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ORIGINAL CONTRIBUTION

Effect of crosslinking on porous poly(methyl methacrylate) produced by phase separation

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Abstract Porous polymethyl methacrylate scaffolds were produced by phase separation during polymerisation in solution, using ethanol as solvent, with monomer/ethanol weight ratios from 80/20 up to 20/80 and different ethylenglycol dimethacrylate contents (1, 5 and 10 wt%) as crosslinker agent. For ethanol weight ratios equal to or lower than 50 wt%, the material presents a homogeneous distribution of dispersed pores. For higher ethanol contents, a highly interconnected porous structure is obtained. The transition from one type of morphology to the other can be also controlled with the amount of crosslinker added in the reactive mixture. Bulk polymethyl methacrylate samples (non-porous) with the same crosslinking densities were also synthesised as reference. The effect of crosslinker is studied by porosity measurements, scanning electron microscopy, dynamic-mechanical spectroscopy and differential scanning calorimetry.

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

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Introduction

Porous polymers can be produced by phase separation during polymerisation in solution. Pores are formed due to the segregation of solvent from the polymer network during the polymerisation process. Phase separation occurring during polymerisation is called syneresis according to Dušek [1, 2]. This phase separation can occur as macrosyneresis or as microsyneresis. Macrosyneresis is related to the unswelling of the growing network when phase separation occurs. The system is transformed into a suspension of polymer spherical particles dispersed in a liquid phase formed by unreacted monomer and solvent. Two continuous phases co-exist, one of them formed by loosely connected polymer spherical particles and the other by solvent. On the other hand, microsyneresis takes place when the segregation of solvent forms disperse domains inside the growing network. For the lowest solvent contents, pores are not interconnected. However, microsyneresis can yield an interconnected pore structure for moderate solvent contents and in the monomer/solvent ratio close to the transition to macrosyneresis the typical *honeycomb* structure can be obtained.

The problematics of macro- and microsyneresis has been met already in other acrylate and methacrylate polymers. Porous poly(2-hydroxyethyl acrylate) (PHEA) networks were produced by phase cseparation during polymerisation in ethanol and methanol in our laboratory in previous studies [3, 4]. Phase separation occurred as microsyneresis up to quite high solvent contents because those solvents were good ones for that hydrophilic polymer. Poly (hydroxyethyl methacrylate) (PHEMA) sponges produced by macrosyneresis during the polymerisation of hydroxyethyl methacrylate copolymerised with different multifunctional monomers in water have been proposed as

biocolonizable scaffold material for the anchoring ring or a cornea prosthesis [5, 6]. The adhesion of the polymer particles of these PHEMA scaffolds was very weak, yielding very poor mechanical properties when swollen in water. In a previous work of ours, porous polymethyl methacrylate, PMMA, was obtained by phase separation during polymerisation in ethanol [7]. For high ethanol contents, the PMMA sponges had a high porosity with well-interconnected pores, with the structure characteristic of macrosyneresis. However, phase separation occurs as microsyneresis when low ethanol contents are used in the polymerisation process, giving rise to a structure with disperse pores. The influence of the monomer/ethanol ratio on the morphology, mechanical and thermal properties, and on the size of the polymer microparticles in the case of macrosyneresis was studied. The main difference between PMMA and PHEA or PHEMA sponges is the hydrophobic character of PMMA, which improves cell adhesion and mechanical properties. The hydrophobic character of these scaffolds was modified by hydrophilic plasma grafting [8, 9].

In this present work, the effect of the crosslinking density of the polymer network on the structure of the macroporous PMMA is studied. Chirila et al. found a great dependence of the pore morphology with the amount and chemical structure of the crosslinking agent in the polymerization of PHEMA in solution using water as solvent [10]. Previous studies of PHEA polymerised in solution in methanol also showed this dependence [4].

