Influence of the Polymer Molecular Weight on the Microstructure of Hybrid Materials prepared by γ-irradiation

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Abstract

Hybrid materials have been the object of intense research due to their potential for biomedical applications as well as in other fields. They are usually prepared by sol-gel but the method of gamma irradiation of the precursors is an alternative avoiding the addition of any other chemicals. The study of the hybrids prepared by this method has been progressing to understand the impact of different variables on the microstructure. In this work, the influence of the polymer's molecular weight on the microstructure of the materials is investigated. Hybrids were obtained from a mixture of polydimethylsiloxane (PDMS) silanol terminated, tetraethylorthosilicate (TEOS) and zirconium propoxide (PrZr) in the wt% composition 20PDMS-73TEOS-7PrZr varying only the PDMS molecular weight. The obtained materials are homogeneous, transparent and flexible and their microstructure was analysed by Scanning Electron Microscopy (SEM) and Small Angle Neutron Scattering (SANS). It was found that different microstructures were obtained, depending on the polymer molecular weight.

1. Introduction

Hybrid materials are excellent candidates to use as bioactive materials (Chen et al., 2000; Tsuru et al., 1997; Yabuta et al., 2003). They are usually processed by the sol-gel method where chemical bonds are established between the organic and the inorganic constituents promoted by the use of solvents and catalysts (Brinker and Scherer, 1990). Alternatively, the authors use gamma-irradiation to process these materials from a mixture of precursors and without the addition of any other chemical (Gomes et al., 2006). The gamma radiation produce reactive sites in the PDMS chains and in the alkoxide molecules and chemical reactions proceed from these active sites (Gomes et al., 2007; Gomes et al., 2008). The irradiation method is particularly suitable for biomedical applications as it provides sterilized materials and free of chemical products other than those derived from the precursors.

The samples have been prepared in the system PDMS-TEOS-PrZr (polydimethylsiloxane, tetraethylorthosilicate and zirconium propoxide, respectively). The study of the hybrids so prepared has been progressing to understand the impact of variables such as the dose rate, total dose or the influence of TEOS or PrZr content on the microstructure (Gomes et al., 2007; Lancastre et al., 2012). It was found that the microstructure of the hybrids consists of inorganic clusters interconnected by polymer structures (Falcão et al., 2003). The inorganic clusters develop predominately by monomer-cluster growth from the inorganic precursors (TEOS and PrZr) as they condense on the reactive sites (Gomes et al., 2008). The irradiation of PDMS promotes crosslinking of its chains with the evolution of gases such as methane, ethane and hydrogen (Miller, 1960). As PDMS is silanol terminated (Si-OH) highly reactive OH radicals are formed (Billmeyer Jr, 1984; Allen et al., 1974).

The present work aims to study the influence of the PDMS weight average molecular weight (Mw) on the microstructure of the hybrids with the composition (in wt%) 20PDMS-73TEOS-7PrZr prepared by gamma irradiation. The PDMS Mw varied from 4200 to 43500 g.mol^{-1}.This system has been thoroughly studied by the authors to fully characterize the hybrid materials prepared by γ–irradiation. The choice of a larger content in the inorganic component follows the trend known in the composition of the natural bone. As for the PrZr content, it was found that its presence guarantees a good thermal stability to the hybrid sample (Gomes et al., 2009).

Small Angle Neutron Scattering (SANS) technique was used to characterise the obtained samples at the nm scale, as in the present case X-rays are not suitable

(Hammouda, 2010; Grillo, 2008). This is due to contrast reasons or to high absorption of the sample when it contains high contents of heavy elements (Zr) in the composition. Scanning Electron Microscopy (SEM) was also used for complementary characterization of the samples at the µm scale.

2. Experimental section

2.1. Materials

Commercially available polydimethylsiloxane (PDMS), silanol terminated, p.a. reagent, from ABCR, tetraethylorthosilicate (TEOS), purity 99%, from Riedel-de Haën and zirconium propoxide (PrZr), 70 wt.% solution in 1-propanol, p.a. reagent, from Aldrich were used as received to prepare the hybrid materials.

2.2. Hybrid materials preparation

The precursors PDMS, TEOS and PrZr were used to prepare the hybrid materials in the wt% composition 20PDMS-73TEOS-7PrZr without addition of any solvent or other product, only varying their PDMS weight average molecular weight (Mw). The precursors were thoroughly mixed and sealed in a N_2 atmosphere. All samples were irradiated at the ^{60}Co irradiation facility, UTR (Andrade et al., 1995), located at the Nuclear Technological Campus of IST, to a total dose that was enough for its gellification using the same dose rates (15 and 30 kGyh^{-1}) and irradiation conditions as described previously (Gomes et al., 2006). The samples are referred as Mx, where x represents the Mw value of the polymer in units of hundred g.mol^{-1}. The PDMS Mw used in the preparation of the samples was 4200 g.mol^{-1} (sample M42), 18000 g.mol^{-1} (sample M180), 26000 g.mol^{-1} (sample M260), 36000 g.mol^{-1} (sample M360) and 43500 g.mol^{-1} (sample M435).

