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Positron annihilation studies of nanoholes and microphase formation control of a PMMA + MMA + TEGDMA system

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Abstract

Positron annihilation lifetime spectroscopy (PALS) was applied for the study of a set of PMMA (polimethyl-methacrylate) + MMA (methyl-methacrylate) + TEGDMA (triethyleneglycol-dimethacrylate) blends prepared by two synthesis routes (standard and phase separation methods). The aim was to investigate the correlation between free volume and miscibility of the compounds. PALS measurements were performed in order to determine contents and sizes of free volume on the 'standard' and 'phase-separation' polymers; important differences in the behavior of the free volume composition curves were found, which are explained in terms of the formation of microregions in the phase separation material. When considering simple binary interchain interaction, the mean free volume hole fraction in a blend was computed in terms of an interaction parameter (β) that might be correlated to the Flory–Huggins interaction parameter (χ). This suggests that local free volume properties of polymer in blends are very important for local packing and segmental arrangements. We have re-encountered the task of defining miscibility depending upon the scale of observation: we observed distinct phases in the micrometer scale while still nothing can be discerned in the nanometer scale. We conclude that it is possible to produce a PMMA + TEGDMA blend with the presence of a low fraction of MMA/TEGDMA copolymer situated at the interphase between the PMMA and TEGDMA regions allowing a higher degree of compatibility of the components.

Keywords: PMMA + TEGDMA system; Microphase formation; Nanoporosity

1. Introduction

In the last two decades [1] polymer science and engineering have found in positron annihilation lifetime spectroscopy (PALS) a very useful method for determining a number of physico-chemical quantities at a nanoscopic level. It has been well demonstrated [2] that positron (e^+) and positronium (Ps) annihilation events are very sensitive to the molecular environment in which they occur, so PALS has evolved as a suitable material characterization technique. In particular, free volume concentrations and average free volume sizes are important quantities detectable by this technique (via a suitable model). In polymers, attention has been paid to free volume quantities, which determine several mechanical properties of technological interest (as impact strength and elastic moduli) [3]. The existence of free volume nanoholes in polymers has been postulated for more than four decades [4]. It has been demonstrated that molecular motion in the bulk state depends on the presence of free volume holes. In polymers, local free volume holes arise due to the irregular packing in the amorphous state (static) and to the molecular relaxation of polymer chains and terminal ends (dynamic). According to the common view, positronium (Ps) formed inside a polymer annihilates from its ground state within a spherical well potential modelling a nanohole of the polymer free volume. Therefore the positron and positronium annihilation signals are found to be contributed mainly from free volume nanoholes in a polymer. Positrons emitted from ^{22}Na radioisotope enter into the polymer and may combine with an electron of the medium to form either *para*-positronium (*p*-Ps) or *ortho*-positronium (*o*-Ps). In vacuum, *p*-Ps annihilates with a lifetime of 123 ps by emitting two gamma rays, whereas *o*-Ps lives much longer (142 ns) and annihilates with the emission of 3γ. In materials *o*-Ps mainly annihilates through the so-called pick-off mechanism (e^+ in *o*-Ps annihilates with an external electron of opposite spin and not with the e^- belonging to the Ps atom) shortening considerably its lifetime, up to 1 ns. This lifetime is

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Table 1
Chemical compositions of the different reacting mixtures

Casting syrup (g) (30 wt% PMMA)	20	18	16	14	13	12	10	8	6	4	2	0
TEGDMA (g)	0	2	4	6	7	8	10	12	14	16	18	20

very sensitive to the molecular environment, especially to the empty spaces existing between molecules. In polymers, free volume quantities have proven to be closely related to its mechanical properties, so it becomes interesting to investigate this correlation based upon positron annihilation.

It is a common point of view that many mechanical properties of polymers can be significantly improved by a process of blending [5]. Miscibility and phase-separation phenomena of polymer blends have been studied with academic as well as with technological purposes in order to predict and enhance the material properties [6]. It is important to understand the underlying factors of blending at the molecular level. The investigation of the correlation between free volume and miscibility represents a possibility in this line of research [7]. Unfortunately, only a few number of techniques are available for characterizing free volume nanoholes due to the very small size of intermolecular spaces. In this connection PALS (in spite of not being yet a very popular tool) has proven to be a powerful probe to test free-nanospaces [8].

