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ORIGINAL CONTRIBUTION

Macroporous poly(methyl methacrylate) produced by phase separation during polymerisation in solution

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Abstract Polymethyl methacrylate (PMMA) sponges were obtained by polymerization in a solution with monomer/ethanol ratios up to 20:80. The material obtained after the elimination of the solvent present a homogeneous distribution of dispersed pores up to a monomer/ethanol ratio lower than 40:60. For higher ethanol contents in the reacting mixture, the morphology of the sponge corresponds to a network of PMMA microparticles, leaving large empty spaces leading to highly porous structure. The monomer/ethanol ratio during polymerization has a large influence on the porosity, thermal, and mechanical properties of the material and, for large solvent contents, on the size of the polymer microparticles.

Keywords Macroporous polymers · Poly(methyl methacrylate) · Scanning electron microscopy · Dynamic mechanical spectroscopy · Differential scanning calorimetry

Introduction

When a polymer network is synthesised in the presence of a diluent starting from a monomer/solvent mixture in a ratio that exceeds the solvent absorption capacity of the polymer network, phase separation takes place in some intermediate state of the polymerization process, between a swollen polymer network and a liquid mixture of the solvent and the remaining monomer. As a result, the elimination of the solvent after full monomer conversion produces a porous polymer network. The formation mechanisms of these porous polymers are not completely understood, and their explanations are qualitative. According to Dušek [1, 2], phase separation occurring during the polymerization process is called *syneresis*. The cross-linking density of the growing network and the solubility parameters of the polymer, and the solvent, monomer, and solvent/monomer mixtures determine the conversion at which phase separation takes place, and in turn, the pore morphology is finally obtained [3]. In the presence of a good solvent for both the monomer and the polymer network, phase separation may take place for high conversions, and the polymer phase consists of the swollen polymer network with the equilibrium solvent content that depends on its cross-linking density. In the presence of a bad solvent of the polymer, phase separation happens at very low conversions due to a change in the nature of the interaction among the system species (from monomer-solvent to polymer-solvent). Whatever the mechanism is, phase separation can happen as *macrosyneresis* or as *microsyneresis*. *Macrosyneresis* is related to the unswelling of the growing polymer network when phase separation occurs. The system is transformed into a suspension of polymer spherical particles diffused in a liquid phase formed by unreacted monomer and solvent. At the final conversion, two continuous phases exist, one of them formed by connected polymer spherical particles and the other by solvent.

On the other hand, *microsyneresis* consists of a separation of solvent forming disperse domains inside the

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growing network. Pores are not interconnected for low solvent contents used in the polymerization process. However, for high solvent contents, the pore size increases so much that they connect with the others obtaining the typical structure known in the porous material literature as *honeycomb* structure.

Thus, the polymerization of a polymer network in a given solvent yields a pore architecture corresponding to *macrosyneresis* (spherical interconnected or adhered polymer particles) or *microsyneresis* (dispersed or interconnected pores in a continuous polymer matrix), depending on the solvent content added in the reactive mixture, and beyond a certain amount of solvent, it is possible to pass from *microsyneresis* to *macrosyneresis*.

Poly(hydroxyethyl methacrylate) (PHEMA) white sponges produced by *macrosyneresis* during the polymerization of hydroxyethyl methacrylate copolymerized with different multifunctional monomers in water at monomer/water ratios around 20:80 have been proposed as biointegrable materials for the anchoring ring or a cornea prosthesis [4, 5]. The mechanical properties of these materials are poor mainly when swollen in water due to the loose adhesion between the polymer particles. In previous studies of our group, porous poly(2-hydroxyethyl acrylate) (PHEA) networks were synthesised by polymerization in the presence of ethanol and methanol [6, 7] using ethylene glycol dimethacrylate (EGDMA) as cross-linker. Because these alcohols are good solvents of PHEA, the phase separation occurs as *microsyneresis* up to high monomer/solvent ratios as in the 2-hydroxyethyl methacrylate/water polymerization.

In this work, macroporous polymer networks of poly(methyl methacrylate) (PMMA) cross-linked with EGDMA were polymerized in the presence of a bad solvent for the polymer network (ethanol) to study the influence of the amount of solvent on the PMMA particle size and the mechanical properties of the resulting macroporous sponge. These macroporous materials could be used in biomedical applications where a very porous interconnected structure is required to produce biointegrable materials. The difference with respect to the PHEMA sponges proposed in references [4, 5] is the hydrophobic character of PMMA that improves cell adhesion.