The gellification of these samples under gamma irradiation involves the formation of a 3D network via crosslinking of the PDMS chains: the longer the PDMS chain the easier is the crosslink between chains. Finally the hybrid gels were left to dry in air. The obtained samples are monolithic, flexible and transparent.

2.3. Hybrid materials characterization

The microstructure of the samples was characterised by Small-Angle Neutron Scattering (SANS) and Scanning Electron Microscopy (SEM). The SANS measurements were carried out at the *Yellow Submarine* instrument of the Budapest Neutron Centre, Hungary. The experiments were performed using two wavelengths

and two sample-detector distances to cover a Q range $(Q = (4\pi/\lambda)\sin(\theta)/2)$ from 0.005 to 0.4 Å^{-1}. All measurements were carried out at room temperature and atmospheric pressure. Scattering intensities were normalised for sample thickness and transmission, and corrected for detector efficiency by the use of an incoherent scatterer. The BerSANS data reduction software has been used (Keiderling, 2002). The resulting SANS scattering curves were then analysed and fitted by least squares refinement using Origin7.5 program.

The micrographs of the samples, at μm scale, were obtained using the *SEM-Hitachi SU-70* instrument at Aveiro University, Portugal.

3. Results and Discussion

For the specific system 20PDMS-73TEOS-7PrZr under study, where the PDMS content (in wt%) is fixed and only its Mw is changed, the parameters that vary are the polymer chain length (its end-to-end distance) and the number of OH groups (PDMS is silanol (Si-OH) terminated, i.e., there is one OH group for each extremity of the polymer chain). As the PDMS Mw increases the chain length increases, there are a smaller number of chains in the sample, but with longer chain length. Thus, there are fewer OH groups in samples prepared with high Mw PDMS than in samples having PDMS with low Mw.

The microstructural studies in the hybrid samples involved the collection of the SANS intensities where the scattering of neutrons is due to the contrast between the inorganic oxide and PDMS chains or empty pores. Since polymer chains and pores are indistinguishable for the SANS technique, the contrast will be reported as to be between the oxide regions and heterogeneities (Gomes et al., 2008).

Fig. 1 shows the SANS spectra obtained for the prepared samples in a I (Q) plot to show the presence or absence of a broad peak in the scattering curves.
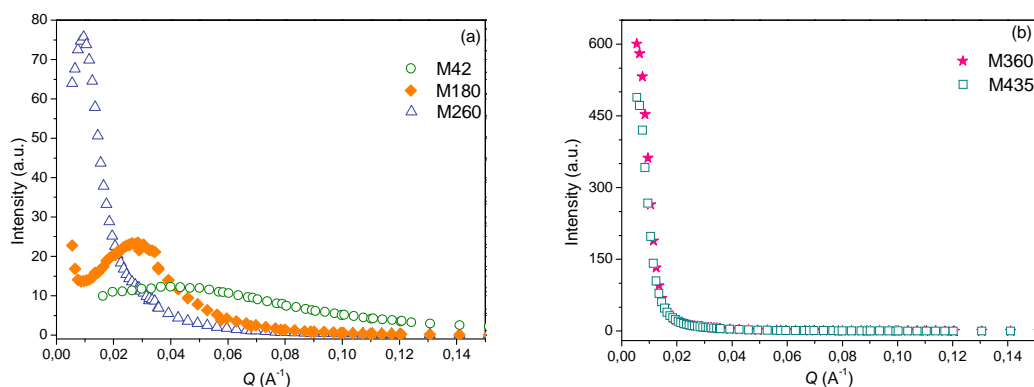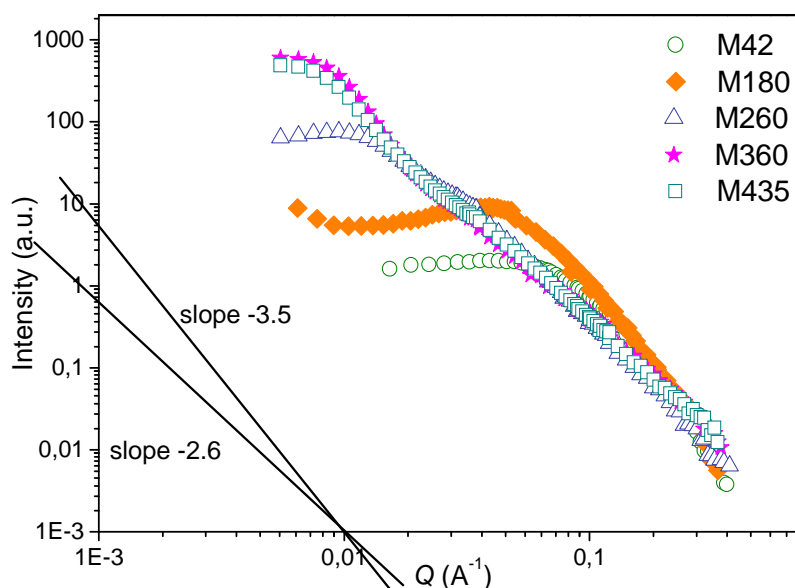
Fig. 1. SANS spectra of 20PDMS-73TEOS-7PrZr hybrids prepared with Mw ≤ 26000 g.mol^{-1} (a) and Mw > 26000 g.mol^{-1} (b).