Several studies have been reported on the effect of addition of miscible and immiscible foreign compounds to the size, content and size distribution of free volume by the blending [9–11]. Some of the present authors (Velázquez et al. [12]) synthesized a number of PMMA/MMA + TEGDMA blends of different chemical composition employing the conventional method of initiation by thermal decomposition of benzoyl peroxide (PB) and induced decomposition of PB through *N*,*N*-dimethyl-*p*-toluidine as initiator processes, characterized the microstructure of these polymers by scanning electron microscopy (SEM) and studied their thermal behavior by differential scanning calorimetry (DSC). In the present work, we focus on the free volume effects on PMMA–MMA–TEGDMA blends prepared by two synthesis techniques (‘conventional or standard method’ and ‘phase-separation method’) [27]. Free volume contents may enhance or inhibit the degree of miscibility of the components present in the blend in accordance to well-accepted thermodynamic criteria [13].

2. Experimental

2.1. Synthesis of the blends

For the synthesis of the polymeric materials first, casting syrup was prepared by dissolving polymethyl methacrylate (PMMA) (average M_w 120,000) in methyl methacrylate (MMA) monomer in concentration of 30% by weight of the polymer. This syrup was mixed with triethylene glycol dimethacrylate (TEGDMA) monomer in different proportions from 0 to 100% by weight. Each of the mixtures were mixed separately with a mechanical stirrer until a single phase was obtained. Then the mixtures were bottled and stored under refrigeration until the polymerization reactions were completed. Table 1 summarize all the chemical composition of the reacting mixtures.

When the polymerization reaction was carried out, 5 g of one of the mixtures was withdrawn and placed inside a test tube, 8-mm diameter and 50 mm long. Then, 50 mg (1% by weight) of benzoyl peroxide (BPO) were added as initiator. The mixture was mixed until the BPO was completely dissolved, and the solution was placed in a thermal bath at 70 °C to start the reaction. When the viscosity was considerably increased by visual inspection, the test tube was taken off from the warm bath and the reaction was completed in another bath at room temperature. This process, called ‘conventional reaction’ was done with all of the reacting mixtures.

An alternative method (that we have called ‘phase-separation method’) to carry out the polymerization consisted of taking another 5 g of a mixture in a test tube and then adding 50 mg of BPO. When the BPO was dissolved 5 mg (0.1% by weight) of *N*,*N*-dimethyl-*p*-toluidine (DMPT) were added and the reaction began immediately and was completed inside a bath at room temperature. This fast reaction was also carried out with all the mixtures.

2.2. Morphology characterization by scanning electron microscopy

Samples of both types of polymer in each of the composition listed in Table 1 were coated by sputtering with a gold target. Then, the samples were observed in the SEM employing 20 kV in the accelerating voltage and secondary electron images were obtained.

2.3. Thermal behavior by differential scanning calorimetry

DSC analyses were carried out for all the polymers to determine thermal parameters such as glass transition temperature (T_g) and degradation temperatures. Each analysis was made with a 10 mg sample, using a heating rate of 3 °C/min, a temperature range from room temperature till 550 °C and aluminum oxide fine powder as reference.

2.4. Positronum annihilation measurements

The positron source consisted of a droplet of ^{22}Na from a carrier-free neutral solution (activity: 0.3 MBq), dried between two Kapton foils (thickness 1.08 mg/cm^2), which were afterwards glued together. The source was inserted within two identical layers of a specimen in a typical ‘sandwich’ configuration. The thickness of the specimens was sufficient to stop all the injected positrons. Positron annihilation lifetime spectra were collected through a conventional coincidence set-up, having a resolution of about 300 ps. All the measurements were performed at room temperature and in a vacuum granted by a rotary pump (<2 Pa). Each spectrum contained about 10^7 counts. Three spectra for each sample were collected. Deconvolutions were carried out through the computer code LT [Kansy], with a suitable correction for the positrons annihilated in the Kapton.

