Positron Lifetime Distributions and Free Volume Parameters of PEO/PMMA Blends Determined with the Maximum Entropy Method

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ABSTRACT: The temperature dependence of the average free volume hole size and its distribution in blends of poly(methyl methacrylate) and poly(ethylene oxide) were studied by positron annihilation lifetime spectroscopy. Measurements at room temperature, 70 °C, and 110 °C all indicate that the average ortho-positronium lifetime (τ_3), and thus the free volume hole size of the blends, shows a positive deviation from additivity of the values of the pure components. Mean ortho-positronium (o-Ps) lifetimes and intensities were calculated with the POSITRONFIT program, while o-Ps lifetime distributions were obtained from evaluations made with a recently introduced program based on Bayes' theorem and the maximum entropy principle. o-Ps lifetime distributions were successfully calculated for all measured spectra and offer valuable additional information about the structure of the studied blends. At 70 °C, the distributions seem to reflect the lifetimes in a blend of binodal composition. Large differences in width of the o-Ps lifetime distributions as a function of blend composition and temperature are observed.

Introduction

Polymer blends are combinations of at least two polymer components which are miscible on a molecular scale or form immiscible or phase-separated heterogeneous multiphase systems. Miscibility in polymer blends is usually judged on the basis of the existence of a single glass transition temperature measured by differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA). These methods are, however, sensitive only to heterogeneities larger than approximately 50 nm in domain size.[1] Solid state NMR has been reported to be capable of a more refined assurance of miscibility at the segmental level.[2−4]

A polymer blend that has been reported to be miscible in the melt state is poly(ethylene oxide)/poly(methyl methacrylate) (PEO/PMMA).[5−7] The structure and crystallinity of these blends have been studied with DSC and optical microscopy, as well as with a variety of other techniques, e.g., dilatometry,[5,8] SAXS and SANS,[8−12] infrared dichroism, birefringence and rheological studies,[,6,14−17] IR spectroscopy,[7,8] NMR,[4,19] and ESR spectroscopy.[20] Although miscibility in the melt state has been reported, the solid state properties are composition-dependent, as demixing and crystallization takes place. Extensive crystallization studies of PEO/PMMA blends have been performed by several groups.[5,7,11,13,18,21,22] Martuscelli *et al.*[5] showed that up to a content of about 40 wt % PMMA, blend films are completely filled with PEO spherulites, while no separated domains of PMMA can be observed. This observation suggests that for such compositions the PMMA molecules are incorporated together with amorphous PEO in interlamellar regions of PEO spherulites. For blends containing 50% PEO or less, the spherulite dimensions are drastically reduced. However, blends with a PEO content below 20 wt % show no evidence of crystallinity. On the basis of SANS and SAXS measurements, Russell *et al.*[12] suggested that a pure amorphous PEO phase is located between the crystalline lamellae and the mixed amorphous phase.

Single glass transition temperatures (T_g) have been reported over the whole PEO/PMMA composition range.[5−7] The T_g's were measured immediately after a quench of the blends from the melt to at least −100 °C. Li and Hsu[7] showed, however, that samples containing less than 50% PEO, which were crystallized up to 30 days at room temperature, gave two T_g's in a DSC run. This implies that phase separation of the two polymers can take place at room temperature. IR measurements showed that no spectroscopic changes could be detected after 3 days for blends with more than 50% PEO, while crystallization continued at room temperature even after 3 days for samples with less than 42% PEO. DSC studies of melt mixed PEO/PMMA blends containing 38% PEO were carried out as a function of time and indicated that crystallization after phase separation continues even after several weeks at 28.6 °C.[23,24]