The larger intensity is observed in the low Q region for all samples, and it increases with the Mw value. However, the curves differ in the presence or absence of a peak: in the hybrids with Mw ≤ 26000 g.mol^{-1} there is a broad peak whose position (Q_0) shifts to lower Q as the PDMS Mw increases (Fig. 1a); in hybrids with larger Mw the peak is absent within the covered Q region (Fig. 1b).

A broad peak in the SANS scattering is usually associated to short range order in the spatial arrangement of the particles/heterogeneities in the sampled volume. Its shift to lower Q values is easily understood if the distance between the ends of a polymer chain increases. As mentioned above, the increase in the PDMS Mw translates in fewer numbers of polymer chains with longer lengths. Since each chain is silanol terminated (one OH group for each extremity), the distance between these two hydroxyl groups increases.

The characteristic distance, given by $d = 2\pi/Q_0$, coincides with the average particle diameter for a packed particle system. In the present materials this could be attributed to the spatial arrangement of the inorganic oxide regions or grains (Gomes et al., 2008).

Fig. 2 shows the spectra obtained in a log-log plot for all samples to show the different slope values.

Fig. 2. SANS spectra in a log-log plot of 20PDMS-73TEOS-7PrZr hybrids prepared with different PDMS Mw.

The curves in Fig. 2 show a plateau in the low Q region followed by an asymptotic descendent with a given slope value. The slope informs on the interface type (smooth or fractal) between the matrix of inorganic oxide regions and the heterogeneity. The apparent slope values were found to be – 2.6 (samples M260 and above) and – 3.5 (samples M42 and M180). The values show that the inorganic oxide regions that develop in samples M260 and above are mass fractal type objects ($2 < n < 3$), consisting of an open oxide network. On the other hand, the inorganic oxide regions in samples M180 and M42 are surface fractal type ($3 > n > 4$), i.e, the oxide network is dense but with rough surface (Brinker and Scherer, 1990). In both cases, the inorganic regions, which develop from the active sites at the polymer chain end (Falcão et al., 2003), grow predominately by monomer-cluster growth under reaction limited conditions (Brinker and Scherer, 1990).

The broad peak fitting model was applied to the SANS data. This model provides the peak position (Q_0) and ultimately the average diameter size of the oxide regions ($d = 2\pi/Q_0$) can be calculated through (Hammouda, 2009)

$$I(Q) = A/(Q^n) + C/(1+(|Q-Q_0|.L)^m) + B \quad (1)$$

In this way, the first term is related to the asymptotic region where the parameter n is the slope value. The parameter n was fixed to the apparent slope value found in the SANS log-log curves (-2.5 and -3.6). The second term is associated to a Lorentzian type curve with a peak centred at Q_0. Note that when $m = 2$ this term is a proper Lorentzian function where L is its FWHM. The parameters A and C are scaling factors and B the background.

Table 1 shows the function parameters obtained for the best fit for each sample.

Table 1 Function parameters values obtained during fitting to Eq. (1) where d is calculated from the peak position: $d = 2\pi/Q_0$.

|	M42	M180	M260	M360	M435
n	3.5	3.5	2.6	2.6	2.6
$Q_0 \times 10^{-3}$ (Å^{-1})	39	26	9.6	7.5	6.8
d (Å)	161	242	654	838	920

The fitting of samples M360 and M435 provides the peak position (Q_0) which could not be identified within the covered Q region. Care must be taken with the interpretation of the n values for actual materials due to eventual polydispersity. In fact, if the size distribution is narrow it will not change the asymptotic behaviour but in many fractal systems this is not the case (Martin et al., 1987). In the following it is assumed a narrow size distribution for the present samples.