2.5. Average sizes and free volume contents.

ortho-Positronium (*o*-Ps) is utilized as an accurate probe to determine the free volume size and content since the *o*-Ps lifetime ($\tau_3 \sim$ a few nanoseconds) is correlated to the average free volume radius R (nm) and free volume fractions (f%), respectively. Free volume sites in polymers are represented by an infinite spherical well of radius R where e^+ and Ps particles may be localized before they annihilate. The well-known free volume model by Tao [14] provides the mathematical relationship between the *o*-Ps lifetime τ_3 and the hole radius R.

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \tag{1}$$

where ΔR is an empirical parameter equal to 1.656 Å [15]. The above formula has been widely used among positron researchers as well as an equation relating the *o*-Ps intensity (I_3) with the concentration of free volume holes. A quantity closely related to the previous parameters is the free volume fraction, which might be defined as the average hole size (determined by Eq. (1)) multiplied by the hole concentration. It has been proven [8,16] that I_3, the *o*-Ps intensity, increases with an increase in population of free volume sites due to a higher *o*-Ps formation and trapping rate. The fractional free volume f (%) is described as the product of the nanohole volume V_f and I_3 as [17,18]

$$f_{\mathrm{app}} = CV_f I_3, \tag{2}$$

where V_f is calculated from the value of τ_3 in Eq. (1) assuming a spherical volume equation $V_f = (4/3)\pi R^3$ and C is a constant quantity determined by PVT measurements above and below T_g. The validity of this approach has been confirmed by comparing PALS data against independent free volume values estimated from bulk volume temperature data, using the scaling constant [16]. Care needs to be taken when using Eq. (3) to determine the free volume. This equation will only be valid for polymers that do not contain groups which inhibit Ps formation. Exposure of the sample to the radiation source may also lead to a decrease/increase in the I_3 values and need to be taken in consideration. Such effects can be considerable at low temperatures [19]. However, we do not consider radiation effects from the positron source of primary importance in order to interpret our measurements, since the exposure dose for each sample was negligible (a few Grays). The I_3 parameter depends on the number of electrons in the positron track and on the concentration of free volumes. Only in some cases where it has been shown that the former contribution is unchanged, I_3 can be used directly as a quantity proportional to hole concentrations, so we should interpret that the quantities in Eq. (2) are empirical parameters (In fact, this last equation was employed in the present computation of fractional free volume). An alternative way of determining free volume fractions without using I_3 have also been proposed by Dlubek et al. [20]. Bandzuch et al. [21] assume

$$f = V_f \tag{3}$$

Because there are increasing indications [22–24] that I_3 is affected by many different parameters, the approach presented here must be considered of semi-empirical character. However, the main conclusions of the present work are largely independent of assuming Eqs. (2) or (3).

It has been suggested [25] that in miscible blends, the variations of free volume related to blending are due to the interaction between dissimilar chains and the segmental conformation and packing component polymers for van der Waals type blends, i.e. blends involving only weak interaction. Miscibility in these systems is believed to result from specific interactions which lead to a negative free energy of mixing. Changes in mobility can be explained by considering changes in free volume with a greater degree of free volume between molecular chains and at chain ends leading to a greater ease of chain mobility. Free volume includes both static (interstitial) and dynamic (density fluctuation) contributions. If we consider a simple binary interchain interaction, we may express the free volume hole fraction in a blend as [26]:

$$f_{\mathrm{v}} = f_{\mathrm{v}1}\phi_1 + f_{\mathrm{v}2}\phi_2 + \beta f_{\mathrm{v}1}\phi_1 f_{\mathrm{v}2}\phi_2, \tag{4}$$

where $f_{\mathrm{v}1}$ and $f_{\mathrm{v}2}$ are the free volume fractions in pure polymers 1 and 2 and ϕ_1 and ϕ_2 are the molar fractions. β is a parameter that could be related to the interaction between dissimilar chains.

3. Results and discussion

Fig. 1 shows comparative secondary-electron images from SEM of both types of polymers. It is possible to observe remarkable differences of morphology. For the conventional polymer a continuous matrix is present, this is a possible evidence of a single phase. In the case of phase-separated polymer, the morphology consists of an arrangement of particles. Those particles are microdomains with different chemical compositions, some of them are made of PTEGDMA, others consist of PMMA and another fraction could be formed by TEGDMA–MMA copolymer.