Materials and methods

Materials

Polymer networks of PMMA with varying porosity were synthesised by bulk polymerization and polymerization in the presence of ethanol. Polymerization took place at room temperature under UV light using 0.2 wt.% of benzoin (from Scharlau 98% pure) as photoinitiator and EGDMA (from Aldrich 98% pure) as cross-linker. The monomer (methyl methacrylate, MMA, from Aldrich 99% pure) and the cross-linking agent were purified by vacuum distillation. Macroporous PMMA networks with different degrees of porosity were obtained by varying the solvent content in the initial reactive mixture. Thus, the solvent weight ratios chosen in the monomers/solvent initial blends were 80:20, 50:50, 40:60, 30:70, and 20:80, in which the monomers' (MMA/EGDMA) weight ratios were 99:1. Hereafter, in order to be coherent with former publications [8, 9], these porous samples will be designated by PMMA followed by the cross-linker content, the bar (/), the solvent content, and the first letter of the solvent name (ethanol). For example, PMMA1/60E designates the PMMA sample synthesised with MMA/EGDMA weight ratio 99:1 and monomer/ethanol weight ratio 40:60. A bulk PMMA sample (nonporous) was synthesised starting from a mixture of MMA and EGDMA monomers in 99:1 weight ratio, which will be called hereafter as PMMAB1. The polymerization took place in a mould that consisted of two glass plates with a rubber spacer that allowed the preparation of polymer sheets between 1 to 3 mm thick. The low molecular weight substances remaining in the samples after polymerization were extracted in boiling ethanol for 24 hours. Afterwards, the solvent was allowed to evaporate partially from the samples at room temperature and atmospheric pressure. This step is necessary to avoid sample cracking during the drying process. Finally, the samples were dried at 160 °C in vacuo to constant weight.

Specific volume and porosity

A Mettler Toledo AX205 balance with a sensitivity of 0.01 mg and a density accessory kit was used to measure the specific volume of the dry bulk polymer networks by weighing a sample in the air and immersing in *n*-octane at 25±0.5 °C. The specific volume of the sample PMMA1/20E was also determined with this method, as it is nonporous. The result obtained for a series of pieces of the same sample was reproducible within $\pm 0.002\ \mathrm{cm}^3\ \mathrm{g}^{-1}$.

The specific volumes of the porous polymers cannot be determined with the same method as in bulk polymers due to their porosity. Nevertheless, their apparent specific volumes (v_{app}) can be calculated after measuring their three linear dimensions with a micrometer, and then weighing the sample. The porous samples were cut with a metal cutter with approximate dimensions of 1×0.5×0.2 cm. Four pieces of each porous polymer were measured, and the mean and the standard deviation of v_{app} were calculated for each sample.

The porosity of the dry porous polymers (P_{d1}) can be determined from their apparent specific volumes

$\left(v_{\mathrm{app}}=\left(V_{\mathrm{pores}}+V_{\mathrm{b}}\right)/m_{\mathrm{b}}\right)$ and the specific volumes of the same bulk polymers (v_{b}) as:

$$P_{\mathrm{d1}}=\frac{V_{\mathrm{pores}}}{V}=\frac{v_{\mathrm{app}}\cdot m_{\mathrm{b}}-V_{\mathrm{b}}}{v_{\mathrm{app}}\cdot m_{\mathrm{b}}}=\frac{v_{\mathrm{app}}-v_{\mathrm{b}}}{v_{\mathrm{app}}}, \tag{1}$$

where V_{b} and m_{b} are the volume and mass, respectively, of bulk polymers.

The volume fraction of pores was also gravimetrically determined by swelling the porous polymers in liquid ethyl acetate and in water for 48 hours at 25 °C. Ethyl acetate is a good solvent of PMMA and is able to swell this polymer network. Therefore, the fraction of pores determined with this solvent is the porosity of the swollen polymer (P_{s}). Water is a bad solvent of PMMA, and its capacity of swelling this polymer is practically negligible. The porosity determined with this solvent was called P_{d2}.

The volume fraction of pores filled with ethyl acetate in the swollen porous samples was estimated considering that the swollen porous materials consisted of two phases: One phase is formed by the polymer network with absorbed solvent, whose behavior can be assumed equal to the bulk polymer with the same cross-linking density, occupying a volume V_{swollenb}; the other phase is formed by pure liquid ethyl acetate, occupying the volume of pores V_{pores}.

