

EFFECT OF POLY(SILICON-BUTYL-ADIPATE) COPOLYMERS COMPOSITION ON SEVERAL CHARACTERIZATION ASPECTS

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المخلص

في هذا الورقة تم دراسة تأثير التركيب الكيميائي (محتوى السيلكون خصوصا) على درجة البلور والحجم الحر والتركيب المورفولوجي لسلسلة من البوليمرات المزدوجة والمكون من جزئيين؛ الأول هو السيلكون والثاني هو بيوتيل ادبيت (PSBA) وهو بولي (سيلكون بيوتيل ادبيت). حيث تم الحصول على درجة البلور من جهاز الأشعة السينية ذي الزاوية المتوسطة بينما استخدم مجهر القوى الذرية للحصول على التركيب المورفولوجي للعينات المدروسة في حين تم قياس الحجم الحر باستخدام المطياف الذي يقيس عمر الإبادة للبويزترون. وللقيام بهذه العملية كان من الواجب حساب الحجم الحر في البوليمرات الأساسية المكون للبوليمرات المزدوجة وهي بولي السيلكون والبولي بيوتيل ادبيت. تم تحليل النتائج المتحصل عليها للبوليمرات الأساسية باستخدام ثلاثة مكونات للحصول على أفضل معادلة تمثل هذه النتائج إلا أنه في حالة سلسلة البوليمرات المزدوجة، وللحصول على أفضل تمثيل، كان من الضروري استخدام أربعة مكونات. مناقشة النتائج كانت مركزة على سلسلة البوليمرات المشتركة من حيث تأثير التركيب الكيميائي على المعاملات المرتبطة بعمر الإبادة للبويزترون وبالتالي تأثير الاختلاف في التركيب على الحجم الحر لهذه البوليمرات. أظهرت النتائج أن المعاملات المرتبطة بعمر الإبادة للبويزترون يمكن أن تستخدم لدراسة التركيب المورفولوجي بين سلاسل البوليمرات خصوصا أطوال عمريين للإبادة (τ_3 و τ_4) والكثافة المقابلة لهما (I_3 و I_4). ومن خلال هذه الدراسة تم الربط بين هذه العوامل وتركيب البلوري المتواجدة في هذه البوليمرات وكذلك انفصال في الأطوار.

ABSTRACT

In this paper the effect of the chemical composition (silicon content), on the morphological structure, degree of crystallinity and free volume in Poly(silicon-butyl-adipate) (PSBA) Copolymer, were investigated. The copolymer series morphology and crystallinity percent (ω_m) were studied using and atomic force microscopy (AFM), wide-angle X-ray diffraction (WAXD) respectively. Positron Annihilation Lifetime Spectroscopy (PALS) was used to measure the free volume in a series of PSBA copolymers as well as in the silicon and BA homopolymers was measured using positron annihilation lifetime spectroscopy (PALS). The free volumes of the homopolymers were determined by analyzing the lifetime (LT) spectra using three-components fit. On the other hand, the LT spectra of the PSBA copolymer series were analyzing using four-components fit. The effects of the chemical composition (silicon content), on the o-Ps annihilation parameters and thus on the free volume of the PSBA copolymers, were investigated. The results indicated that positron annihilation characteristics (the longest lifetime components (τ_3 and τ_4) and their intensities (I_3 and

I₄) are very useful for studying the effect of the morphological parameters (microphase separation and crystallinity) on the free volume in the copolymer series.

KEYWORDS: Poly (Silicon-Butyl-Adipate); Morphology; Atomic Force Microscopy; Wide-Angle X-Ray Diffraction; Free Volume.

INTRODUCTION

The semicrystalline copolymer morphology has recently attracted much attention because the ability of these copolymers to have considerable morphological wealth [1-3]. This wealth of morphology results from two main factors. The first is the driving force for microphase separation between dissimilar segments, especially in the melt. This promotes the formation of nanoscale domains such as lamellae, spheres and cylinders. The second factor is the driving force for the crystallization of a segment. This promotes the formation of alternating amorphous and crystalline layers [4].