Analyses from DSC show quite different thermal behaviors for each type of polymer. Fig. 2 shows thermograms from the polymers [27]. The conventional copolymer has one T_g at 130 °C, a strong evidence of a single phase. Besides, this polymer present exothermic peaks at 250 and 378 °C. Those peaks were produced in different stages of the copolymer degradation. The phase-separation polymer shows two

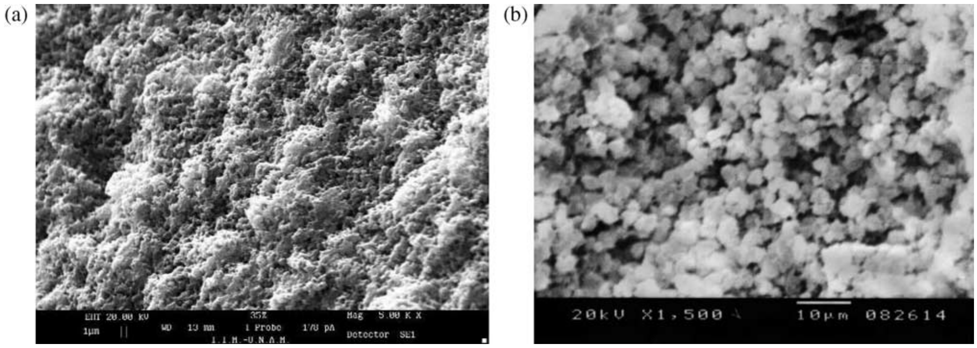

Fig. 1. Scanning electron microscopy micrographs of the two types of polymer blends studied here. (a) Micrograph of a conventional polymer containing casting syrup 30% of PMMA and 30% of TEGDMA. In this polymer one TEGDMA–MMA copolymer was produced and the morphology of a single matrix is formed, and (b) shows a micrograph of a phase-separation polymer containing casting syrup 30% of PMMA and 30% of TEGDMA. Notice the large number of particles that make up the polymer bulk.

different T_g's, one at 102 °C that could be produced by PMMA microdomains and the second one at 150 °C that correspond to PTEGDMA microdomains. Also, this polymer has a broad endothermic peak at 250 °C, possibly produced by a decarboxylation reaction and other chemical changes, but the nature of this thermal transition is still under study. Other three peaks appeared at 348, 378 and 440 °C. These last three peaks concern degradation of PMMA, TEGDMA–MMA copolymer and PTEGDMA microdomains, respectively. Maybe the copolymer fraction was rather small to determine its T_g in these polymers, but large enough to observe its degradation temperature.

Table 2 shows the annihilation parameters τ_i, I_i for $i=1,2,3$ of the polymeric blends resulting from PALS measurements, whereas Table 3 contains the free volume quantities computed from Eqs. (1), (2) and (4). The positron lifetime spectra were decomposed into three components. The first component with the shortest average lifetime $0.15<\tau_1<0.24$ (ns) is partly due to *p*-Ps annihilations but the main contributions come from free positrons annihilated in the bulk. There are two types of annihilation events (in the bulk and at the interphase) that are averaged together and we do not posses a mathematical method to decompose it, however this lack of information is not important for our purposes of computing free volume. Only the third component τ_3 is used for the computation of the average free volume radii in accordance to well-accepted criteria [14]. The second component with an intermediate average lifetime $0.36<\tau_2<0.54$ (ns) is attributed to e^+ annihilations in the outer cores of polymeric chains and to positron particles trapped in free volume holes between PMMA and TEGDMA microregions. The third component is associated to the *o*-Ps annihilations in the voids between the chains forming the polymer and it represents the longest lifetime $1.86<\tau_3<2.22$ (ns). The corresponding sub-nanoholes form what can be called inter-chain free volume. Variations of *o*-Ps lifetime τ_3 with chemical concentration for two kinds of polymers are shown in Fig. 3.