Materials and methods

Materials

Poly(methyl methacrylate) (PMMA) with varying porosity and crosslinking density was synthesised by radical polymerisation of the monomer in the presence of ethanol. Polymerisation took place at room temperature under UV light using 0.2 wt% of benzoin (from Scharlau 98% pure) as photoinitiator and ethylene glycol dimethacrylate (EGDMA, from Aldrich 98% pure) as crosslinker. The monomer (methyl methacrylate, MMA, from Aldrich 99% pure) and the crosslinker 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 50/50, 40/60, 30/70 and 20/80, in which the monomers (MMA/EGDMA) weight ratios were 99/1, 95/5 and 90/10 for each solvent content. Hereafter, to be coherent with former publications [7–9], these porous samples will be designated by PMMA followed by the crosslinker content, the bar /, solvent content and the first letter of the solvent name (ethanol). For example, PMMA10/70E designates the PMMA sample synthesised with MMA/EGDMA weight ratio 90/10 and monomer/ethanol weight ratio 30/70. A series of bulk PMMA samples (non-porous) with different crosslinking densities was synthesised starting from a mixture of MMA and EGDMA monomers in 99/1, 95/5 and 90/10 weight ratios, which will be called hereafter as PMMAB1, PMMAB5 and PMMAB10. Polymerisation took place in a mould that consisted of two glass plates with a rubber spacer what allowed to prepare polymer sheets between 1 and 3 mm thick. The low molecular weight substances remaining in the samples after polymerisation were extracted in boiling ethanol for 24 h. 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 volumes and porosities

A Mettler Toledo AX205 balance with a sensitivity of 0.01 mg with density accessory kit was used to measure the specific volume of the dry bulk polymer networks by weighing a sample in air and immersed in n-octane at 25± 0.5 °C. The result obtained for a series of pieces of the same sample was reproducible within ±0.002 cm^3g^{-1}.

The specific volumes of the porous polymers cannot be determined with the same method as 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 approximately dimensions: 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 $\left(v_{app} = \left(V_{pores} + V_b\right)/m_b\right)$ and the specific volumes of the same bulk polymers (v_b) as

$$P_{d1} = \frac{V_{pores}}{V} = \frac{v_{app} \cdot m_b - V_b}{v_{app} \cdot m_b} = \frac{v_{app} - v_b}{v_{app}} \quad (1)$$

where V_b and m_b are the volume and the mass of the 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 h 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 capability of

swelling this polymer is practically negligible. The porosity determined with this solvent is 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 behaviour can be assumed equal to the bulk polymer with the same crosslinking 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

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

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

$$P_s = \frac{V_{\text{pores}}}{V_{\text{swollenb}} + V_{\text{pores}}} = \frac{v_{\text{eacetate}} \cdot (w - w_b)}{v_{\text{swollenb}} \cdot (1 + w_b) + v_{\text{eacetate}} \cdot (w - w_b)}, \tag{3}$$

where w is the equilibrium solvent uptake of the porous sample after immersion to constant weight (48 h), 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 ($w_b = m_{\text{eacetate}}/m_{\text{polymer}}$) after immersion to constant weight (48 h) of the swollen bulk sample with the same crosslinking density. The v_{swollenb} was estimated assuming null excess volume in the polymer/ethyl acetate blend,

$$v_{\text{swollenb}} = v_{\text{eacetate}} \cdot \omega_b + v_b \cdot (1 - \omega_b), \tag{4}$$

where v_b is the specific volume of the non-porous sample with the same crosslinking density in the dry state and ω_b is the mass fraction of ethyl acetate in the sample, calculated as $\omega_b = w_b / vlldelimiterspace(1 + w_b)$.