Semicrystalline polymers as well as amorphous polymers contain cavities or holes of atomic and molecular dimension, which arise because of irregular molecular packing in the amorphous phase. These holes and cavities are called *free volume*. Over the past fifteen years, the free-volume hole properties in polymeric materials have been investigated by researchers using positron annihilation lifetime (PAL) spectroscopy [5-7]. A fraction of positrons injected into polymeric materials combine with electrons to form ortho-positronium (O-Ps) which survives up to a few nano-seconds (ns) in the free-volume holes of a few Angstrom (Å) in size. The measured o-Ps lifetime is found proportional to the hole size and the relative intensity of the o-Ps component among others provides a measure of the hole population. The localization of a-Ps into the holes in polymers renders the unique capability of PAL spectroscopy in sampling the free volume alone [5-6]. The relationship between the positron lifetime annihilation and the molecular characteristics of semicrystalline polymers has been the subject of vast number of academic research studies [8].

The observations of various authors on the relationship between the o-Ps lifetime and the molecular structure of semicrystalline polymers can be summarized as follows. For several semicrystalline polymers, the changes in the crystalline regions do not affect the lifetime of the o-Ps destruction. The lifetime spectra of the polymers are best resolved in three components, similar to the amorphous polymers. This has led to the conclusion that there is only one long-lived component ($\tau_3 \cong 1.5-4$ ns), regardless of the presence or absence of the crystalline phase. Some examples of semicrystalline polymers in this group are polyethyleneterephthalate (PET) [9] and polypropylene [10]. On the other hand, four lifetime components have been found for polyethylene (PE) [6], polyamides [7], polytetrafluoroanethylene [10] and 1,4-polybutadiene [11]. In this group of semicrystalline polymers two long-lived o-Ps components were obtained, where the first ($\tau_3 \cong 1$ ns) is attributed to o-Ps annihilation in the chain folded regions, and the second ($\tau_4 \cong 2.4-4$ ns) is attributed to pick-off annihilation of o-Ps entrapped in the free volume in the pure amorphous phase of the polymer. In the case of polyurethane/urea membranes obtained through the introduction of two soft segments, polypropylene oxide and polydimethylsiloxane, two long components (lifetimes τ_3 and τ_4) were ascribed to two Ps states decaying in different regions. The detection of the two long lifetimes in these membranes indicated the coexistence of two phases corresponding to separate domains of the two soft segments of the polydimethylsiloxane and polypropylene oxide membranes [12].

In this work a series of Poly (silicon-butyladipate) (PSBA) copolymer was chosen in order to investigate the effect of the chemical composition (silicon content), on the copolymer morphology, crystallinity and free volume. The silicon and BA homopolymers free volumes and PSBA copolymer series free volume were determined using Positron Annihilation Lifetime Spectroscopy (PALS). Furthermore the copolymer series morphology were imaged using AFM while, the crystallinity percent (ω_m) were studied using wide-angle X-ray diffraction (WAXD).

EXPERIMENTAL WORK

Characterization Techniques

Positron annihilation lifetime spectroscopy (PALS)

Positron lifetime measurements were performed at University of Stellenbosch (South Africa) using a fast-fast coincidence system with a time resolution of 240.34 ps full width of half-maximum (FWHM) and a total of 1024 channel. The radioactive source (^{22}Na) was placed between two pieces of sample, for each sample, and wrapped very carefully in aluminium foil to ensure that the positrons interacted effectively with the material. The duration of each measurement was 80 min maximum, during which time 1×10^6 counts were collected. Two identical samples, approximately $2.5 \times 10 \times 10 \text{ mm}^3$, were sandwiched around a positron source, made by evaporating carrier-free $^{22}\text{NaCl}$ solution onto aluminium foil.

Atomic force microscopy (AFM)

AFM images were obtained at University of Stellenbosch (South Africa) using a multimode AFM model no. MMAFMLN, with a Nanoscope IIIa controller from Veeco, operating in non-contact mode, and using a low resonance frequency silicon cantilever with a resonance frequency of about 60 kHz and a spring constant of $k = 50 \text{ N/m}$. The substrate containing the polymer samples was attached to the sample holder with double-sided adhesive tape. All experiments were carried out under ambient conditions. The scan rate was set in the range of 0.5 to 0.7 Hz. Topography and phase images were captured simultaneously for the tapping mode.

