Miscibility of Styrene–Maleic Anhydride and Styrene–Acrylonitrile Blends Studied by Positron Annihilation Lifetime Spectroscopy

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ABSTRACT: Blends of melt-mixed styrene–maleic anhydride and styrene–acrylonitrile copolymers were examined with respect to miscibility and free volume parameters. Differential scanning calorimetry, dynamic mechanical analysis, scanning electron microscopy, and positron annihilation lifetime spectroscopy were used to judge blend miscibility. It was found that blends containing copolymers with similar amounts of styrene were miscible. Positron annihilation lifetime spectra of all blends were evaluated with the POSITRONFIT and the MELT program, where the latter can be used to obtain lifetime distributions. The mean o-Ps lifetimes (or hole sizes) of the blends were found always to be between those of the pure constituents. Pronounced negative deviations of the o-Ps intensity from weighted averages were measured in miscible blends but not in immiscible ones. Immiscible blends exhibit, on the basis of MELT evaluations, unsymmetric and broader o-Ps lifetime distributions than do miscible blends.

Introduction

There is great industrial interest in polymer blends since blending is a relatively simple way to create materials with a wide variety of properties. To what extent a polymer pair is miscible determines the morphology of the blend, which in turn affects the mechanical properties of the material. The term miscible is used to describe blends that are homogeneous at a molecular level.[1] The miscibility of polymer blends is defined by the technique used and is often judged by studying the glass transition temperature (T_g) by differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA). These techniques are sensitive to approximately 10 nm in domain size.[1] The existence of one T_g between those of the constituent materials indicates miscibility, while two T_g's at the original positions are evidence of a completely immiscible blend. If two T_g's are found, which are shifted toward each other from the original values, the blend is termed partially miscible.

Blends of styrene–maleic anhydride (SMA) and styrene–acrylonitrile (SAN) copolymers have previously been shown to form miscible blends when the MA and AN contents do not differ too greatly.[2–6] Single glass transition temperatures were measured with DSC and DMA. Since neither SMA nor SAN is miscible with polystyrene,[3] interactions between MA and AN might be expected. Paul and Barlow[7] used an extended interaction model to theoretically analyze the miscibility of SMA and SAN blends. They found that, for high molecular weight copolymers, miscibility is possible only if the binary interaction parameter for the mixing of MA and AN units is less than zero. This suggests that MA and AN must interact exothermically with each other. This proposal was later confirmed by heat-of-mixing

experiments using low molecular weight liquid analogues.[5] It is known that SMA copolymers have a strong tendency toward alternation but that a more random nature of the macromolecular chains is obtained at higher styrene contents. Because of the low reactivity ratio of maleic anhydride, it is difficult to homopolymerize MA to high molecular weights. In SMA copolymers as well, the maximum MA content that it is possible to obtain is approximately 50 mol %. According to Kim et al.,[5] the more or less alternating SMA copolymers seem not to differ from those of more random structure with respect to miscibility with SAN copolymers. The same group[5] also measured volume changes upon mixing SMA and SAN copolymers and found a maximum volume contraction at high SAN contents with a tendency toward volume expansion at high SMA contents.

Positron annihilation lifetime spectroscopy (PALS) is a technique that can be used to give a measure of the angstrom scale free volume hole sizes in polymers. In PALS measurements, positrons from a radioactive source are used to probe the material. When a positron enters a polymer sample, it can annihilate as a free positron with an electron in the material. The lifetime of a free positron in a polymer is often 0.3–0.5 ns. The positron can also form a bound state called positronium (Ps) together with an electron in the material. If the spins of the positron and electron are antiparallel, parapositronium (p-Ps) with a lifetime of 0.125 ns is formed. In orthopositronium (o-Ps), the spins of the positron and electron are parallel. The lifetime of o-Ps is longer than that of p-Ps and free positrons, and equals 1–5 ns in polymers. The positron in o-Ps annihilates via pick-off of an electron of opposite spin from one of the surrounding atoms. The pick-off annihilation lifetime is inversely proportional to the overlap of the positron and electron wave functions, and can therefore be related to the size of the low electron density site at which the annihilation occurs. A semiempirical equation can be used to calculate an average free volume hole radius from the measured o-Ps lifetime (τ_3):[8,9]