The volume fraction of pores filled with water was calculated in the same way. In this case, due to the hydrophobic behaviour 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 non-isolated pore 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 previous to 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. A size distribution bar graph, the mean, and the standard deviation were determined from these measurements. 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 analyser 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 250 °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 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 volumes of the bulk (non-porous) PMMA samples at 25±0.5 °C and the apparent specific volumes of the macroporous PMMA networks (v), the porosities in the dry state determined from the apparent specific volumes (P_{d1}) and from swelling in water (P_{d2}), and the porosities in the swollen state determined from swelling in ethyl acetate (P_s) are shown in Table 1. These results show that the effect of crosslinking on the specific volume of bulk PMMA is practically negligible within the experimental uncertainty ($v \approx 0.860$ cm^3/g). In most of the samples, the porosity in the dry state determined by swelling in water (P_{d2}) is smaller than that determined from the apparent specific volumes (P_{d1}). This means that there is a number of isolated pores that are not accessible to water. For high monomer/ethanol ratio, 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 during polymerization, the contrary effect is observed due to the swelling of the polymer microspheres, which decrease the volume fraction of pores.

The particle size analysis, DMS, DSC and SEM results of polymethyl methacrylate polymerised with 1 wt% of EGDMA and monomer/ethanol weight ratios from 80/20 up to 20/80 were presented in reference [7]. These results

Table 1 Characteristic parameters of the PMMA networks: specific volumes of bulk PMMA and apparent specific volumes of porous PMMA with different crosslinking densities and porosities at 25 °C±0.5 (v), porosities in the swollen state determined from swelling in ethyl acetate (P_s), porosities 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 temperatures of the maxima of the loss tangent curves (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
PMMA1/50E	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	–
PMMAB5	0.858±0.002	0	0	0	127.5	148.1
PMMA5/50E	1.160±0.029	51	26	–	138.4	159.4
PMMA5/60E	2.418±0.047	62	65	60	138.8	160.0
PMMA5/70E	3.569±0.081	66	76	68	134.8	159.4
PMMA5/80E	4.374±0.121	68	80	81	134.2	–
PMMAB10	0.861±0.002	0	0	0	130.5	157.0
PMMA10/50E	1.802±0.056	55	52	–	152.0	171.0
PMMA10/60E	2.826±0.050	61	70	72	151.0	172.7
PMMA10/70E	3.719±0.095	71	77	72	154.6	173.1
PMMA10/80E	4.567±0.161	75	81	83	145.5	–

will be compared with those obtained in the samples with higher crosslinking density of the present paper.

Figures 1 and 2 show the effect of crosslinking on the morphology when phase separation occurs as microsyneresis (50 wt% of ethanol) or macrosyneresis (70 wt% of ethanol), respectively. For low ethanol contents, the effect of crosslinking on the PMMA microstructure is quite apparent, porosity increases rapidly with increasing cross-

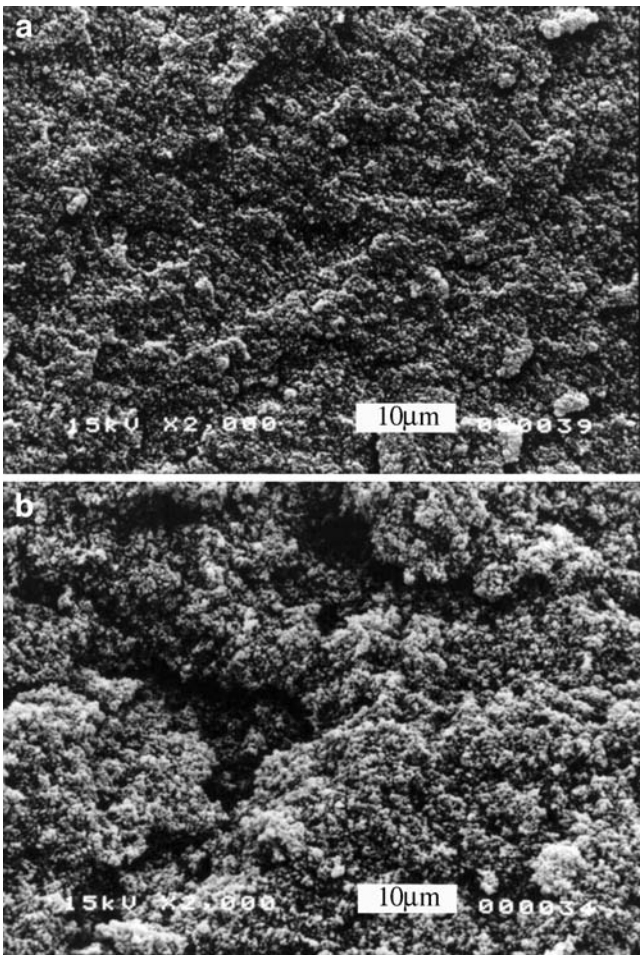

Fig. 1 SEM micrographs of porous PMMA polymerised with 50 wt% of ethanol and two crosslinker contents: 5 (**a**) and 10 (**b**) wt% of EGDMA. Both micrographs have the same magnification