Wide-angle X-ray diffraction (WAXD)

WAXD was performed at iThemba LABS (South Africa) on a Bruker AXS D8 ADVANCE diffractometer at room temperature, with filtered $\text{CuK}\alpha$ radiation, using a LynxEye position sensitive detector. All samples were scanned at diffraction angles (2θ), ranging from 5° to 50° , with a step size of 0.02° . The samples were prepared by casting films of 10 wt % copolymer solutions in THF on mica substrates to form thin films with a thickness of about 0.5 mm. From the WAXS data, the percentage of crystallinity was calculated by peak deconvolution and subsequent determination of the relative areas under the amorphous halo and the crystalline peaks of the X-ray diffraction scan. The ratio of the area under the crystalline peaks (I_c) to the total (amorphous + crystalline) area (I_{tot}) gave the degree of crystallinity (ω_m).

Data Analysis of Positron Annihilation Spectrum

Each positron annihilation spectrum, with a summit height of approximately 1×10^6 counts, was obtained at room temperature. Mathematically, using the PATFIT computer program, the spectra were analysed as the sum of exponentials. The following procedure was used to analyse the LT spectra. The lifetime spectra for each

sample of the homopolymers were first analysed in terms of three lifetime components. The magnitudes of the three lifetimes τ_1 , τ_2 and τ_3 suggest that they originate mainly from the annihilation of p-Ps, free positron and o-Ps, respectively. The last parameter with the respective intensity (τ_3 and I_3) are the most important ones, because their analysis will determine the free volume and the physical–chemical characteristics of the media where the positron annihilation occurs [13]. The following equation is obtained by Tao and Eldrup, which shows the relationship between o-Ps lifetime (τ_3) and free volume radius.

$$\tau = \frac{1}{2} \left[\frac{1}{\left(1 - \frac{R}{R_0}\right) + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right)} \right] \quad (1)$$

where R is the hole radius and R_0 is the infinite spherical potential radius, and $R_0 = R + \Delta R$, where ΔR is an empirical parameter [14, 15]. In the Tao-Eldrup model a spherical pore (here holes of irregular shape are treated as spheres for simplicity) is described by a rectangular potential well with spherical symmetry. The Tao-Eldrup model was extended later to other hole shapes (as cubes, cuboids, cylinders and large holes) as well as different potential shapes [16].

Analysis of the measured spectra of PSBA copolymer by four lifetime components was also attempted. The analysis was first applied without any constraints where the shortest of the four lifetimes was scattered in the range 0.1 and 0.3 ns, with very large variances fit. This lifetime is consistent with that of the p-Ps lifetime. In order to reduce the scatter of the points the final four lifetime analyses were carried out by fixing the intrinsic p-Ps lifetime at 0.125 ns.

RESULTS AND DISCUSSION

The percentage of crystallinities of the BA, silicon homopolymers and the copolymer series are obtained from the **WAXD** analysis and shown in Table (1). There was a significant reduction in the crystallinity of the copolymers as the silicon content in the copolymer series was increased. The degree of crystallinity of the copolymers (ω_m), was calculated based on the BA content (weight fraction).

Table 1: Characteristics of the investigated silicon and BA homopolymers and the PSBA copolymer series (M_n for silicon segment in the copolymers =2000 g/mol).

Sample	Silicon in feed (wt %)	Crystallinity ω_m (%)
PBA	0	43.6
PSBA-101	5	39.5
PSBA-102	10	35.8
PSBA-103	25	30.9
PSBA-104	40	23.9
PSBA-105	60	16.2
Silicon	100	0

Figure (1 and 2) shows the phase images of **AFM** for the PBA homopolymers and PSBA copolymer series. In Figure (1a) small part of spherulites of PBA crystal is shown, which show clear formation of lamellae inside the spherulitic crystal from which the spherulites are made.