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

It is assumed in this model that the free volume holes are infinite spherical potential wells of radius R_0. An electron layer exists in the region $R < r < R_0$, where $R_0 = R + \Delta R$. For polymers, the value of $\Delta R = 1.66$ Å appears to be a good approximation.[10] A long o-Ps lifetime thus corresponds to a large hole size, while a shorter lifetime corresponds to smaller holes. With PALS, it is possible to probe free volume sites of a radius of 1−10 Å.

Several PALS studies of polymer blends—both miscible[11−15] and immiscible[11,13,16]—have been published. Generally, the o-Ps lifetimes of blends show a negative deviation from those of the starting materials (or are approximately linearly additive) in miscible blends.[11−15] The o-Ps formation probability (I_3), however, shows no systematic tendency in the different miscible systems. The picture is not clear for immiscible blends. Both τ_3 and I_3 have been reported to deviate both positively and negatively from linear additivity.[11,13,16] A particular difficulty exists in blends with crystallizable constituents, where crystallization and changes in crystallinity[17] can affect the o-Ps lifetime and intensity.

The conventional means for determining miscibility in a blend system is, as mentioned earlier, performed by measuring the glass transition temperature(s) with, e.g., DSC, DMA, or dielectric measurements. Nuclear magnetic resonance is sometimes also used to judge miscibility. With PALS, it is possible to obtain T_g values by measuring the hole size change as a function of temperature. However, this method is time-consuming and gives less accurate values for the glass transition temperature than the methods mentioned above. In addition to average hole sizes (lifetimes), lifetime distributions and intensities can also be extracted from positron lifetime spectra. A prediction of the appearance of lifetime distributions in amorphous blends, where the distributions of the original polymers differ sufficiently from each other with respect to lifetime, can be made. For a miscible system, a single Gaussian-like distribution between those of the two original ones is expected, because the blend is homogeneous on the molecular level. On the other hand, an immiscible blend is expected to exhibit a broader distribution as a consequence of the different phases and interphases present in the blend. This gives us reason to believe that studies of o-Ps lifetime distributions should give indications of blend miscibility on a molecular scale. Furthermore, the o-Ps intensity (o-Ps formation probability) may be expected to differ between miscible and immiscible blends. In the case of SMA and SAN copolymers, I_3 is determined by the concentration of MA and AN units present in the polymer chains owing to inhibition[18] and can be described according to eq 2,[19]

$$I_3 = I_3^0 \left[A + (1 - A)/(1 + \sigma C)\right] \quad (2)$$

where I_3^0 is the o-Ps yield at $C = 0$, C is the concentration of scavenger in mol/dm^3, A is a constant related to the saturation value of I_3, and σ is a fitting parameter called the inhibition constant. The I_3 of immiscible systems is supposed to be a weight average intensity based on a simple composite model[20]

$$I_{3,im} = w_A I_{3,A} + w_B I_{3,B} \quad (3)$$

where $I_{3,im}$ is the theoretical intensity of the immiscible blend, w_A and w_B are the weight fractions of components A and B, and $I_{3,A}$ and $I_{3,B}$ are the respective theoretical o-Ps intensities of the pure components calculated from eq 2. Miscible blends can have an o-Ps intensity that differs from a weighted average because of synergistic inhibition effects, changes in positron and positronium mobility, and changes in free volume fraction.