Privalko *et al.*[8] concluded from PVT (pressure−volume−temperature) measurements that PEO/PMMA miscibility is a result of specific interactions between the components, which results in homogeneity of the melt at a macroscopic level of the order of the coil size, and that the external volume shows a negative deviation from additivity over the whole composition range. It was concluded from SAXS measurements that, despite miscibility at the "macrolevel", the studied blends exhibited significant composition fluctuations at a segmental level. Other authors[5] obtained specific volumes of PEO/PMMA mixtures at temperatures higher than that of PEO melting by dilatometric measurements. Except for a few blends, a positive excess volume of mixing was found. Wu[14] calculated average free volumes of several different blends from WLF parameters. The results indicate an expansion of free volume upon blending PEO with PMMA. The above results are in some cases contradictory. Further investigations are needed to explain the behavior of this complicated blend system. Positron annihilation lifetime spectroscopy is a technique that gives information on the segmental level and may contribute to the understanding of the

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behavior of these blends.

Positron annihilation lifetime spectroscopy (PALS) can be used to probe the free volume hole size of polymers. By introducing positrons from a radioactive source into a polymer sample and measuring the lifetime of the positrons, conclusions can be drawn about the free volume hole sizes in the polymer. There are at least three different ways for the positron to annihilate with an electron in the sample. It can annihilate as a free positron with an electron in about 0.3–0.5 ns. The positron can also capture an electron from the material and form a bound state, called a positronium “atom”. In para-positronium (p-Ps), the spins of the two particles are antiparallel, leading to very fast annihilation (0.125 ns). Ortho-positronium (o-Ps), in which the spins are parallel, has a mean lifetime of 142 ns in vacuum. In polymers, the o-Ps lifetime is shortened to 1–5 ns, because the positron picks off an electron of opposite spin from the surrounding medium. A PAL spectrum of a polymer is usually found to consist of three different mean lifetimes: τ_1, τ_2, and τ_3, corresponding to the different annihilation processes described above. Each lifetime also has a relative intensity, I_1, I_2, and I_3, proportional to the probability of each process. It has been shown that o-Ps is preferentially localized in holes or regions of low electron density.[25] The probability of the pick-off process is directly related to the electron density of the cavity wall and inversely associated with the free volume hole radius, which can be calculated by a semiempirical equation:[25]

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \tag{1}$$

PALS has been shown to be a useful technique for studying polymer blends.[26–33] Both positive[26,33] and negative[27,30,32] deviations from free volume additivity have been reported. There are several complications, except for crystallization, that can be expected when mixtures of polymers or filled polymers are studied with the positron annihilation technique. When investigating the temperature dependence of blends, it is important to be aware that the polymers most probably have different thermal expansivities. If the polymers are not miscible on the molecular level, there will be interphases or interfaces between the two phases that will affect the results; the size of the different phases can also probably affect the positronium formation and annihilation probabilities. It may even be possible that the positrons and positronium atoms prefer to diffuse to one of the phases. In filled polymers, the particle size and distribution of particles in the matrix are of importance. As concerns semicrystalline polymers, it has been shown that the o-Ps annihilates in the amorphous phase and that the o-Ps intensity decreases with increasing crystallinity.[34–36] The most supported model for positronium formation is the spur model, in which the Ps formation process is dominated by the radiation chemistry in the spur. For example, I_3 decreases in several polymers during long-term source radiation exposure,[37–39] and the presence of polar groups also leads to reduced o-Ps formation.[40–41] The interpretation of I_3 as a measure of the number of holes[42] can, therefore, in some cases, be questioned.

The most commonly used program for evaluations of positron lifetime spectra is called POSITRONFIT[43] and gives mean lifetimes and intensities. Recently, programs extracting positron lifetime *distributions* from lifetime measurements have been developed.[44,45] A program called CONTIN,[46] which uses a Laplace inversion technique, has for instance been used to study hole size distribution changes in an epoxy polymer at different temperatures and pressures.[46,47] A recently developed program that gives distributions is called MELT and uses a Bayesian method and the maximum entropy principle. This program was developed by Shukla *et al.*[45,48] It has been shown that average values obtained with MELT agree well with POSITRONFIT values when studying lifetimes shorter than 0.5 ns.[45] In a recent study of polymers we showed that average o-Ps lifetimes and intensities calculated with the two methods also agree well with each other over a large intensity and lifetime range.[49] Simulated spectra have been evaluated with both CONTIN and MELT, and a comparison of the results obtained shows that MELT is very suitable for resolving polymer spectra.[50]

The purpose of the present study is to investigate PEO/PMMA blends with a spectroscopic method, sensitive to changes at the angstrom scale, not used for these blends before. It is also important to compare the lifetime results obtained with the two programs, POSITRONFIT and the recently developed MELT. The lifetime distributions are studied as a function of composition and temperature.