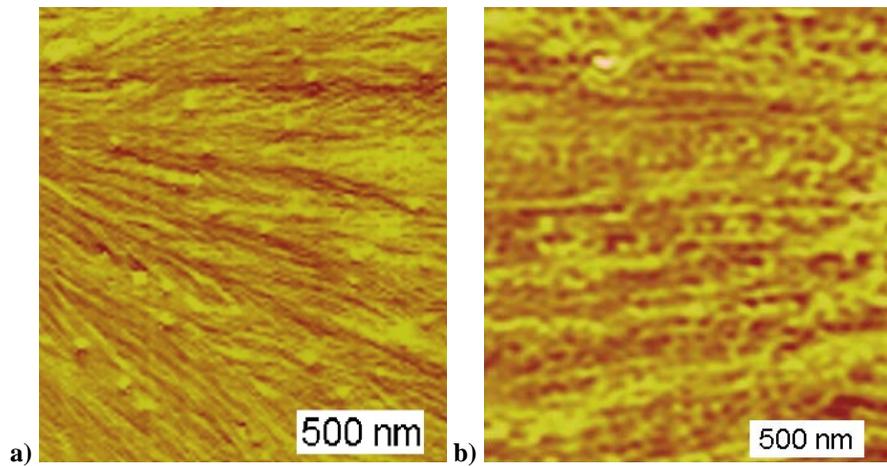


Figure 1a: a) Spherulitic crystal in PBA homopolymers sample, b) Spherulitic crystal and silicon spherical domains in PSBA-101 sample.