In a previous study,[18] we reported free volume properties of SMA and SAN copolymers of different compositions determined by PALS. The aim of this study is to examine miscible and immiscible blends of SMA and SAN with positron lifetime measurements to investigate how the free volume parameters obtained are influenced by blend miscibility. It is advantageous to use SMA/SAN blends as a model system, since miscible and immiscible blends can be prepared by changing the composition. The copolymers and their blends are also amorphous, which means that no crystalline parts exist that can further complicate the system.

Experimental Section

Materials and Sample Preparation. Styrene−maleic anhydride and styrene−acrylonitrile copolymers of different compositions (Table 1) were used. Blends of the copolymers were prepared by melt-mixing them at 190 °C for 10 min in a Brabender Plasticorder AEV 330. Three series of blends, named A, B, and C, were prepared. Series A blends are 50/50 wt % blends of SAN25 (25 wt % AN) and SMA of varying MA concentrations. The series B blends are 50/50 wt % blends of SMA24 (24 wt % MA) with SAN of different AN contents. In the C blends, SMA24 and SAN25 are mixed in 10/90, 20/80, ..., and 90/10 wt % compositions. Prior to blending, the polymers were dried under vacuum at 80 °C for at least 15 h. All blends were pressed into 2 mm thick samples at 190 °C and cooled between cold aluminum plates for 10 min. Rectangular samples for dynamic mechanical analysis (DMA)

Table 1. Molecular Weights and Supplier Names for the Polymers Used

polymer	MA or AN content (wt%)	T_g (°C)[a]	M_w (kg/mol)[b]	source
SMA8	8	114	224	Monomer-Polymer Dajac Labs
SMA14	14	130	50	Monomer-Polymer Dajac Labs
SMA22	22	147	110	DSM Research
SMA24	24	153	110	DSM Research
SMA28	28	161	110	DSM Research
SMA32	32	173	110	DSM Research
SMA50	50	202	50	Scientific Polymer Products
SAN22 (Luran 368R)	22	109	210	BASF
SAN25 (Luran 358N)	25	107	170	BASF
SAN33 (Luran 378P)	33	109	150	BASF

[a] According to DSC measurements in ref 20. [b] Molecular weights of SAN measured with size exclusion chromatography and calibration with narrow polystyrene standards. Other molecular weight data are values according to the supplier.

Table 2. Glass Transition Temperatures from DSC and Maximum Tan δ Temperatures of Series A Blends

blend composition	T_g (°C) from DSC	$T_{\tan\delta,\max}$ (°C) from DMA
SMA8/SAN25	110	122
SMA14/SAN25	109 and 129	115 and 138
SMA22/SAN25	124	136
SMA24/SAN25	126	138
SMA28/SAN25	127	144
SMA32/SAN25	118	129 and 182
SMA50/SAN25	101	111 and 192
SMA24/SAN22	126	
SMA24/SAN25	126	
SMA24/SAN33	115	123 and 154

measurements were prepared by compression molding as described above. Between processing and measurements, the samples were stored in a desiccator to prevent moisture uptake.

Differential Scanning Calorimetry. The glass transition temperatures of the blends were measured using a Perkin-Elmer DSC-7 instrument. Each sample was heated to approximately 20 °C above the respective T_g with a heating rate of 40 °C/min. The sample was then quenched to 40 °C, and the second heating run of 10 °C/min was used to determine T_g as the midpoint of the heat flow change. All measurements were calibrated against indium.

Dynamic Mechanical Analysis. Rectangular torsion bars were analyzed in the solid state with a Rheometrics RDA II instrument in the oscillatory torsion mode. Temperature sweeps were performed at a heating rate of 2 °C/min; the angular frequency was 1 rad/s, and a shear strain of 0.2% was used. The glass transition temperature was determined as the tan δ peak temperature, $T_{\tan\delta,\max}$, since it was not possible to obtain the more appropriate temperature at G'' maximum in all cases.

Density Measurements. A Micromeritics multivolume pycnometer 1305 working with helium gas was used to determine densities (at 22 °C) of the compression molded samples. Melt-pressed samples of approximately 1 g, free from visible bubbles or pores, were studied.