Experimental Section

Materials and Sample Preparation. The PEO used in this study had a density of 1210 kg/m^3 and a viscosity average molar mass of 200 000 according to the supplier (Scientific Polymer Products, Inc.). The atactic PMMA 6N (ρ = 1190 kg/m^3) (Röhm GmbH), containing approximately 6% methyl acrylate groups, had an $\bar{M}_n$ of 47 000 g/mol and an $\bar{M}_w$ of 90 000 g/mol, determined by size exclusion chromatography measurements. Prior to blending, the homopolymers were dried in a vacuum oven for at least 24 h. The PEO was dried at room temperature, while the temperature used for PMMA was 60–65 °C. PEO/PMMA blends were prepared by melt mixing in a Brabender Plasticorder at 180 °C operating at 40 rpm for 10 min. In this way 14 different blend compositions (by volume) were prepared. The pure homopolymers were treated in the same way as the blends. After mixing, the blends were compression molded at 190 °C into samples with a thickness of 2 mm and a diameter of 25 mm. The samples were allowed to cool to room temperature slowly. Between processing and measurements, the samples were stored in a desiccator to prevent moisture uptake.

Spectroscopic Measurements and Data Analysis. A fast–fast coincidence system with CsF crystals was used for the PALS measurements at room temperature. The source consisted of ^{22}Na deposited between two 8 μm thick Kapton foils. It had an activity of 2.2 MBq, which gave a count rate of approximately 1100 cps. The time resolution could be determined to be 280 ps by using a ^{60}Co source. The channel width during the measurements was 23.6 ps. The source was placed between two identical pieces of the material under study, and five spectra containing 2.5–3 × 10^6 counts each were collected for every blend and homopolymer. The measurements were all performed 1–4 weeks after molding.

Additional measurements at higher temperatures and at room temperature were performed at the Materials Department at Risø National Laboratory in Denmark. A conventional fast–fast spectrometer comparable with the one described above was used. The channel width of the spectrometer was 26.8 ps and the overall time resolution was about 250 ps. Kapton foils were used for the ^{22}Na source in this case as well, which gave a count rate of approximately 100 cps. Positron measurements were performed on the two pure polymers and on four different blend compositions running the following temperature cycle: room temperature, 70 °C, 110 °C, and room temperature. All the polymer samples in this study were 1 year old. Approximately 2 × 10^6 counts were collected for each spectrum.

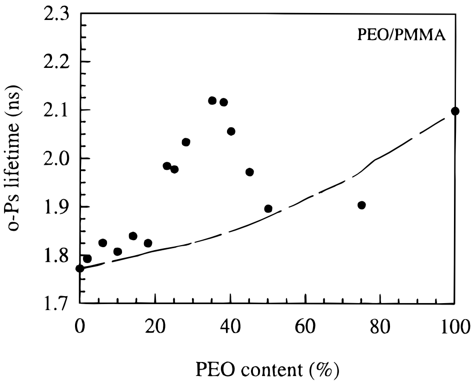

Figure 1. Average o-Ps lifetime dependence of blend composition at room temperature.

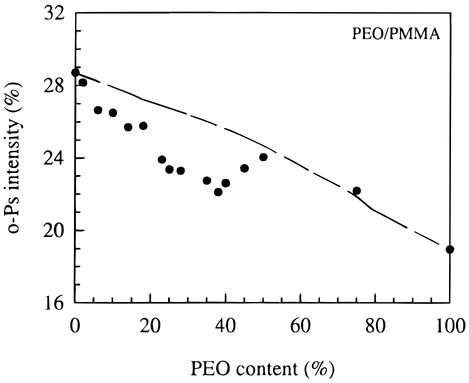

Figure 2. Average o-Ps intensity dependence of blend composition at room temperature.