It is interesting to notice that lifetimes and corresponding hole volumes are different for the two pure PMMA samples (composition 100%, Table 2). This is probably so since MMA mixed with PMMA polymerized with a very high polymerization rate when DMP was used as a promoter to initiate the reaction, thus, the molecular weight produced would be lower than those obtained in a conventional reaction, which is rather slower. The lower molecular weight for phase separated polymer would then produce a lower glass trasition temperature, as it was registered by DSC measurements.

Figs. 3–6 show the plots of the *o*-Ps intensities (I_3), nanoholes radii R, the free volume fractions of the blend f_{app} and the beta parameter β, respectively, versus the composition of the blends. In particular, Fig. 6 shows that for intermediate values of composition the β parameter for phase separation blends assumes negative values. This means that the free volume fraction of the blend f_v is less than the weighted sum of the free volume fractions of pure polymers f_{v1} and f_{v2}, and in this case the blend does not favor the formation of larger interchain spaces enhancing the compactness of molecules in the polymer.

Indeed, if the so called β parameter is directly correlated to the χ Flory–Huggins parameter, then a negative value of β would correspond to a stronger attractive interaction between PMMA and TEGDMA chains, while $\beta>0$ would mean

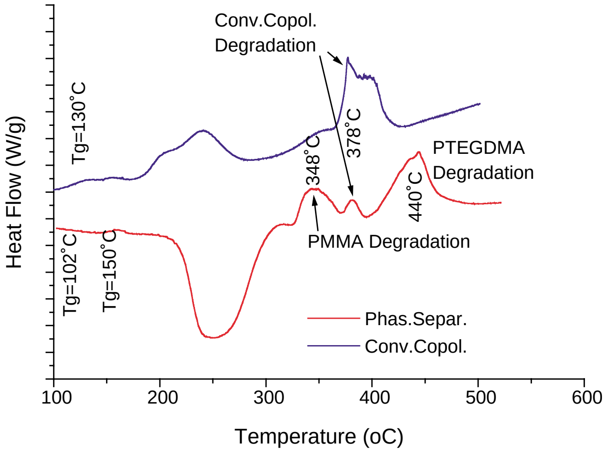

Fig. 2. Comparative DSC thermograms from sample of the two types of polymers. Both polymers had the same chemical composition, casting syrup (30 wt% PMMA) and 30 wt% of TEGDMA, but different thermal behavior. Conventional copolymer (upper line) has one T_g, and phase-separation polymer has two T_g's.

Table 2
Positronium annihilation parameters τ_i, I_i, $i=1,2,3$ for the polymers as a function of the composition ϕ

ϕ	τ_1	I_1	τ_2	I_2	τ_3	I_3	σ_3	χ_2
(a) Conventional polymer								
1.00	0.18	23.6	0.41	45.3	1.86	31.1	0.29	1.08
0.90	0.20	33.8	0.45	38.4	2.05	27.8	0.31	1.06
0.80	0.16	18.7	0.39	49.9	2.16	31.4	0.55	1.09
0.70	0.21	32.8	0.47	39.1	2.13	28.1	0.13	1.19
0.65	0.21	29.7	0.44	41.1	2.15	29.2	0.36	1.07
0.50	0.19	25.2	0.42	45.2	2.15	29.5	0.41	1.11
0.40	0.20	25.6	0.41	44.4	2.08	30.1	0.45	0.96
0.10	0.24	45.1	0.54	29.3	2.10	25.5	0.20	1.08
0.00	0.23	37.8	0.48	35.6	2.04	26.6	0.24	1.10
(b) Phase-separation polymer								
1.00	0.20	36.4	0.45	35.2	2.22	28.3	0.38	1.11
0.90	0.19	26.1	0.44	44.3	2.20	29.7	0.09	1.18
0.80	0.18	23.0	0.41	46.0	2.11	31.0	0.41	1.19
0.70	0.19	26.3	0.42	43.9	2.02	29.8	0.36	1.12
0.65	0.17	19.3	0.40	51.2	1.97	29.5	0.38	1.07
0.50	0.15	14.0	0.36	53.8	1.98	32.3	0.62	1.14
0.40	0.17	19.6	0.39	50.2	2.02	30.3	0.48	1.05
0.10	0.19	31.4	0.38	43.2	2.05	25.4	0.56	1.17
0.00	0.20	31.3	0.44	41.6	2.07	27.1	0.43	1.07