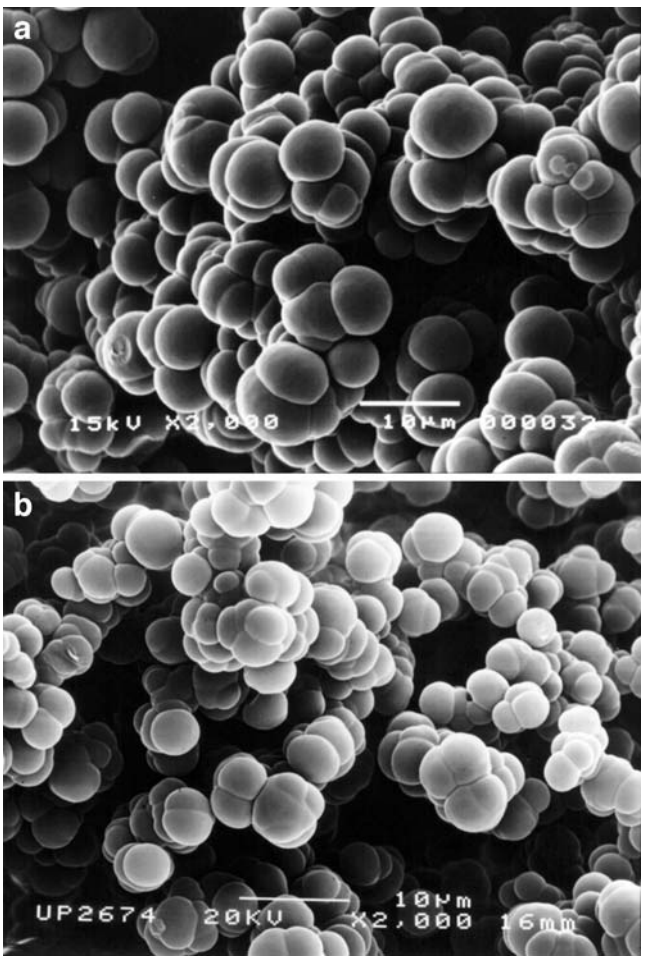

Fig. 2 SEM micrographs of macroporous PMMA polymerised with 70 wt% of ethanol and two crosslinker contents: 5 (**a**) and 10 (**b**) wt% of EGDMA. Both micrographs have the same magnification

linking density. Thus, sample PMMA10/50E has the highest porosity in microsyneresis (see Fig. 1 and Table 1). The size of the particles produced by macrosyneresis was determined from the SEM micrographs (Fig. 2). A value of 4.5±1 microns was found independently of the crosslinking density of the polymer network.

The temperature dependence of the real part of the elastic modulus and the loss tangent of bulk PMMA and porous PMMA polymerised with 5 and 10 wt% of crosslinker are shown in Figs. 3 and 4, respectively. The temperatures of the maxima of the loss tangent curves (T_α) are shown in Table 1. These DMS measurements show that the loss tangent peaks of the porous PMMA samples polymerised in the presence of ethanol are shifted to higher temperatures with respect to bulk PMMA for similar crosslinker contents. Different experiments were performed to ensure that this shift was not due to remaining solvent in the bulk polymer networks. This shift was confirmed in bulk samples drastically dried at 180 °C in vacuo until constant weight, bulk samples with lower thickness and also in bulk samples that after polymerisation were directly dried in vacuo without being washed in ethanol. The samples polymerised with 80 wt% of ethanol were too brittle to allow dynamic-mechanical experiments.