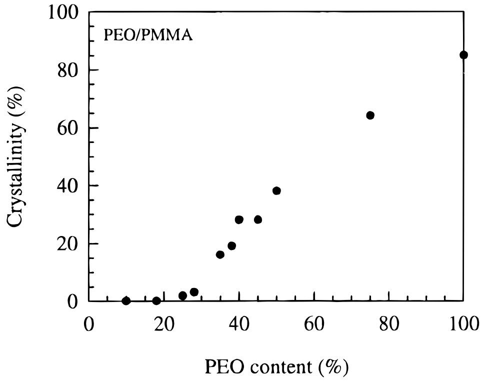

Figure 3. Crystallinity of the blends determined with DSC.

The well-known program POSITRONFIT[43] was used to analyze the spectra into three mean lifetime components. No source correction was made for the room temperature spectra measured in our laboratory. The MELT program, which besides average lifetimes and intensities also gives lifetime distributions, was used. In the MELT program, it is not possible to fix the number of lifetimes or the value of any lifetime or intensity. This means that all spectra are evaluated without constraints. Although it is possible to make a source correction, that was not done in this study. The maximum entropy, α, was set to a constant value of 10^{-6} for all evaluations. The temporal origin, t_0, was varied within one channel for each set of data, and the fit giving a χ^2 close to one and the highest probability value $p(\alpha)$ was chosen as the best fit and used for further comparisons of lifetime distributions. The same spectra were evaluated both with POSITRONFIT and MELT. For the spectra measured at different temperatures, source correction was used for all POSITRONFIT evaluations, but no constraints were applied. The same single spectra were used for the MELT calculations without any source corrections.

Differential Scanning Calorimetry Measurements. To obtain the heat of fusion of the blends, DSC measurements were run on a Perkin-Elmer DSC-7. All measurements were calibrated against indium, and a heating rate of 10 °C/min was used. To calculate the degree of crystallinity, the heat of fusion of 100% crystalline PEO, which equals 203 J/g,[51] was used. The samples were stored in a dry atmosphere for 6 months before the DSC measurements.

Results and Discussion

o-Ps Mean Lifetimes and Intensities at Room Temperature. The influence of the amount of PEO on the mean o-Ps lifetime in PEO/PMMA blends at room temperature is shown in Figure 1. With increasing PEO content, the lifetime increases from the low value of pure PMMA (1.77 ns) to the higher value of pure PEO (2.10 ns). A maximum in the lifetime values can be observed between approximately 25 and 50% PEO. The o-Ps lifetime becomes much larger than what can be expected from simple additivity of the lifetimes of the homopolymers at each composition. By adding spectra of the pure constituents in ratios of their weight fractions, spectra of simulated immiscible blends were constructed and evaluated with POSITRONFIT. The result of this exercise is shown as a dotted curve in Figure 1, and it can be observed that it does not coincide with a straight line of additivity. This result suggests that, even in a completely immiscible blend, the mean free volume hole size as determined with PALS cannot be expressed by a simple rule of mixtures. Furthermore, despite the existence of two distinct mean lifetimes of 1.77 and 2.10 ns in the simulated spectra of immiscible blends, POSITRONFIT predicts only one new mean o-Ps lifetime between the values of the pure constituents. The lifetime of the constituents seems to be too close to be separated by the POSITRONFIT procedure. The o-Ps intensity, I_3, as a function of PEO content is shown in Figure 2, together with the results of the simulated immiscible blends. Below 40% PEO, the decrease in I_3 is faster than for simulated immiscible blends. This reflects the o-Ps formation probability change and means that the local environment of the positrons and positronium atoms has been changed and is different from that of the pure components. However, above 50% PEO, the o-Ps intensity of the blends seems to be comparable with that of a demixed system.