The equilibrium solvent uptake is

$$w=\frac{m_{\mathrm{solvent}}}{m_{\mathrm{drypolymer}}}, \tag{2}$$

and thus, the volume fraction of pores in the swollen porous polymer can be calculated as

$$P_s=\frac{V_{\mathrm{pores}}}{V_{\mathrm{swollenb}}+V_{\mathrm{pores}}}=\frac{v_{\mathrm{eacetate}}\cdot\left(w-w_{\mathrm{b}}\right)}{v_{\mathrm{swollenb}}\cdot\left(1+w_{\mathrm{b}}\right)+v_{\mathrm{eacetate}}\cdot\left(w-w_{\mathrm{b}}\right)}, \tag{3}$$

where w is the equilibrium solvent uptake of the porous sample after immersion for 48 hours; v_{eacetate} is the specific volume of ethyl acetate (1.11 cm^3/g at 25 °C); v_{swollenb} and w_{b} are the specific volume and the equilibrium solvent uptake $\left(w_b=m_{\mathrm{eacetate}}/m_{\mathrm{polymer}}\right)$, respectively, after immersion for 48 hours of the swollen bulk sample with the same cross-linking density. The v_{swollenb} was estimated assuming null excess volume in the polymer/ethyl acetate blend,

$$v_{\mathrm{swollenb}}=v_{\mathrm{eacetate}}\cdot\omega_{\mathrm{b}}+v_{\mathrm{b}}\cdot\left(1-\omega_{\mathrm{b}}\right), \tag{4}$$

where v_{b} is the specific volume of the nonporous sample with the same cross-linking density in the dry state, and ω_{b} is the mass fraction of ethyl acetate in the sample, calculated as $\omega_{\mathrm{b}}=w_{\mathrm{b}}/(1+w_b)$.

The volume fraction of pores filled with water was calculated in the same way. In this case, due to the hydrophobic behavior of the PMMA network, the air located in the pores was extracted at high vacuum before immersion in liquid water. In this way, it is expected that any nonisolated pore will be filled with water.

Microscopy

Scanning electron micrographs (SEM) were taken in an ISIDS-130 microscope at an accelerating voltage ranging from 15 to 20 kV. The cryogenic fracture cross-sections of the samples were sputtered with gold before observation. An estimation of the distribution of particle size was obtained from SEM micrographs. The diameter of around 50 microspheres of each picture was measured. Only the samples with clear spherical particles were analysed.

Dynamic mechanical spectroscopy

Dynamic mechanical spectroscopy (DMS) was performed in a Seiko DMS 210 dynamic mechanical analyzer at a frequency of 1 Hz in the tension mode. The temperature dependence of storage modulus (E') and loss tangent (tan δ) was measured from room temperature up to 230 °C with a heating rate of 1 K/min. DMS experiments were conducted on dry samples of prismatic shape.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed in a Perkin-Elmer Pyris 1 apparatus. The temperature of the calorimeter was calibrated with water, cyclohexane, and *n*-octadecane. The melting heat of indium was used to calibrate the heat flow output. DSC measurements were performed on dry samples. The glass transition temperature was taken from the inflexion point of the heating scan.

Results

The specific volume of PMMAB1 and the apparent specific volume of macroporous PMMA at 25±0.5 °C (v), the porosity in the dry state determined from the apparent specific volume (P_{d1}) and from swelling in water (P_{d2}), and the porosity in the swollen state determined from swelling in ethyl acetate (P_{s}) are shown in Table 1.

The porosities of the samples in the dry state, determined from swelling in water (P_{d2}), are smaller than those determined from the apparent specific volumes (P_{d1}). This means that the sample contains a number of isolated pores, occupying a volume fraction up to 8%, that are not accessible to water. In particular, in the sample polymerized with 50 wt.% ethanol, the apparent specific volume indicates the presence of an 8% volume of pores, but no water penetrates in the sample. For low ethanol contents,

Table 1 Characteristic parameters of bulk PMMA and PMMA polymerized in the presence of different ethanol contents (20, 50, 60, 70, and 80 wt.%): specific volume of bulk PMMA and apparent specific volumes of porous PMMA at 25 °C±0.5 (v), porosity in the swollen state determined from swelling in ethyl acetate (P_s), porosity in the dry state determined from the apparent specific volumes (P_{d1}) and from swelling in water (P_{d2}), DSC glass transition temperatures in the dry state (T_g), and the temperature of the maximum of the loss tangent (T_α)

Sample	v (cm^3/g)	P_s (%)	P_{d1} (%)	P_{d2} (%)	T_g (°C)	T_α (°C)
PMMAB1	0.862±0.002	0	0	0	119.6	140.6
PMMA1/20E	0.860±0.002	14	0	_	124.0	140.8
PMMA1/50E	0.933±0.008	45	8	_	129.9	147.0
PMMA1/60E	2.807±0.011	61	69	63	130.2	147.8
PMMA1/70E	2.880±0.157	61	70	70	130.8	147.5
PMMA1/80E	4.272±0.105	66	80	75	131.1	_

the porosity in the swollen state (P_s) is greater than in the dry state (P_{d1}) because the sample swells in ethyl acetate, opening the collapsed porosity. However, for high ethanol contents, the contrary effect is observed due to the swelling of the polymer microspheres that decreases the volume fraction of pores (Table 1).