The DSC thermograms show a single glass transition in these materials (Fig. 5). In good agreement with the temperature shifts observed in the DMS main relaxation, PMMA polymerised in the presence of ethanol has a glass transition temperature higher than bulk PMMA (Table 1).

Discussion

When the ethanol content is equal or below 50%, the segregation of the solvent during polymerization yields isolated pores dispersed in the continuous polymer matrix (microsyneresis). This is clearly proved by the fact that water is not able to penetrate in the pores and the value of the pore fraction P_{d2} is zero independently of the amount of crosslinker added (Table 1). Nevertheless, the apparent density of the sample allows to calculate a pore fraction that rapidly increases with crosslinking density, from 8% in PMMA1/50E to 52% in PMMA10/50E. It is worth noting that the pore fraction of the latter practically equals the

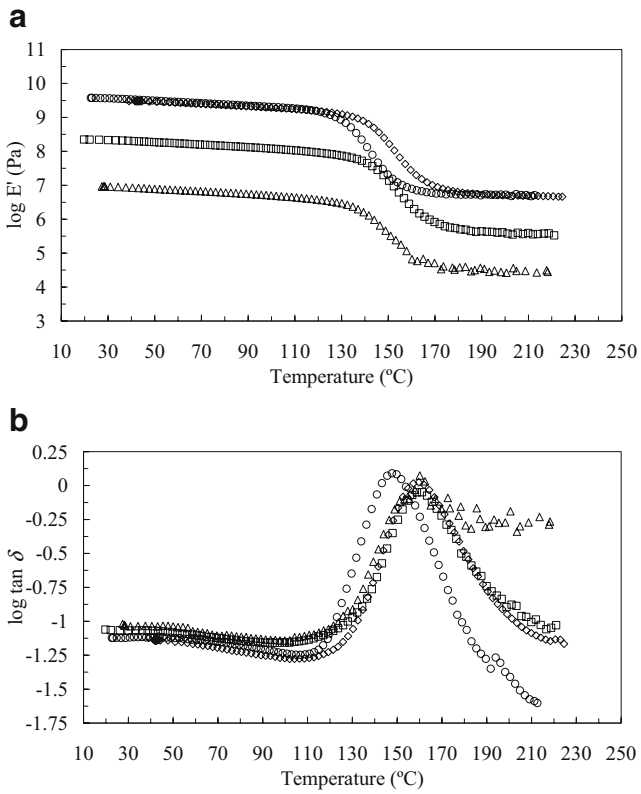

Fig. 3 Temperature dependence of the real part of the elastic modulus (**a**) and the loss tangent (**b**) of PMMA polymerised with 5 wt% EGDMA: bulk PMMA (*open circle*) and PMMA polymerised with 50 (*open diamond*), 60 (*open square*) and 70 (*open triangle*) wt% of ethanol. Only one point out of ten is plotted to obtain a clearer representation