repulsive interaction. It is quite interesting to note that the conventional polymer always presents positive values of β, and that is to say that blending tends to create larger concentrations of free volume which agrees well with the repulsion between chains of polymers 1 and 2.It is worthwhile try to understand the differences between these behaviors: β is always positive in the conventional polymer whereas changes of sign in a complex form in the phase-separation polymer. We think this is not due to statistical error but due to the fact that additivity does not always holds for the phase separated polymer because there is a physico-chemical factor that makes packaging of molecules to be more complex in the phase-separation polymer and it is the formation of a low fraction of MMA/TEGDMA copolymer localized at the interphase between the PMMA and TEGDMA phases. This interfacial zone contributes to the detected annihilation signal of both τ_i, I_i and up to now we have no way of isolate the annihilation components of this zone. By the other hand, the free volume radii results show that both types of polymers have about the same size of nanopores. Normally, the o-Ps lifetime decreases as the molecular weight (M_w) increases up to about 50,000: then it stays unchanged as M_w increases further [28]. Since the blends here considered have $M_\mathrm{w} > 50{,}000$, then the different values of τ_3 could be interpreted in terms of molecular structure and its packing in the polymer.

Table 3
Nanohole radius R (nm), nanohole volume V_f (nm^3), apparent free volume fraction f_app(%) and beta interaction parameter for the polymers as a function of the composition ϕ of the blend

ϕ	R	V_f	f_app	β
(a) Conventional polymer				
1.00	0.271	0.0833	2.59	0.0000
0.90	0.288	0.1000	2.78	0.0170
0.80	0.298	0.1108	3.48	0.1431
0.70	0.295	0.1075	3.02	0.0892
0.65	0.297	0.1097	3.20	0.1383
0.50	0.297	0.1097	3.24	0.1588
0.40	0.291	0.1032	3.11	0.1198
0.10	0.293	0.1053	2.69	0.0054
0.00	0.287	0.0990	2.63	0.0000
(b) Phase-separation polymer				
1.00	0.303	0.1165	3.30	0.0000
0.90	0.301	0.1142	3.39	0.0109
0.80	0.294	0.1064	3.30	0.0140
0.70	0.286	0.0979	2.92	−0.0392
0.65	0.281	0.0929	2.74	−0.0714
0.50	0.282	0.0939	3.03	−0.0005
0.40	0.286	0.0979	2.97	−0.0029
0.10	0.288	0.1000	2.54	−0.0214
0.00	0.290	0.1021	2.77	0.0000

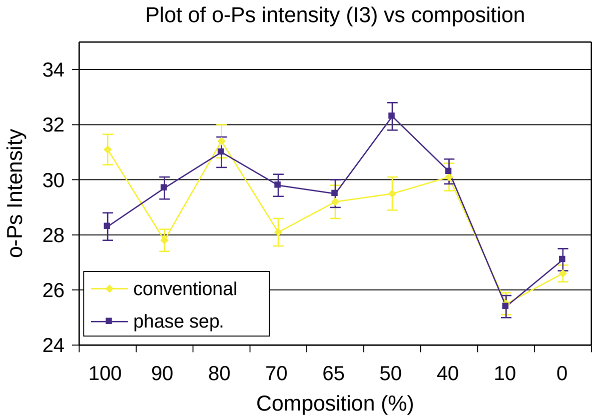

Fig. 3. o-Ps intensity I_3 as a function of the composition ϕ of the blend for each type of polymer.