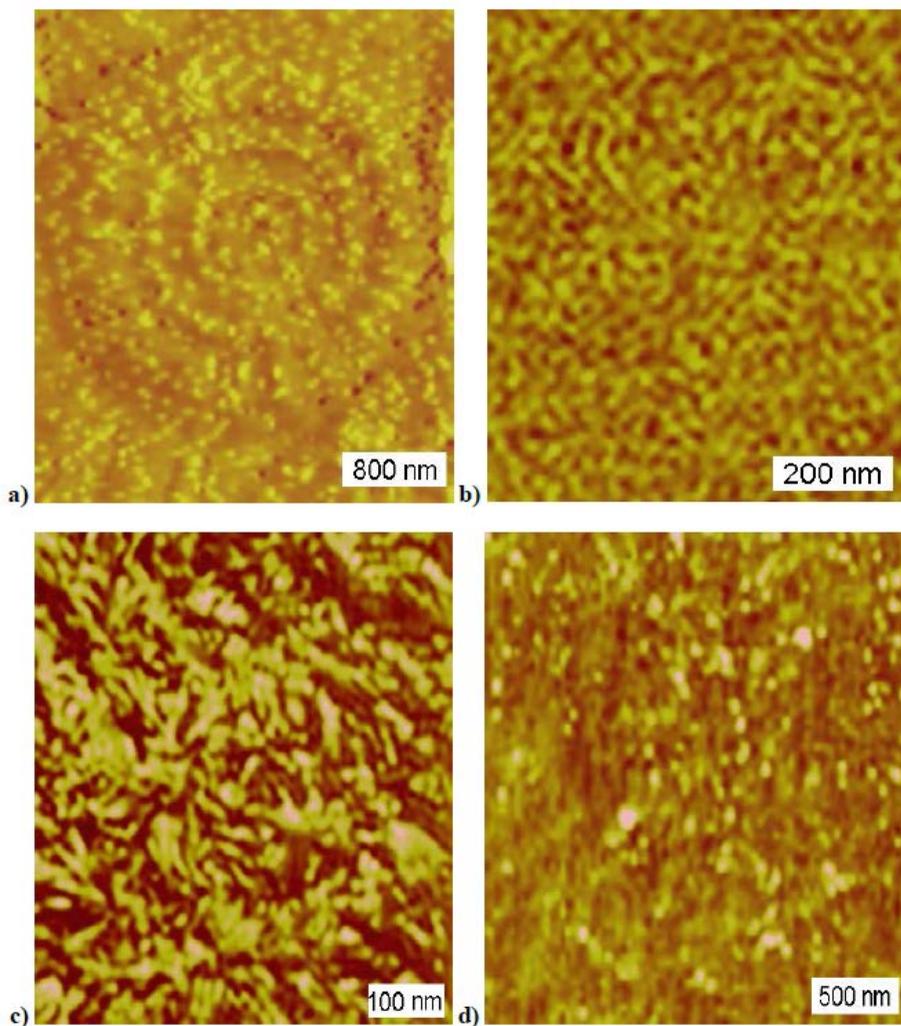


Figure 2: a) Spherulitic crystal and silicon spherical domains in PSBA-102 sample, b) silicon spherical domains only with in PSBA-103 sample, c) bicontinuous phases in PSBA-104 sample, d) BA spherical domains only in PSBA-105 sample.

In the case of the PSBA copolymer series small spherical domains were detected in-between the lamellae inside the spherulitic crystal structure, as shown in Figure 1(b) for PSBA-101 sample and in Figure 1(a) for PSBA-102 sample. The average size or diameter of these domains is approximately 50 ± 10 nm. On the other hand, in Figure 1(a) no domains are seen for PBA homopolymers. Therefore, it is believed that these domains in the copolymer are silicon segments segregated to form small domains or islands (dark spots in the phase images) in the BA segments matrix (the bright region in the phase images).

When the silicon contents increased to 25 wt % in for PSBA-103 sample (Figure 2(b)), no spherulites are detected by AFM on the surface for either type of copolymer. This is most probably due to the presence of relatively smaller amounts of crystallinity in these copolymers, as detected by WAXD, and the decreased probability of the formation of crystals at the interface. However, the silicon domains in PSBA-103 sample is detected and increase in number. As the silicon contents increased to 40 wt % in PSBA-104 sample (Figure 2(c)), the spherical PDMS domains start connecting with each other and a bicontinuous double diamond type of morphology appears in this sample. Upon a further increase in the silicon contents to 60 wt % in PSBA-105 sample (Figure 2(d)) this type of morphology changes to spheres of BA segments surrounded by rubbery phases of silicon.

Table (2) shows the annihilation lifetime of the o-Ps (τ_3) and the corresponding intensity (I_3), that was obtained from analysis of the *PALS* results using three component fit. The suitability of the three-components fit for the Silicon and PBA homopolymers is consistent with that reported in literature for other polymers, such as PET [9]. Both (τ_3 and I_3) are indicative of the relative number of o-Ps annihilations. The radius of the holes, obtained using Eq (1) are also listed in Table (2).

Table 2: The o-Ps characteristics of Silicon and PBA homopolymers determined using the three- components fit

Sample	τ_3^a (ns)	$\Delta\tau_3^a$ (ns)	I_3^b (%)	ΔI_3^b (%)	R^c (Å)	ΔR^c (Å)
PBA	2.34	0.017	21.02	0.101	2.75	0.004
Silicon	4.14	0.009	37.48	0.156	4.32	0.003

^a the average lifetimes of the o-Ps

^b the average intensities of the free volume holes

^c the average radii of the free volume holes

Table (2) shows that the radius of the free volume holes in the silicon polymer (4.32 Å) is about twice as the radius of the free volume holes in the PBA homopolymer (2.75 Å). The relatively small radius of free volume in the PBA homopolymer can be attributed to the crystallinity degree in this polymer, determined using WAXD to be about 43.6% (see Table 1), resulting in a lower o-Ps yield. Therefore, the o-P lifetime and its intensity, as extracted from the lifetime spectra, can provide an indication of the polymer's structure, and eventually provide more information on the region where the o-Ps could be annihilating.

Figures (3a & b) shows the longest o-Ps lifetimes (τ_3 and τ_4) and intensities of the corresponding o-Ps (I_3 and I_4), as obtained after using the four-components fits. In

contrast to the homopolymers, the four-components fit in the copolymer series is necessary in order to understand the complex structure and morphology of such phase separated copolymer series and to have physical meaning of the lifetimes obtained.