Figure 1 shows the SEM micrographs of samples PMMA1/20E, PMMA1/50E, PMMA1/60E, PMMA1/70E, and PMMA1/80E. A seemingly nonporous polymer is obtained in the polymerization with low concentration of ethanol (20 wt.%), whereas a porous polymer is obtained for a 50 wt.% of ethanol. For 60 wt.% of ethanol, the

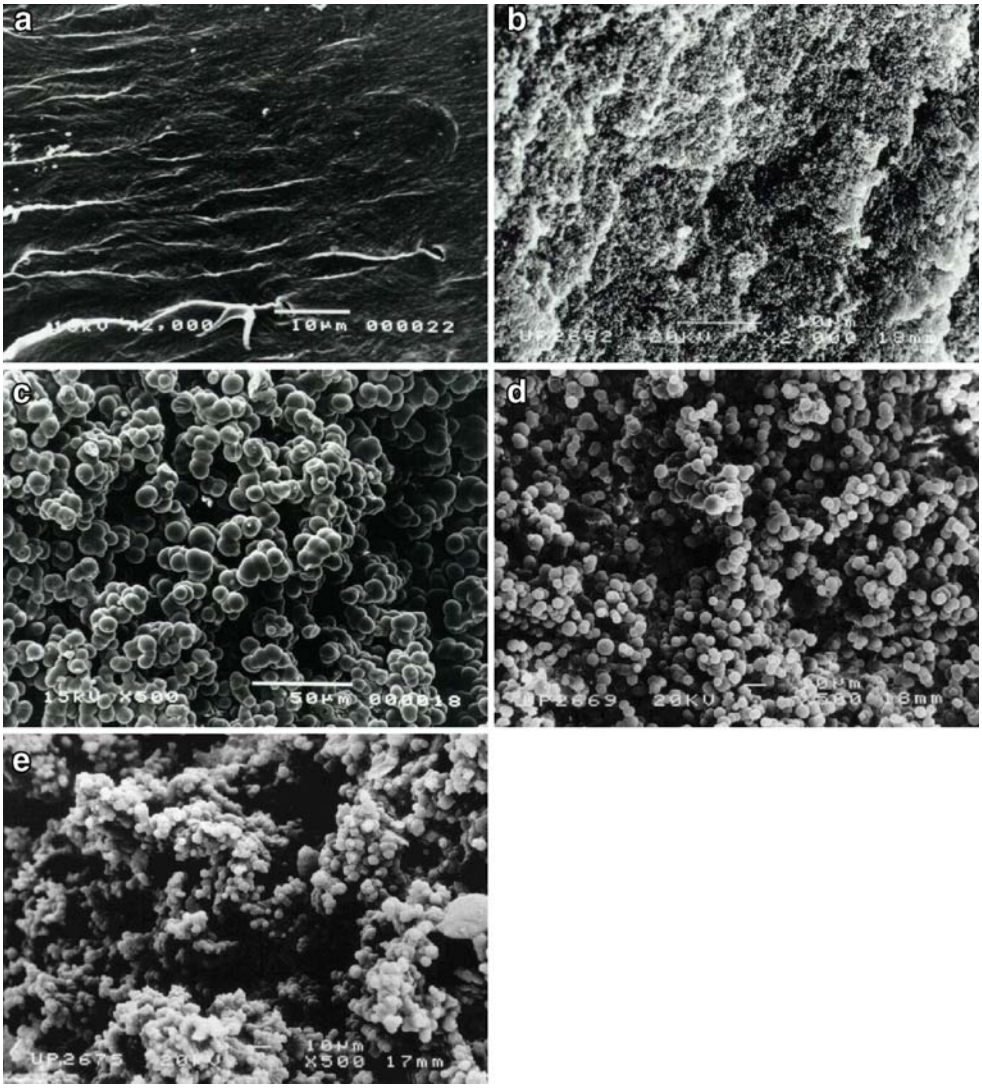

Fig. 1 SEM micrographs of macroporous PMMA polymerized with 1 wt.% of EGDMA and several ethanol contents: 20 (**a**), 50 (**b**), 60 (**c**), 70 (**d**), and 80 (**e**). The dry samples were cryogenically fractured. The samples PMMA1/20E and PMMA1/50E are shown at the same magnification (2,000×). The samples PMMA1/60E, PMMA1/70E, and PMMA1/80E are shown at 500×

transition from microsyneresis to macrosyneresis is produced, and a typical structure with spherical polymer particles joined together is formed. For higher solvent contents, a similar morphology is obtained, but porosity increases and polymer particle diameter decreases with increasing solvent content. The SEM micrograph of sample PMMA1/80E shows the highest porosity and smallest polymer particles (see Fig. 1e).