A similar effect to the "poisoned" Eden Model (Keefer, 1986) might occur in the present system. This model explains the change of the slope value from mass fractal to surface fractal in base-catalysed sol-gel systems of TEOS with different molar ratios of water/TEOS. The gels prepared with higher water ratios showed higher slope values. Alkoxide sites act as poisoned sites when they are unhydrolyzed, so their number and distribution dictates the type of fractal structure that develops.

Although no water is added in the preparation of the present samples, there are silanol groups (Si-OH) whose number decreases with increasing PDMS Mw. These groups could originate water molecules in the reaction medium since ionizing radiation breaks the silanol bonds, producing highly reactive OH radicals and Si active sites (Billmeyer Jr, 1984; Allen et al., 1974). Samples M42 and M180 show the highest slope value (-3.5) and contain a larger number of silanols, that can lead to a higher number of water molecules present in the reaction medium. Therefore, the nature of the oxide network in the hybrids prepared by gamma irradiation depends on the number of silanols present: the condensation reaction becomes more and more incomplete as the number of silanols decreases (high PDMS Mw). This is similar to the lower water/TEOS molar ratio in the sol-gel system mentioned above.

As for the oxide region average diameter size (d) shown in Table 1, its value is found to increase with PDMS Mw. This is expected as the inorganic oxide network develops from the Si active site at the polymer chain end (Falcão et al., 2003). When there are a large number of Si-OH groups, as in sample M42 and M180, there a great number of reactive sites where the inorganic regions can develop from. The microstructure of these samples consists of a large number of relatively small inorganic oxide dense regions with rough surface. As the PDMS Mw increases, the number of chain end active sites decreases, so the microstructure of these materials present a small number of larger oxide regions with an open structure. In both cases, the oxide regions are interconnected by crosslinked polymer chains as these materials swell in a good solvent of the polymer (Falcão et al., 2003).

To confirm whether the grain size increases with the PDMS molecular weight, SEM observation was performed. The micrographs are shown in Fig. 3.
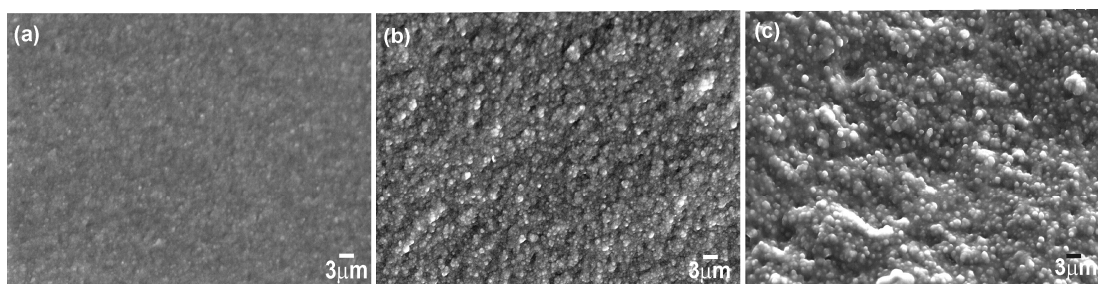
Fig. 3. SEM micrographs of some of the 20PDMS-73TEOS-7PrZr hybrids: (a) M42; (b) M260 and; (c) M435. The scale bar is 3.0 µm.

The SEM micrographs show that the grain size increases with the polymer Mw for the prepared hybrid materials.

This study showed that by varying the molecular weight of the polymer the grain size of the material can be significantly changed. This might have important implications in the design of materials for biomedical purposes, especially when cellular anchoring processes are demanding. Further work is envisaged to proceed with mechanical assays.

4. Conclusions

Hybrid materials with fixed composition 20PDMS-73TEOS-7PrZr but with different PDMS molecular weight were prepared by gamma irradiation of the precursor's mixture. The obtained materials were analysed by SANS and SEM. It was found that the Mw has a major influence on the microstructure at two levels: the average size of the inorganic oxide regions and the fractal dimension of the oxide network. In the materials prepared with low PDMS Mw, a large number of relatively small inorganic oxide dense regions with rough surface (surface fractal type) is obtained, whereas in materials prepared with high Mw, a small number of larger oxide regions with an open structure (mass fractal type) are present. In both cases the oxide regions are interconnected by crosslinked polymer chains. The increasing size of grains in materials prepared with increasing PDMS Mw was confirmed by SEM observation.

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