PEO Crystallinity and Composition in the Amorphous Part of the Blends. The crystallinity of the blends measured by DSC is depicted in Figure 3. The data shown are from the first heating run of samples that were stored in a desiccator at room temperature for half a year since preparation. The crystalline melting peak temperature of pure PEO was determined to be 67 °C, with a melting range between 20 and 80 °C. The crystallinity of pure PEO is 85%, while no crystallinity can be detected in blends with a lower PEO content than 25%. This is in good agreement with what other authors have shown.[5,7,19] The glass transition temperatures of the pure components, measured with DSC, are 95 °C for PMMA and −60 °C for PEO. Glass transition temperature data for PEO/PMMA blends can be found in ref 5−7. The general picture is that for quenched samples, the Fox equation is applicable,

$$\frac{1}{T_g} = \frac{w_a}{T_{gb}} + \frac{w_b}{T_{gb}} \qquad (2)$$

where T_g is the glass transition temperature of the blend, T_{ga} and T_{gb} are the glass transition temperatures

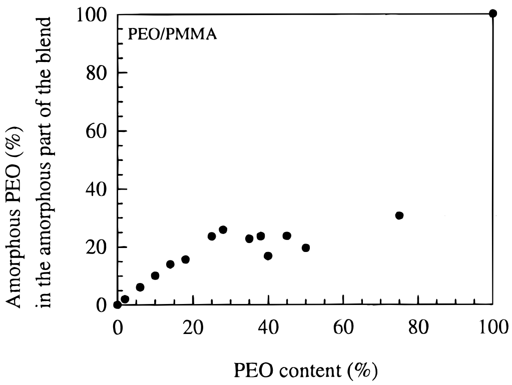

Figure 4. Amorphous PEO in the amorphous part of the blend as a function of blend composition.

of polymers A and B, respectively, and w_a and w_b are the respective weight fractions of polymers A and B in the blend. The equation predicts that the T_g of a miscible blend is somewhat lower than the linear relationship. It follows from eq 2 that, above approximately 35% PEO, the T_g of the blends is below room temperature, while it is above room temperature in blends containing less than 35% PEO.

Figure 4 shows the variation in the amount of PEO in the amorphous part of the blend, calculated from DSC data, as a function of the total amount of PEO. The percentage of amorphous PEO increases linearly up to 25% PEO in the original blend. At approximately this composition, PEO starts to crystallize and the amorphous PEO part decreases slightly. In a sample containing pure PEO, the amorphous part will obviously consist of 100% PEO. At room temperature, the blends consist of a crystalline PEO part *probably* (Russell *et al.*[12] suggests pure amorphous PEO phase surrounding the crystals) surrounded by a PMMA-enriched amorphous phase. Phase separation and demixing by crystallization may be responsible for the observed effects on o-Ps lifetime and intensity shown in Figures 1 and 2. In the range where the free volume effects are observed, we are close to both the glass transition temperature and the crystallization temperature of the blends.[24] This leads to a competition between crystallization, glass transition shift, viscosity, and relaxation, which seems to result in very large free volume sites in blends of certain compositions. The o-Ps intensity dip in Figure 2 could be explained by the composition change in the amorphous part of the blend. The amorphous part will again be richer in PMMA above 25% PEO, and I_3 will increase toward the value of pure PMMA. It has been postulated that the I_3 value is a measure of the crystallinity in the sample and that, in a 100% crystalline polymer, the o-Ps formation probability approaches zero.[34] This has also been shown experimentally for PEEK[34] and PE.[35,36] Other reports have indicated I_3 values above zero for 100% crystalline material, for instance, for HDPE[52] and a random copolyester called ThermX.[28] An extrapolation of the o-Ps intensity in the amorphous blends, i.e., below 25% PEO, gives an I_3 of approximately 8% for 100% amorphous PEO, implying that the intensity resulting from free volume holes connected to crystalline parts could be as much as 11%.