The increase of the ethanol content in the polymerization process of macroporous PMMA produces smaller microspheres (the average particle size is shown in Table 2) with narrower diameter dispersion (the histogram of particle diameter is shown in Fig. 2 for the three samples in which macrosyneresis take place). The increase in the porosity is also apparent (Table 1). The results presented in Fig. 2 and Table 2 were determined from the analysis of the SEM micrographs of samples PMMA1/60E, PMMA1/70E, and PMMA1/80E (Fig. 1c–e). This analysis consisted of measuring around 50-microsphere diameters of each picture. The size distribution bar graph, the mean, and the standard deviation were determined from these measurements.

The temperature dependence of the real part of the elastic modulus and the loss tangent of bulk PMMA and porous PMMA polymerized with different ethanol contents are shown in Fig. 3. The temperatures of the maxima of the loss tangent curves (T_α) are shown in Table 1. The temperature of the maximum shown by samples PMMA1/20E and PMMA1/50E coincides with that of the bulk PMMA. Nevertheless, the loss tangent peak is shifted towards higher temperatures in the three samples in which macrosyneresis takes place. Different experiments were performed to confirm that this feature is not an artifact produced by the plasticization of the bulk sample due to the remaining solvent because difficulty of the solvent to escape from the bulk sample could be greater than that from the macroporous sponges. The result was confirmed in the bulk samples of different thickness drastically dried at 180 °C in vacuo until constant weight and also in bulk samples that after polymerization were directly dried in vacuo without being washed in ethanol.

From 60 wt.% of ethanol, the storage modulus falls dramatically, showing the transition from microsyneresis to macrosyneresis. From 60 to 70 wt.% ethanol, a significant fall is still observed. The samples polymerized with 80 wt.% of ethanol are too brittle to allow dynamic mechanical experiments.

Table 2 Mean microsphere diameters of PMMA polymerized with 1 wt.% of EGDMA and several ethanol contents [60, 70, and 80 wt.%; mean microsphere diameter±standard deviation (ϕ_m)]

Sample	ϕ_m (μm)
PMMA1/60E	7±2
PMMA1/70E	4±1
PMMA1/80E	3±1

The DSC thermograms show a single glass transition in these materials (Fig. 4). In good agreement with the temperature shifts observed of the DMS main relaxation,