Positron Annihilation Lifetime Spectroscopy. Positron lifetime measurements were performed using the same experimental setup as in our previous study.[18] The ^{22}Na source, which was sandwiched between 8 μm thick Kapton foils, had an activity of approximately 1.7 MBq, giving a count rate of 600 cps. The time resolution of the spectrometer was 280 ps as measured with a ^{60}Co source. Five spectra of three million counts were collected for every blend. The measurements were all performed in air at room temperature. The spectra were analyzed with both the POSITRONFIT[21] and the MELT (version 3.0) program.[22] With POSITRONFIT, the spectra were analyzed into three mean lifetimes and intensities. No constraints or source corrections were applied. Evaluations with MELT give not only average lifetimes and intensities but also lifetime distributions. Five spectra were added together for each sample and then evaluated. No source correction or constraints were used. The entropy weight, α, was kept constant and equal to 10^{-6} for all evaluations, and the criteria used in ref 23 were used to choose the best fit.

Results and Discussion

Miscibility Determination. Several complementary methods were used to determine whether the melt-mixed blends were miscible. Glass transition temperatures from DSC measurements of series A and B blends are shown in Table 2. The SMA14/SAN25 blend is the only one exhibiting two T_g's, implying that all the other blends are miscible. However, the A blends containing SMA32 and SMA50 and the series B blend with the highest concentration of AN show only one low T_g close to pure SAN and low ΔC_p values (approximately
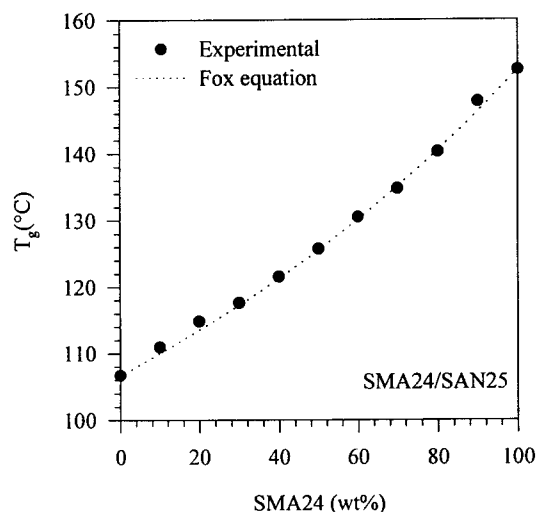
Figure 1. Glass transition temperatures of the series C blends (SMA24/SAN25) measured with DSC. The dotted line corresponds to the prediction by the Fox equation.

half of those expected), for which reason it can be suspected that these three blends are not miscible. The DSC T_g's of the series C blends are shown in Figure 1. All the blends have one glass transition temperature which follows the predicted values according to the Fox equation.[24] DMA measurements were performed on all series A blends and on one of the series B blends. Glass transition temperatures from DMA analysis could not be determined from the G'' maximum for all samples, and the temperature at the tan δ maximum is instead used as the definition of the T_g in Table 2. The $T_{\tan\delta,\max}$ values are ca. 10 °C higher than T_g, as determined from G'' maximum values. The DMA measurements confirm nonmiscibility of the three blends described above. They all have two glass transition temperatures close to those of the original materials. For blends with glass transitions very close to each other, it is not possible to distinguish between one and two T_g's. A way to judge miscibility can then be by optical clarity of the samples if the refractive indices of the two blend components are not too close. An opaque sample indicates immiscibility, while transparency of the sample indicates that the phase domains are smaller than a few hundred nanometers. Scanning electron microscopy can also be used—not to prove that a blend is miscible but to prove immiscibility when two or more phases are observed. Results from optical clarity studies are shown in Table 3, together with miscibility indications resulting from the DSC and DMA studies. In Figure 2, a miscibility map of our melt mixed blends can be observed. This picture of miscibility agrees with earlier studies of SMA/SAN blends.[2−4] It is important to note that the blends in this plot are all 50/50 wt % and that the nine series C blends are gathered at one point.