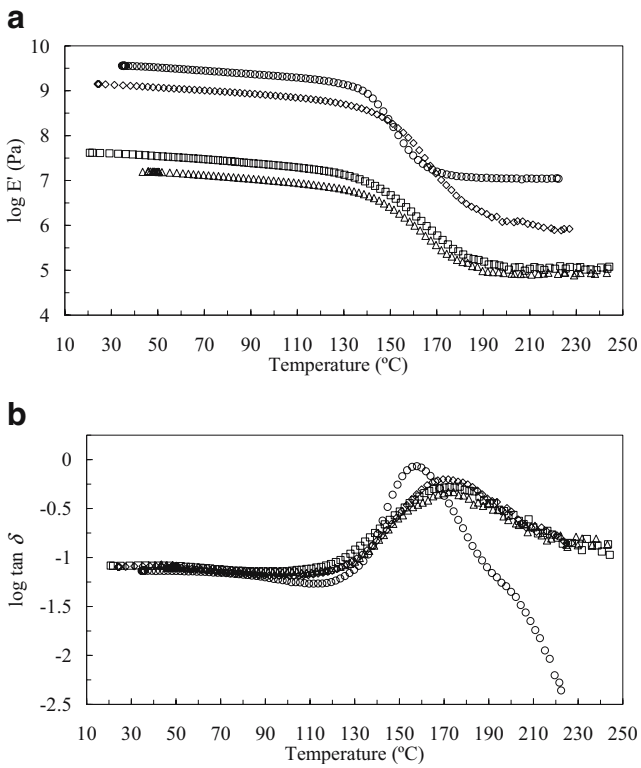

Fig. 4 Temperature dependence of the real part of the elastic modulus (**a**) and the loss tangent (**b**) of PMMA polymerised with 10 wt% of EGDMA: bulk PMMA (*open circle*) and PMMA polymerised with 50 (*open diamond*), 60 (*open square*) and 70 (*open triangle*) wt% of ethanol. Only one point out of ten is plotted to obtain a clearer representation

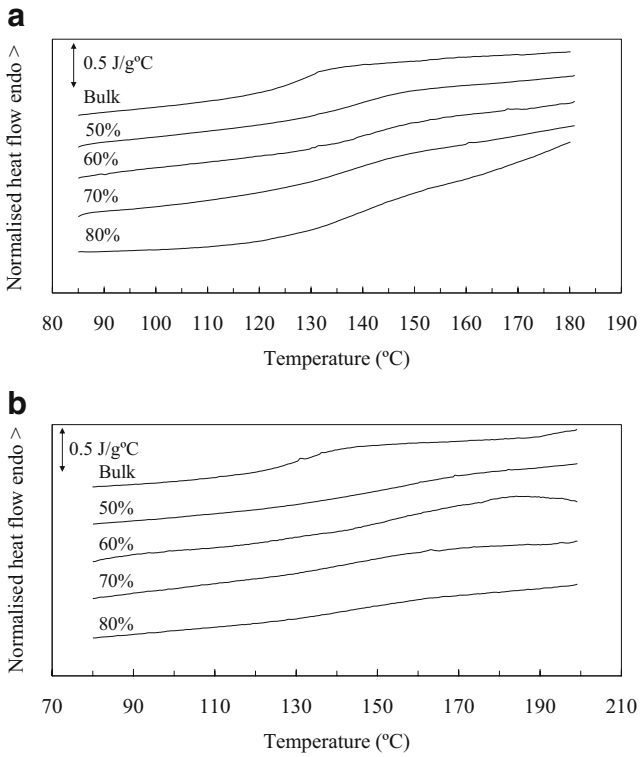

Fig. 5 DSC heating scans of bulk PMMA and PMMA polymerised in the presence of different ethanol contents (50, 60, 70 and 80 wt%) with 5 (**a**) and 10 (**b**) wt% of EGDMA crosslinker

amount of solvent introduced in the reacting monomer/ethanol mixture (a 50% weight fraction of ethanol in the monomer/ethanol mixture corresponds to 54.5% volume fraction). It can be said that all the solvent is segregated from the growing polymer network during the polymerization process in the form of dispersed pores and that the solvent extraction during drying preserves the pore architecture of the sample. Swelling of the samples with low crosslinking density in ethyl acetate increases pore fraction (see the value of P_s in Table 1). In the case of sample PMMA1/50E, porosity increases from P_{d1}=8% to P_s=45%. This means that the droplets of ethanol segregated during polymerization occupy around 45% of the sample volume, slightly below the total amount of ethanol added to the monomer (the rest must be homogeneously mixed with the polymer network at the end of polymerization process) but when ethanol evaporates, the polymer matrix contracts and the volume of the pores diminishes. The same happens in the case of PMMA5/50E sample, but now, the increase of the pore fraction during swelling is smaller: P_{d1}=26% to P_s =51%, but there is nearly no difference between P_{d1} and P_s in the case of sample PMMA10/50E. The ethanol that the networks are able to absorb acts as a plasticizer, and the amount of ethanol that the loosely crosslinked network is able to absorb may decrease the glass transition temperature below room temperature; in this way, the polymer network can contract at the same time that the solvent evaporates, and the pore structure collapses. On the other hand, in the case of highly crosslinked networks, the amount of ethanol absorbed homogeneously in the polymer network is much smaller and vitrification of the polymer network prevents its contraction and the pore volume fraction is maintained after drying. This effect was already reported in polymer scaffolds produced with template techniques [11]. As a