In the complex semicrystalline copolymers with microphase separated morphology the three-components fits has no relevant physical meaning and gives only a more or less sufficient fit to the experimental data. Because of the structures of these semicrystalline PSBA copolymers, positronium can form in both the crystalline (BA region) and amorphous (BA and silicon regions) phases. The possible regions with free volume holes probed by o-Ps in these copolymers are in:

- (1) Open amorphous texture and interfaces in spherulites,
- (2) interlamellar phase and lamellar defects,
- (3) interstitial cavity in the crystalline unit cell [17], and the intermediate phase that forms between the silicon domains and
- (4) the BA dominant phase.

Figure (3) shows the effect of the silicon content on the lifetime (Figure 3(a)) and intensity (Figure 3(b)) of the o-Ps annihilation in the copolymer series, when four-component fits was used to analysis the LT spectra. The values of the lifetime and the intensity depend largely on the silicon content in the copolymers. There is an increases in long-lived component τ_4 and its intensity (I_4) as the silicon content increases.

This can be considered to be an indication of an increase in the free volume in the silicon region. The increase in the τ_4 represents an increase in the size of the free volume holes in the silicon phase. The increase in the intensity in the silicon phase represents an increase in the number of the free volume holes and indicates the higher fraction of o-Ps annihilating in the silicon phase as the silicon content increases. The free volume increases as the silicon phase becomes the dominant phase and the morphology changes from small spherical domains of silicon to larger domains, to bicontinuous phase, and then to small spherical domains of BA in a matrix of silicon as shown from the AFM results. The shortest long-lived component τ_3 and its intensity (I_3) show an unstable increasing trend. This long-lived component (τ_3) can be attributed to the change in the free volume in BA phase. It is also worthwhile considering the possibility that Ps trapping in dislocations or in vacancies that are associated with dislocations in the crystalline region of the BA segment could also affect the o-P characteristics in the PALS.

Therefore, in addition to, the microphase separation, the change in the crystallinity in PSBA copolymer can have influence on the positron annihilation mechanism and increasing in the free volume in the BA region (τ_3) can be an evidence of looser packing of the BA macromolecular chains and of the formation of additional free volume at the phase boundaries. This might offer additional evidence of the formation of o-Ps in both the crystalline and amorphous phases, depending on the material under investigation, as was reported in several articles in the literature [9]. In this case the increasing I_3 as well as I_4 with silicon content is most probably a result of the decreasing crystallinity in the BA phase. The increases in the τ_3 , τ_4 , I_3 and I_4 with an increase in the silicon content shows a nonlinear relationship.

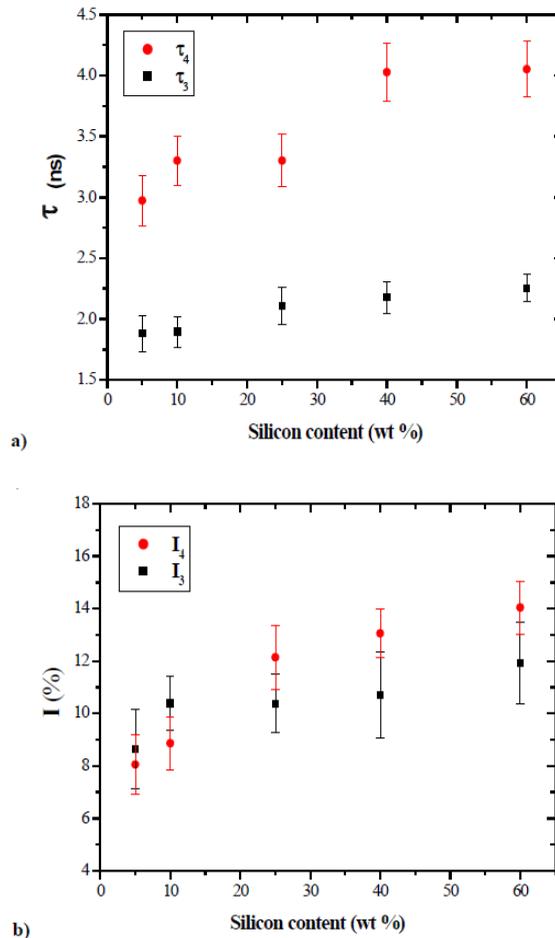


Figure 3: Chemical composition effect on the o-Ps lifetime (τ)(a) and intensity (I) (b) in PSBA copolymer series.