The densities of all blends in the three series show a more or less pronounced positive deviation from linearity when compared with those for the pure blend components. This confirms that there exists some favorable interactions between the SMA and SAN moieties in the blends. Kim *et al.*[3] also observed macroscopic volume contractions in SMA/SAN blends, with the greatest effect near the middle of the miscibility region.

Positron Annihilation Lifetime Measurements. Positron lifetime measurements were performed on all

Table 3. Results of Miscibility Determinations of Series A and B Blends with Different Techniques[a]

blend composition	optical clarity	DSC	DMA	conclusion
SMA8/SAN25	I	(M)	I	I
SMA14/SAN25	I	I	I	I
SMA22/SAN25	M	M	M	M
SMA24/SAN25	M	M	M	M
SMA28/SAN25	M	M	M	M
SMA32/SAN25	M	(M)	I	I
SMA50/SAN25	M	(M)	I	I
SMA24/SAN22	M	M		M
SMA24/SAN25	M	M	M	M
SMA24/SAN33	I	(M)	I	I

[a] Miscibility is indicated with an "M"; immiscible or partially immiscible blends are indicated with an "I". (M) Denotes that it is apparently miscible with this technique.
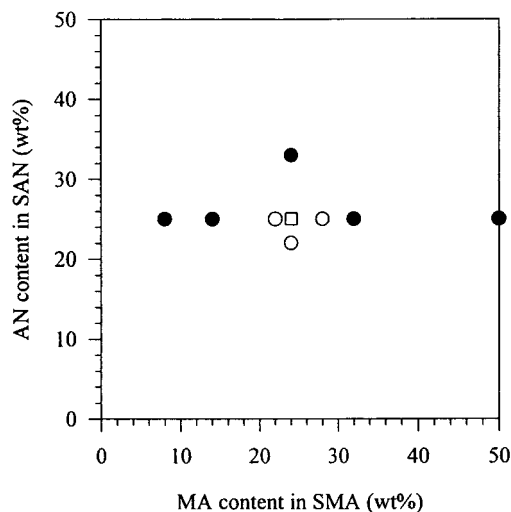
Figure 2. Miscibility map of the 50/50 wt % blends used in this study. Filled circles indicate immiscible blends, unfilled circles mark miscible blends, and the unfilled square corresponds to all nine of the series C blends, which are all miscible.
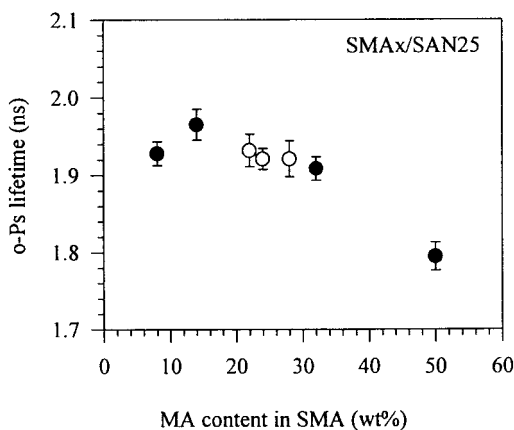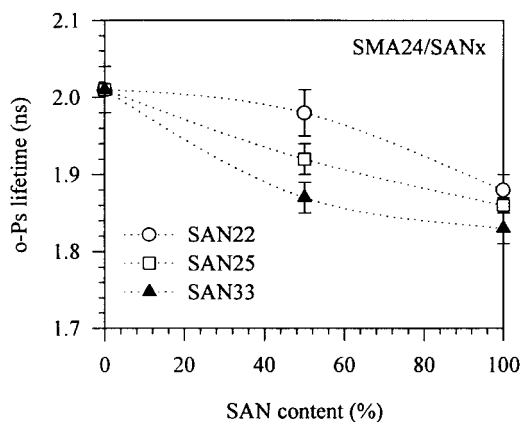