o-Ps Lifetime as a Function of Temperature. Figure 5 shows the variation in the o-Ps lifetime with blend composition at room temperature, 70 °C, and 110 °C. The values were calculated with POSITRONFIT, and the samples were 1 year old at the time of data collection. The room temperature curve still shows the same behavior described earlier. It can be observed that the distinct maximum between 25% and 50% PEO at room temperature is not present at 70 °C, but the o-Ps lifetime over the whole composition range is now even higher above additivity values of the pure constituents, compared with the situation at room temperature. Both at 70 °C and at 110 °C, τ_3 shows a maximum or high plateau before reaching the lower value of pure PEO. The free volume hole size of all blends is larger than what can be expected from a linear relationship between the pure polymers. PEO and PMMA do not seem to have large interactions, or the packing of the molecules is not favorable at these temperatures, since the hole size tends to increase when the chain mobility increases.

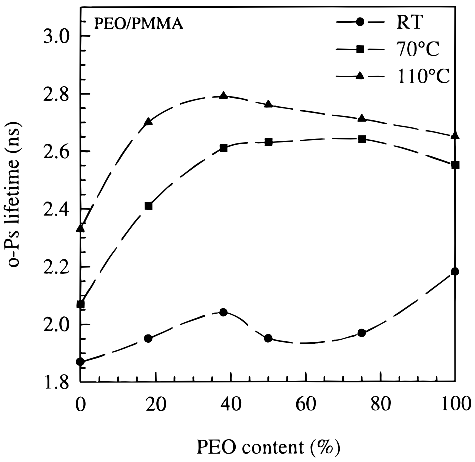

Figure 5. Average o-Ps lifetime dependence of temperature and blend composition. The volume percentage composition calculated at room temperature is not corrected for density changes at higher temperatures.

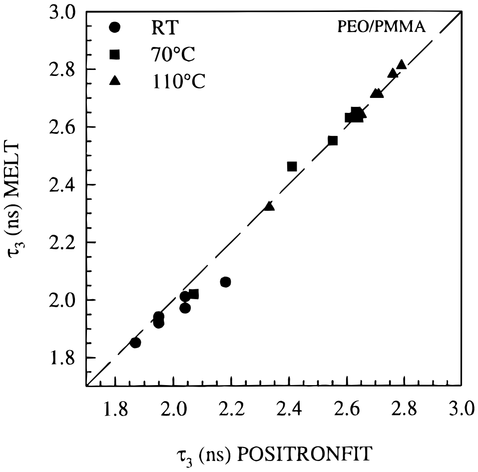

Figure 6. Comparison of average o-Ps lifetimes calculated with POSITRONFIT and MELT. Results are shown for measurements at different temperatures. The dotted line is for guidance only.

o-Ps Lifetime and Positronium Free Volume Hole Size Distributions. Evaluations of all the spectra were performed with the MELT program and gave, besides average lifetimes and intensities, lifetime distributions of the samples. Average values of MELT and mean values of POSITRONFIT evaluations are shown in Figure 6 and are found to agree well with each other. Figure 7 shows free volume hole size distribution curves of six different samples at different temperatures. The distribution change from pure PMMA to pure PEO at room temperature can be observed in

