might reveal the progress of condensation reactions between the alkoxides themselves and/or with the polymer. This is in agreement with the results from elemental analysis [8]. Such restructuring does not occur in the case of pure PDMS for which the relatively narrow exothermic peak is due to pure physical ordering of the polymer chains. However a similar restructuring might occur in the hybrids prepared with larger PDMS mass than that of ALK although the amount of inorganic component present in these samples is relatively small, leading to a faint exothermic peak and no significant endothermic one.

The variation of the position of the exothermic peak temperature, T_{exo}, has been studied and is shown in Fig. 7 as a function of the molar ratio TEOS/PrZr for all prepared samples.

It is found that the temperature of the exothermic peak remains almost constant, at a value T_{exo}~325°C, for compositions with molar ratio TEOS/PrZr<8. For

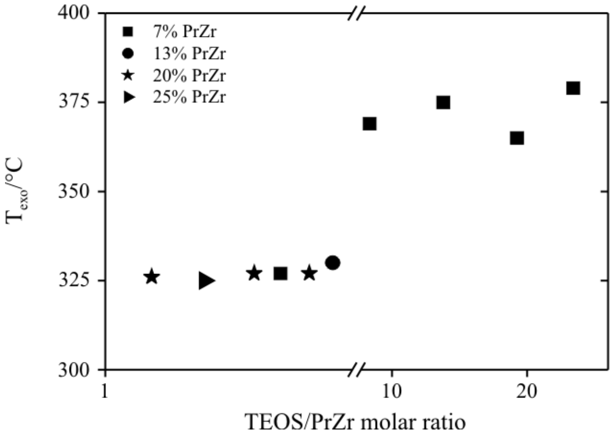

Fig. 7 Variation of the exothermic peak position with the molar ratio TEOS/PrZr

higher values of the molar ratio, the exothermic peak occurs at higher temperatures, T_{exo} in the range 365–380°C. These results suggest the development of two different structures, one of them requiring a larger thermal energy to settle. According to XRD, both are amorphous structures. These results show that Zr, not only acts as a catalyst for the development of the inorganic oxide domains, but it also determines the spatial arrangement in which the inorganic oxide network develops through its relative content in the alkoxide mixture.

Further work is planned to investigate the microstructure of these hybrid materials at the nanometer scale with small angle scattering measurements.

Conclusions

The thermal analysis of materials of the system PDMS/TEOS/PrZr prepared with different relative compositions using γ-irradiation has been performed. The picture emerging from the results of this work is that such hybrids are amorphous nanocomposite materials, made of cross-linked polymer surrounded by inorganic oxide network regions. The material rupture temperature, that is associated to the polymer degradation, occurs in 450–525°C range, depending mainly on the TEOS content used in the precursors mixture. The Zr alkoxide, besides acting as a catalyst for the development of the inorganic component, determines its structural stability, depending on the PrZr relative content in the alkoxides mixture. A more thermally stable structure develops for molar ratios TEOS/PrZr>8. The materials were found to remain amorphous in the whole temperature range 25–650°C.

Acknowledgements

The authors wish to acknowledge support from the Portuguese Foundation for Science and Technology, FCT, in the framework of project POCTI/CTM/44150/2002.

References

1 C. Sanchez, B. Julien, P. Belleville and M. Popall, J. Mater. Chem., 15 (2005) 3559.
2 S. Yano, K. Iwata and K. Kurita, Mater. Sci. Eng. C, 6 (1998) 75.
3 C. Sanchez, Book of Abstracts, SOLGEL 2005 – 13th Int. Workshop on Sol–Gel Science and Technology, UCLA, Los Angeles, USA, August 21-26, 2005
4 C. Sanchez, B. Lebeau, F. Ribot and M. In, J. Sol-Gel Sci. Technol., 19 (2000) 31.
5 F.W. Billmeyer, Textbook of Polymer Science, John Wiley & Sons, Inc., New York 1984.
6 S. R. Gomes, F. M. A. Margaça, I. M. Miranda Salvado, L. M. Ferreira and A. N. Falcão, Nucl. Instrum. Methods Phys. Res., B, 248/2 (2006) 291.
7 S. R. Gomes, F. M. A. Margaça, D. Faria Silva, L. M. Ferreira, I. M. Miranda Salvado and A. N. Falco, Nucl. Instrum. Methods Phys. Res., B, 266 (2008) 1105.
8 S. R. Gomes, F. M. A. Margaça, I. M. Miranda Salvado, J. P. Leal, C. Marques, E. Alves, L. M. Ferreira and A. N. Falco, Nucl. Instrum. Methods Phys. Res., B, 266 (2008) 288.
9 C. M. Mendes, J. C. Almeida, M. L. Botelho, M. C. Cavaco, E. Almeida-Vara and M. E. Andrade, Radiat. Phys. Chem., 35 (1990) 576.
10 K. Dusek and V. Vojta, J. Brit. Polym., 9 (1977) 164.
11 H. Jacobsen and W. H. Stockmayer, J. Chem. Phys., 18 (1950) 1600.
12 S. Candau, J. Bastide and M. Delsanti, Adv. Polym. Sci., 44 (1982) 27.
13 L. M. Ferreira, A. N. Falco and M. H. Gil, Nucl. Instrum. Methods Phys. Res., B, 236 (2005) 513.
14 I. M. Miranda Salvado and J. M. Fernandez Navarro, Bol. Soc. Esp. Ceram. E Vid. 31 C, 7 (1992) 251.
15 F. M. A. Margaça, I. M. Miranda Salvado and J. Teixeira, J. Non-Cryst. Solids, 209 (1997) 143.
16 R. L. Frost and J. M. Bouzaid, J. Therm. Anal. Cal., 89 (2007) 133.
17 A. Migdał-Mikuli and J. Hetmańczyk, J. Therm. Anal. Cal., 91 (2008) 529.
18 E. Franceschi, I. Cascone and D. Nole, J. Therm. Anal. Cal., 91(2008) 119.

Received: May 14, 2008
Accepted: July 8, 2008
OnlineFirst: October 18, 2008

DOI: 10.1007/s10973-008-9223-8