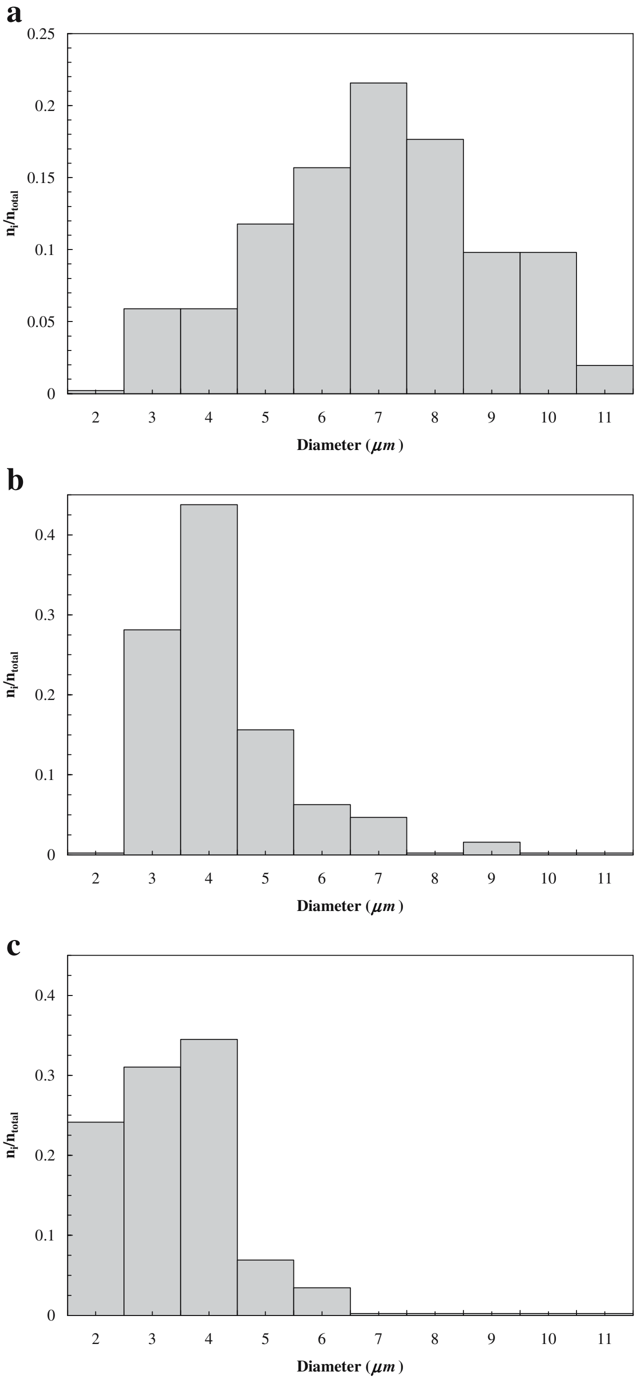

Fig. 2 Microsphere diameter distribution bar graph of porous PMMA polymerized with 1 wt.% of EGDMA and different ethanol contents: 60 (**a**), 70 (**b**), and 80 (**c**) wt.%