Figure (4) shows the effect of the silicon content on the radii of the free volume holes (R_3 and R_4). The smaller value (R_3) corresponds to the free volume holes in the BA phase and the larger one (R_4) to the free volume holes in the silicon phase. Both radii of the free volume holes in Figure 4 increase as the silicon content increase. The increase in the radius obtained for the BA phase in the copolymer when compared with the radius of the free volume holes in the BA homopolymer could be a result of the increase in the dislocations and imperfections in the BA phase in the copolymers due to the silicon segment disruption of the lamella structure, as has been reported using AFM in other type of copolymer series [18]. The change in the degree of crystallinity can lead to a change in the amorphous regions, and subsequently to a change in the lifetime and intensity of the o-Ps annihilations. No clear relationship can be drawn, however, between the degree of crystallinity and the o-Ps characteristics, because in all the PSBA copolymer series the degree of crystallinity decreases as the silicon content increases, which can also affect the o-Ps characteristics.

One can expect a higher free volume to occur due to both the microphase separation and the change in the degree of the crystallinity in the PSBA copolymer. In other words, a high free volume and density is the result of the influence of the silicon regions on the BA amorphous regions, and the BA amorphous regions in turn influence

the neighbouring crystalline structure of the BA region. Furthermore, increasing the silicon content results in widening the amorphous regions in-between the crystalline regions of the BA folding chains in the lamella structure as shown from the AFM results. Obviously broadening the amorphous regions will lead to an increase in the size of the free volume holes in the intermediate region between the crystalline region and the amorphous region, and in the crystalline region.

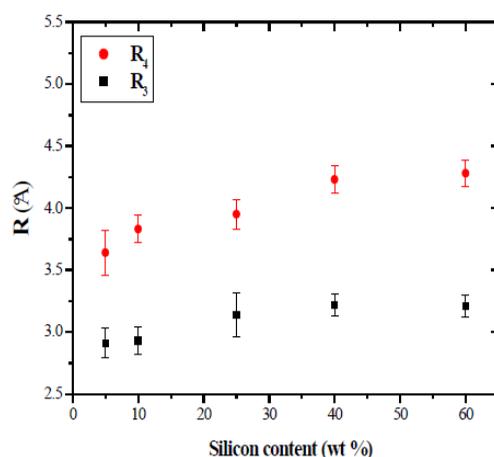


Figure 4: Chemical composition effect on the radius (R) of the free volume holes in PSBA copolymer series.

CONCLUSIONS

The effect of the chemical composition in the series of PSBA Copolymer, on copolymer morphology, crystallinity and free volume were investigated. The free volume in the series was determined using the PALS technique and the results showed increasing the silicon content lead to an increase in the intensity of Ps and the lifetime of the o-Ps. The results also showed that the mean lifetime of o-Ps reflects the size of the free volume holes, and the lifetime of o-Ps found to be very sensitive to changes in the free volume caused by changes in the molecular structure of the copolymers. It has been found, from AFM and PALS results; that the free volume increases as the silicon phase becomes the dominant phase and the morphology changes from small spherical domains of silicon, to bicontinuous phases, and then to small spherical domains of BA in a matrix of silicon. It has also appeared, from AFM, WAXD and PALS results; that the crystal structure has great effect the free volume of the Poly(silicon-butyl-adipate) (PSBA) copolymers.

REFERENCES

- [1] Ekin, A.; Webster, D. C. Library synthesis and characterization of 3-aminopropyl-terminated polydimethylsiloxanes and poly(ϵ -caprolactone)-*b*-polydimethylsiloxanes, *Journal of Polymer Science, Part A: Polymer Chemistry* 2006, 44(16), 4880-4894.
- [2] Rangarajan, P.; Register, R. A.; Adamson, D. H.; Fetters, L. J.; Bras, W.; Naylor, S.; Ryan, A. J.; Dynamics of structure formation in crystallizable block copolymers. *Macromolecules* 1995, 28(5), 1422-1428.
- [3] Loo, Y.-L.; Register, R. A.; Ryan, A. J.; Modes of crystallization in block copolymer microdomains: breakout, templated, and confined. *Macromolecules* 2002, 35(6), 2365-2374.