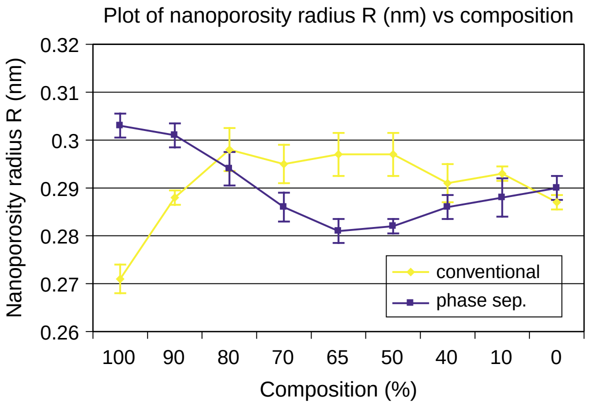

Fig. 4. Free volume radius *R* (nm) as a function of the composition ϕ of the blend for each type of polymer.

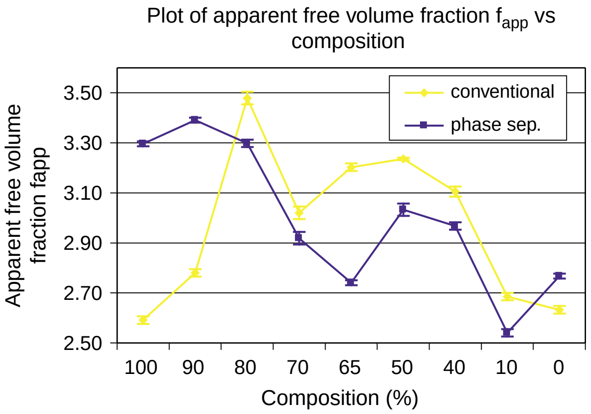

Fig. 5. Apparent free volume fraction f_{app} of the blend as a function of the composition ϕ for each type of polymer.

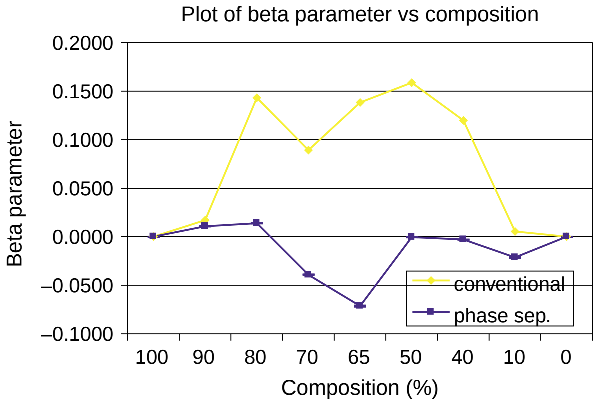

Fig. 6. Beta interaction parameter β as a function of the composition ϕ for each type of polymer.

4. Conclusions

The main conclusions of the present study can be summarized under the following items:

(1) It is well known that positron and positronium annihilation events inside a polymer are very sensitive to the molecular environment in which they occur and what was observed in this study was not an exception. In particular, positronium lifetimes could be used as a probe to test the free volume contents in a polymer sample as well as the existence of sub-nanoholes that are observed in both kinds of polymers considered here.

(2) The free volume fraction (or free volume content) has proven to be well-related to the degree of miscibility of the compounds of a polymer blend. Free volume may enhance or inhibit the compatibility of polymers as a function of the composition of the blend.

(3) Two polymers identical in composition, but synthesized through different routes, present different contents of free volume. The PMMA+MMA+TEGDMA system performed by the 'conventional method' presents on average larger amounts of free volume than the phase-separation polymer. The conventional blend generally has a greater free volume fraction than the free volume fractions of pure polymers 1 and 2, which corresponds to $\beta > 0$ in all range of compositions.

(4) The β parameter (defined in terms of the free volume fractions of the blend and pure polymers 1 and 2) may be correlated to the Flory–Huggins parameter χ (this last parameter is not directly correlated with free volume data in the present work) in the sense that positive values of β would correspond to larger free volume contents produced by a stronger repulsion between PMMA and TEGDMA chains. $\beta < 0$ would be associated to an attractive interaction of the polymer chains that would contract the free volume fraction of the blend.

(5) The possible explanation of the the complex behavior of the free volume fraction observed in the phase-separation polymer may be in terms of a variety of local packing and molecular arrangements due to the presence of a low fraction of MMA/TEGDMA copolymer located at the interphase between PMMA and TEGDMA phases and this is currently being investigated.

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