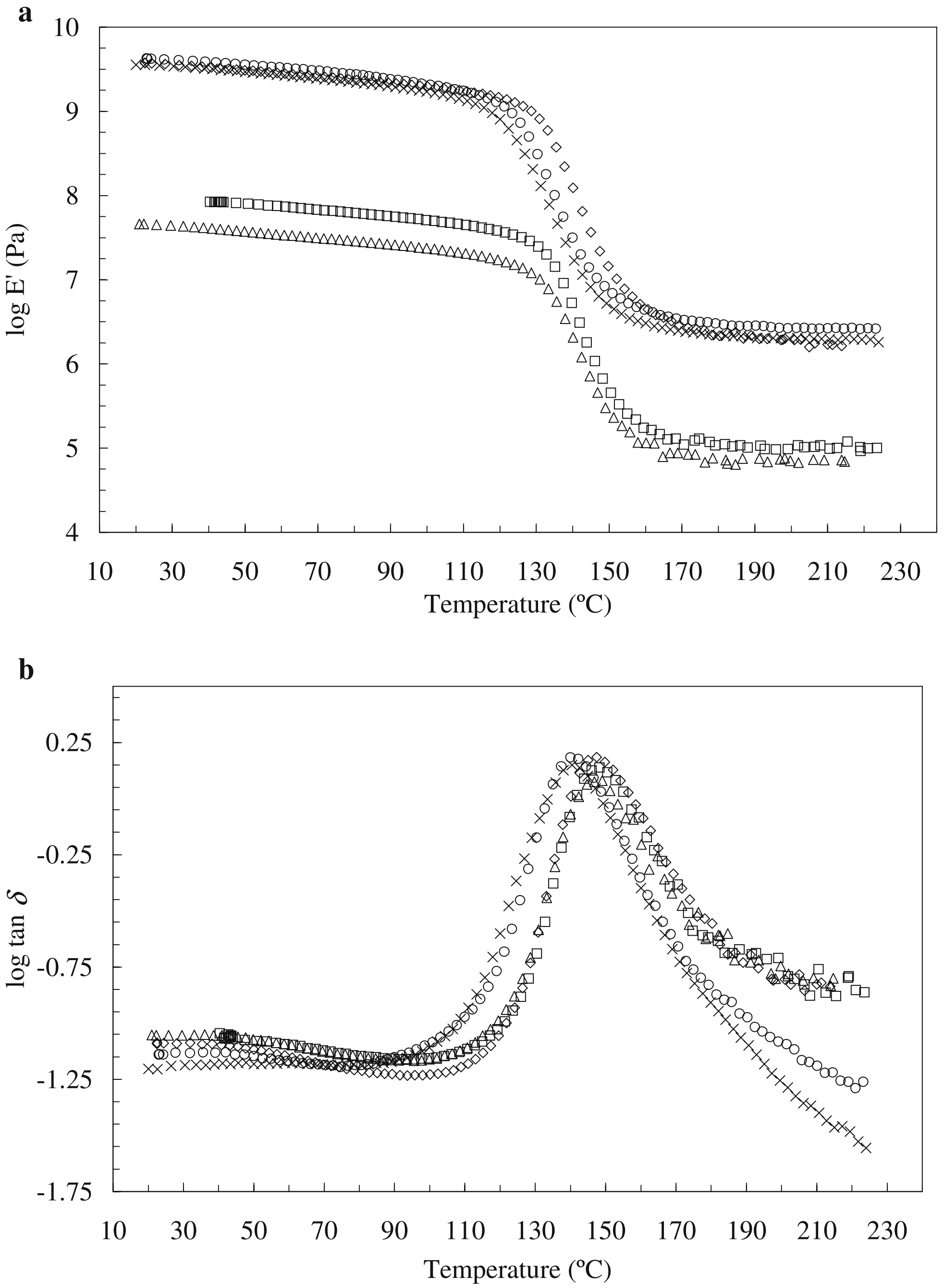

Fig. 3 Temperature dependence of the real part of the storage modulus (**a**) and the loss tangent (**b**) of bulk PMMA (*circle*) and porous PMMA polymerized with 20 (*X*), 50 (*diamond*), 60 (*square*), and 70 (*triangle*) wt.% ethanol. Only one point out of ten is plotted to obtain a clearer representation

PMMA polymerized in the presence of ethanol has a glass transition temperature higher than the bulk PMMA (Table 1).

Discussion

Phase separation takes place during the polymerization of the PMMA network even for high monomers/ethanol concentration. When starting with a mixture containing 20% ethanol, at the end of the reaction, much of the ethanol must be in the form of dispersed droplets. During the evaporation of the solvent, the volume occupied by the ethanol collapses, and the dry network is nonporous as proved by the value of the apparent specific volume P_{d1}. The existence of the collapsed pores is demonstrated when this polymer is swollen in a good solvent (ethyl acetate), the pores reopen and a porosity of 14% is obtained (see Table 1). The same behavior was found in references [6, 7] in the case of PHEA polymerized in the presence of ethanol or methanol. The pores collapse during drying, but when these sponges are swollen in water, the pores open and the porosity of the swollen samples may reach up to 60%. Something similar occurs in the polymerization in the presence of a 50 wt.% ethanol, but in this case, the collapse

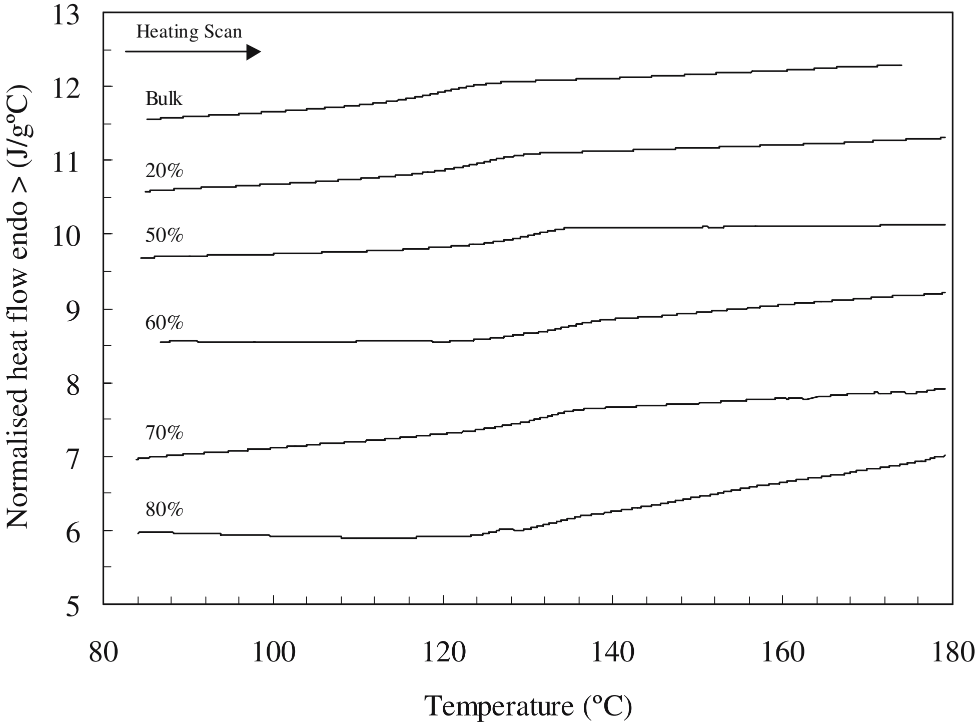

Fig. 4 DSC thermograms for bulk PMMA and PMMA polymerized in the presence of different ethanol contents (20, 50, 60, 70, and 80 wt.%)

of pores is not complete and an 8% porosity was measured in the dry state. Nevertheless, this sample has a porosity of 45% in the swollen state, six times higher than in the dry state.