- [4] Müller, A.; Balsamo, V.; Arnal, M., Nucleation and crystallization in diblock and triblock copolymers. In *Block Copolymers II*, Springer, Berlin / Heidelberg, 2005; pp 1-63.
- [5] He, C.; Suzuki, T.; Shantarovich, V. P.; Kondo, K.; Ito, Y.; Positron annihilation in hypercrosslinked polystyrenes. *Chemical Physics* 2003, 286(2-3), 249-256.
- [6] Danch, A.; Osoba, W.; Stelzer, F.; On the α relaxation of the constrained amorphous phase in poly(ethylene). *European Polymer Journal* 2003, 39(10), 2051-2058.
- [7] Dutta, D.; Bhattacharyya, A.; Ganguly, B. N.; Microstructural study of aromatic polyamide membrane material. *Journal of Membrane Science* 2003, 224(1-2), 127-135.
- [8] Jean, Y. C.; Mallon, P. E.; Schrader, D. M., Principles and applications of positron and positronium chemistry. First ed.; World Scientific Publishing, Singapore, 2003; pp 253-280.
- [9] Li, X.; Gidley, D. W.; Hristov, H. A.; Yee, A. F.; Positronium formation in semicrystalline poly(ethylene terephthalate). *Polymer* 1994, 35(1), 14-17.
- [10] Sánchez, V.; López, R.; Fucugauchi, L. A.; Ito, Y.; Positron-annihilation lifetime study of vapor sorption in polypropylene and polytetrafluoroethylene. *Journal of Applied Polymer Science* 1995, 56(7), 779-791.
- [11] Bartos, J.; Sausa, O.; Bandzuch, P.; Zrubcová, J.; Kristiak, J.; Free volume factor in supercooled liquid dynamics. *Journal of Non-crystalline Solids* 2002, 307-310, 417-425.
- [12] Ferreira Marques, M. F.; Gordo, P. M.; Kajcsos, Zs.; Lopes Gil, C.; de Lima, A. P.; Queiroz, D. P.; de Pinho, M. N.; Positron studies of the temperature-dependence of free volumes in Polydimethylsiloxane /poly(propylene oxide) urethane/urea membranes. *Radiation Physics and Chemistry* 2007, 76 (2), 129–133.
- [13] Li, B.; Xu, D.; Jiang, Z.; Zhang, X.; Liu, W.; Dong, X.; Pervaporation performance of PDMS-Ni²⁺+Y zeolite hybrid membranes in the desulfurization of gasoline. *Journal of Membrane Science* 2008, 322(2), 293-301
- [14] Tao, S.J.; Positronium Annihilation in Molecular Substances. *Journal of Chemical Physics*, 1972. 56(11): p. 5499-5502.
- [15] Eldrup, M., Lightbody D., and Sherwood J.N.; The temperature dependence of positron lifetimes in solid pivalic acid. *J. Chemical Physics*, 1981. 63(1-2): p. 51-58.
- [16] Bug, A.L.R., Deng, Q., F. and Jean Y.C.; Simulation of positronium: Toward more realistic models of void spaces in materials. *J. Radiation Physics and Chemistry*, 2007. 76(2): p. 237-242.
- [17] Cheng, M.-L.; Sun, Y.-M.; Chen, H.; Jean, Y. C.; Change of structure and free volume properties of semi-crystalline poly (3-hydroxybutyrate-co-3-hydroxyvalerate) during thermal treatments by positron annihilation lifetime. *Polymer* 2009, 50(8), 1957-1964.
- [18] Abdallah A. B. E, Peter M.; Microscopic surface and bulk morphology of semicrystalline polydimethylsiloxane - polyester copolymers, *Journal of applied polymer science* 2010, 155(3), 1518-1533.