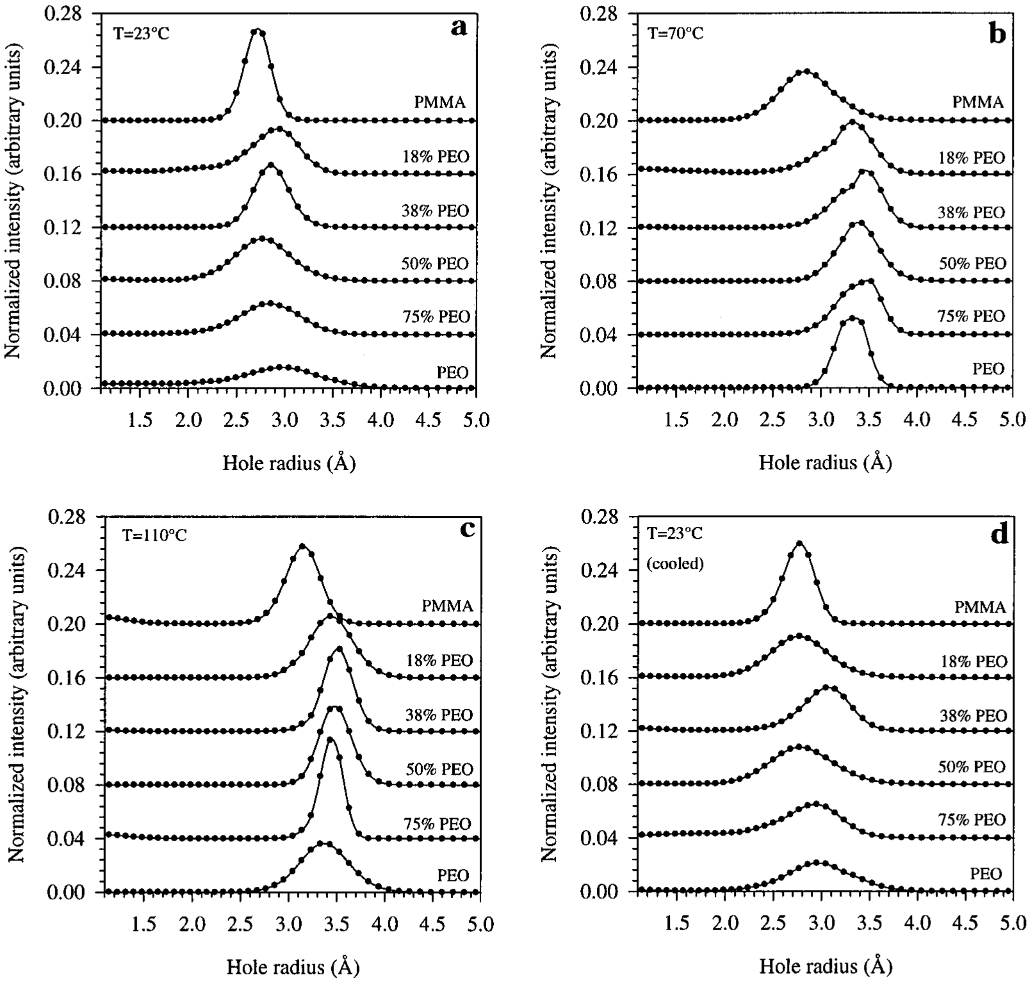

Figure 7. Free volume hole size distributions for the pure polymers and a few of the blends after different temperature treatments, calculated with MELT: (a) room temperature, samples aged for 1 year, (b) 70 °C, (c) 110 °C, and (d) samples just cooled from 110 °C to room temperature.

Figure 7a. The hole size distribution of PMMA is quite narrow, the PEO peak is extremely broad, and the blends have distribution widths between those of the pure polymers. Figure 7b shows the distributions at 70 °C. The PEO crystals have melted at this temperature, and the distributions are changed and shifted toward larger hole sizes, in agreement with the o-Ps lifetimes in Figure 5. The pure PMMA hole size distribution is quite broad at this temperature and has a tail stretching out toward larger radii. The blend containing 18% PEO shifts to higher values because of the PEO influence but, at the left side, the distribution has an unsymmetric appearance. For the blend with 38% PEO, the left side is even more unsymmetric and seems to show two distributions lying close to each other. It is interesting to see that the MELT program is actually sufficiently powerful to resolve the two separate distributions. That a double distribution appears at these blend compositions suggests that the two polymers are phase separated at the conditions used. The PEO crystals are melted, but the mobility of the polymer chains is too low to allow the PEO-rich parts to mix homogeneously within the measurement time. The 75/25 blend also shows this double distribution behavior. The 110 °C curves in Figure 7c show the free volume hole size distributions of the melted samples, which are narrower but at even larger radii. Pure PMMA is above T_g at this temperature. Only a single distribution appears, indicating that the system is more homogeneous. After melting, the samples were cooled to room temperature again; the cooling time was approximately 15 min. Immediately afterward, positron spectra were again collected. The distributions of these spectra are shown in Figure 7d. All blends show broader distributions in the second room temperature measurement than in the first. This demonstrates how slow the rearrangements on the molecular level are. The full width at half maximum (FWHM) of the o-Ps lifetime distribution for the homopolymers and their blends is reported in Table 1. Results from the whole temperature cycle are included.