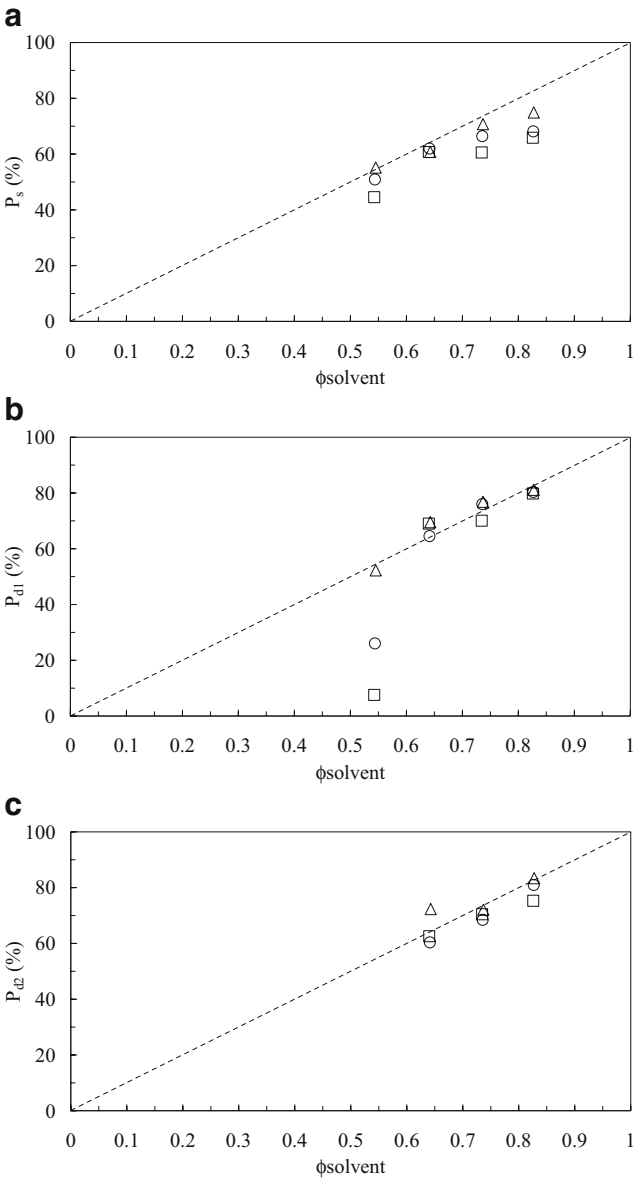

Fig. 6 Porosity in the swollen state [P_s (**a**)] and in the dry state determined from the apparent specific volumes [P_{d1} (**b**)] and from swelling in water [P_{d2} (**c**)] as a function of the solvent volume fraction ($\varphi_{solvent}$) of porous PMMA with 1 (*open square*), 5 (*open circle*) and 10 (*open triangle*) wt% of EGDMA crosslinker. The *discontinuous straight line* indicates pore volume fraction=solvent volume fraction (−)

consequence of the pore collapse, the storage modulus curve of PMMAB5 and PMMA5/50E dry samples are very similar (Fig. 3a). However, the storage modulus of PMMA10/50E falls dramatically with respect to that of PMMAB10 (Fig. 4a).

For high solvent contents (macrosyneresis), the effect of cross-linking is attenuated. No significant changes were found between the average PMMA particle sizes and the diameter distribution bar graphs (results not shown).