The transition from microsyneresis to macrosyneresis occurs between 50 and 60% ethanol. A typical structure with spherical polymer particles joined together is formed for ethanol contents greater than 60% (see Fig. 1). The porosity obtained in the dry sponge increases with increasing solvent during polymerization, going from 69 to 80%, a feature that can be related to the decrease of the size of the PMMA microspheres. It is worth nothing that the volume fraction of pores measured by the weight of the water absorbed in the immersion in liquid water is slightly smaller than that deduced from the apparent specific volume. This means that, in spite of the structure of adhered microspheres, a number of pores are isolated and cannot be filled by liquid water. When the sponge is immersed in ethyl acetate, the expansion is not *affine*. The volume ratio of microspheres/volume of pores decreases significantly.

The pore architecture of the samples polymerized with 60, 70, or 80 wt.% ethanol is very irregular. It is difficult to give a figure of the pore size, but it can be said that the open spaces are interconnected ranging from 10 to 100 μm.

The dynamic mechanical properties were measured in the dry samples. Thus, the pores in PMMA1/20E are collapsed, and the porosity in PMMA1/50E is quite small. The elastic modulus in these two samples is nearly the same as in the bulk polymer, both in the glassy and rubbery states (Fig. 3). In the case of the sponges produced by macrosyneresis, the elastic modulus falls around two orders of magnitude with respect to bulk PMMA, but the sample is still able to sustain the force applied. In these samples, the deformation under the applied stress is mainly determined by the adhesion between the PMMA microspheres, as the deformation of each individual microsphere is much smaller than that of the sponge.

The PMMA polymerized in the presence of ethanol has a glass transition temperature higher than the bulk PMMA (see Table 1 and Fig. 4). The main dynamic mechanical relaxation is consequently shifted towards higher temperatures, too, when the monomers/solvent ratio decreases in the reactive mixture. The effect is apparent both in the real component of the elastic modulus and the loss tangent plots of Fig. 3. The effect is not related to the microstructure of the material because the increase in T_g with respect to the bulk polymer starts in the sample PMMA1/20E (around 4.5 °C), and in PMMA1/50E, the glass transition temperature is nearly the same than in the sponges polymerized with higher ethanol concentration (around 10 ° above that of the bulk PMMA). As a consequence, it must be the changes in the topology of the network due to polymerization in solution that alter the kinetics of the propagation and termination reactions during free radical polymerization [10, 11]. Unfortunately, the uncertainty inherent to the measurement of the elastic modulus of highly porous materials impedes a quantitative analysis of the elastic modulus in the rubbery plateau that would give some insight in the influence of the solvent on the network structure of the macroporous material that could explain the changes in the glass transition temperature with respect to the bulk polymerized PMMA.

The PMMA sponges synthesised in this work by polymerization in solution with high ethanol/monomer ratios present a morphology similar to that of poly(2-hydroxyethyl methacrylate) sponges polymerized in the presence of high water contents by Chirila et al. [12, 13] who reported that the mechanical resistance of these samples were extremely poor. In our case, the samples are consistent enough to allow mechanical characterization, and their modulus is quite high, taking into account the high porosity of the sponges (Fig. 3). The difference between PMMA and PHEMA sponges must lie in the different adhesion between microparticles, perhaps, due to the hydrophilic character of PHEMA. Anyway, the improvement of the aggregation of the PMMA microspheres is necessary for any application in which these materials must sustain mechanical forces. Coating by plasma polymerization is a suitable way to increase interparticle adhesion and, besides, can be used to modify the chemical characteristics of the pore surface. The synthesis and characteristics of PMMA macroporous materials coated with plasma polymerized PHEA will be published elsewhere [8, 9].

Conclusions

The polymerization of PMMA under UV light with EGDMA as cross-linker and in the presence of 60 or more wt.% of ethanol gives rise to a structure of spherical polymer particles typical of macrosyneresis. For lower ethanol contents, microsyneresis takes control in the phase separation process and the porous PMMA structures have part of the pores collapsed. This collapsed pores open when the samples are swollen in ethyl acetate, increasing very much the porosity of the sample. For high ethanol contents, however, the porosity of the samples decreases in the swollen state because of the PMMA microspheres swelling. The effect of the solvent content is very strong on the synthesis of macroporous PMMA. The increase of the ethanol content in the polymerization process produces smaller PMMA microspheres with narrower diameter dispersion and more porosity.

The storage modulus decreases very sharply with increasing porosity for ethanol contents greater than the critical one (60 wt.%). The glass transition and the main dynamic mechanical relaxation are shifted towards higher temperatures in the networks polymerized in the presence of ethanol with respect to the bulk PMMA.

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