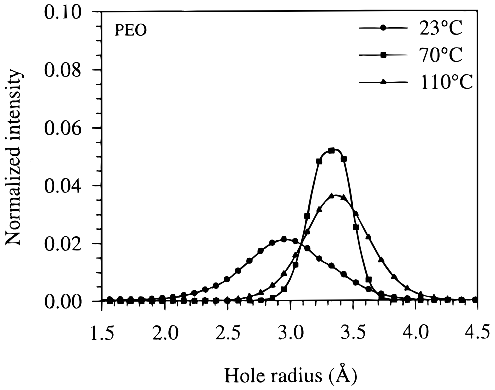

Figure 8. Free volume hole size distributions of PEO as a function of temperature.

Figure 8 shows the free volume hole size distributions of pure PEO at different temperatures. The small radii

Table 1. Variation in Full Width at Half-Maximum of o-Ps Distributions at Different Temperatures

PEO content, %	FWHM, ps			
	23 °C	70 °C	110 °C	23 °C, cooled
0	360	700	510	360
18	640	680	750	750
38	450	730	530	680
50	680	640	580	790
75	790	730	410	810
100	1100	530	810	980

on the left side of the very broad room temperature distribution originate from o-Ps atoms annihilating in small free volume sites, probably in areas constrained by crystals, at crystal surfaces, and at defects in the crystals. It is interesting to note that the distribution changes shape dramatically at 70 °C. The smallest holes of the room temperature distribution have disappeared because the crystals are replaced with melted material of larger free volume hole size. The hole size distribution is now narrower and located at larger radii. A rise in temperature to 110 °C makes the distribution become broader on the right-hand side. PMMA is a completely amorphous polymer which (in the glassy state) at room temperature shows a narrow distribution, reflecting that the free volume holes are small and of rather equal size. As the temperature is raised to 70 °C and 110 °C, the distribution broadens. The largest change in distribution width between aged and unaged samples at room temperature is found in the PEO/PMMA 38/62 blend. The distribution of a 1-year-old sample can be compared to the distribution of the same sample just cooled from 110 °C to room temperature (see Figures 7a and d). The old sample shows a narrower distribution that is placed at smaller radii. The nonaged sample shows a broader distribution that is shifted toward larger hole sizes.

Conclusions

In this study, we report o-Ps lifetimes and free volume hole size distributions in PEO/PMMA blends as a function of temperature and blend composition. We found that lifetime distributions could be obtained for all measured spectra by using the recently introduced MELT program. At room temperature, the PEO/PMMA blends show a larger mean o-Ps lifetime between 25 and 50% PEO than can be expected from simple additivity of the values of the homopolymers. At 70 °C and 110 °C, a positive deviation from additivity can be observed for all blend compositions. POSITRONFIT and MELT average τ_3 values show good agreement for the measurements performed at room temperature, 70 °C and 110 °C. Measurements performed on pure PEO at room temperature and above the crystalline melting temperature show that a part of the o-Ps atoms annihilate in small holes closely connected to crystals. The main part of the samples examined show only one free volume hole size distribution; exceptions are some of the blends at 70 °C. At this temperature, the hole size distribution seems to reflect the free volume holes in a blend of binodal composition and, to our knowledge, this has never been shown with the PALS technique before. We conclude that MELT is a valuable method that can be used to extract additional information on free volume hole size distributions in polymers.

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