The pore fraction measured from the value of the apparent density of the samples, P_{d1}, equals the volume fraction of ethanol in the monomer/ethanol reactive mixture, ϕ_{solvent}, as shown in Fig. 6. Independently of the crosslinking density of the PMMA network, the volume fraction of the solvent in the mixture with the monomer is the same as the volume fraction of the empty space in the polymer sponge finally obtained. On the other hand, the pore fraction determined by water sorption practically equals ϕ_{solvent} as well, indicating that there are no isolated pores in the sponge due to the pore architecture of the sponge (above 50 wt% ethanol).

When porous PMMA samples formed by macrosyneresis are swollen in ethyl acetate (a good solvent for PMMA), the pore fraction measured decreases (see Table 1 and Fig. 6a). The polymer microspheres increase their volume when swollen, thus occupying a part of the empty space between them. In this way, the porosity of the swollen sample is always below the amount of ethanol added in the polymerization, ϕ_{solvent}, as emphasized in Fig. 6 by the straight line $P_s=\phi_{\text{solvent}}$.

PMMA polymerised in the presence of ethanol has a glass transition temperature higher than bulk PMMA polymerised with the same crosslinker content (see Table 1 and Fig. 5). The same effect was found in the DMS results where the temperature of the maximum of loss tangent is higher for PMMA polymerised in the presence of ethanol than for bulk PMMA polymerised with the same crosslinker content (see Table 1 and Figs. 3 and 4). The storage modulus of all the porous PMMA samples starts falling from the lowest temperature of the experiment because of the well-known secondary β relaxation. The α peak of porous PMMA polymerised with 5 and 10 wt% of crosslinker is for all the samples around 12÷14 °C higher than in bulk PMMA polymerised with the same crosslinker content. This effect is not related to the microstructure of the material because the increase in T_g with respect to the bulk polymer occurs in PMMA polymerised with 50 wt% of solvent (microsyneresis) and in porous PMMA polymerised with higher ethanol contents (macrosyneresis). Therefore, this increase must occur due to changes in the topology of the network due to polymerisation in solution that alters the kinetics of the propagation and termination reactions during free radical polymerisation [12, 13].

The effect of crosslinking on the dynamic-mechanical properties and glass transition of macroporus and bulk PMMA is evident. The main relaxation (□ peak) of the loss tangent broadens and shifts to higher temperatures with increasing crosslinking density. Glass transition temperature increases with increasing crosslinker content. These results are expected since co-operative conformational rearrangements of the main chains become more difficult as the crosslinking density increases.

The PMMA scaffolds synthesised in this work with high ethanol contents and different crosslinker contents have a morphology similar to that of poly(2-hydroxyethyl methacrylate) polymerised in the presence of high water contents in references [14, 15]. However, the mechanical resistance of these PHEMA sponges is extremely poor. The porous materials here prepared are mechanically consistent enough to allow dynamic-mechanical characterisation and their modulus is quite high taking into account the high porosity of the sponges (Figs. 3 and 4). The adhesion and mechanical properties of these hydrophobic scaffolds can be improved by hydrophilic plasma grafting [8].

Conclusions

Phase separation during polymerization of a PMMA network in presence of ethanol produces a porous material. The solvent segregation takes place by macrosyneresis if the ethanol content is above 50% by weight in the monomer/ethanol reactive mixture, and through microsyneresis for 50% by weight or less ethanol. The amount of ethanol at which the transition from microsyneresis to macrosyneresis takes place seems to be independent of the crosslinking density of the network.

The crosslinking density of the polymer network plays an important role in the formation of the pore architecture mainly when the pores are formed by microsyneresis because the ability of the polymer network to contract while the solvent is extracted reduces the pore fraction in loosely crosslinked networks. On the contrary, high crosslinking density drastically diminishes the amount of solvent homogeneously absorbed by the polymer network at the end of the polymerization process and allows solvent extraction without pore collapse.

Comparing samples with the same crosslinking density, bulk PMMA has the maximum of the main dynamic-mechanical relaxation or the glass transition temperature measured by DSC always at lower temperatures than macroporous PMMA.

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