Figure 3. Orthopositronium lifetimes of the series A blends evaluated with POSITRONFIT. Different SMA copolymers melt-mixed with SAN25.

the blends. In Figure 3, the mean o-Ps lifetimes (τ_3) from POSITRONFIT evaluations of the series A blends can be observed. The τ_3 values increase slightly with higher MA concentration in the beginning, but then show a pronounced decrease. This effect of MA content on τ_3 has already been shown to exist in pure SMA copolymers[18] and was explained by the change in sequence length distribution with changing MA content. At high styrene contents, the copolymer has a random
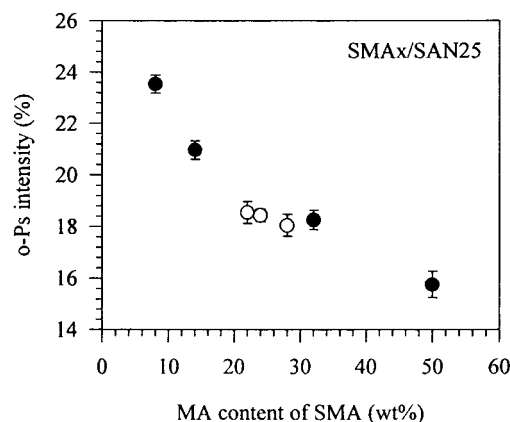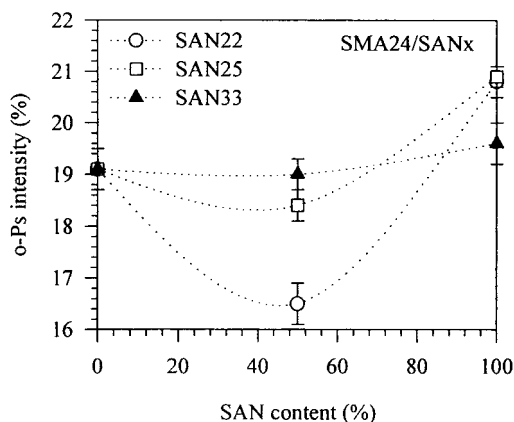

Figure 4. Orthopositronium intensities in series A blends evaluated with POSITRONFIT. Different SMA copolymers melt-mixed with SAN25.
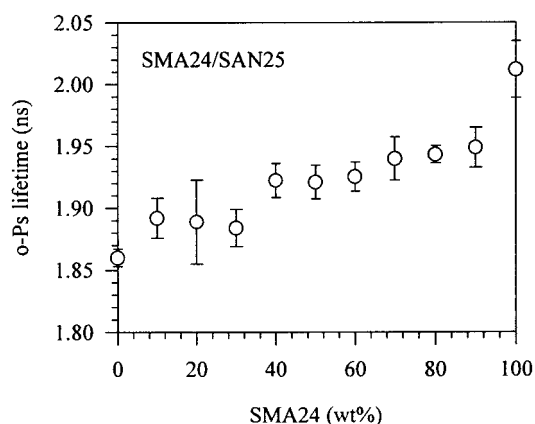

Figure 5. Orthopositronium lifetimes of the series B blends evaluated with POSITRONFIT. Different SAN copolymers melt-mixed with SMA24. The dotted lines are for guidance only.

structure that becomes more perfectly alternating with increasing MA content.[5,25] An alternating structure makes it easier for the polymer chains to pack more closely and the measured o-Ps lifetime will thus decrease. The hole size changes observed in the blends are probably also a result of changes in the packing efficiency in a similar way. In comparison with the lifetimes of the pure constituents (not shown here), the blends show τ_3 values very close to linear additivity. Figure 4 shows the o-Ps intensities of the A blends. A large decrease in I_3 with increasing MA content in the SMA copolymers can be seen. The same behavior was observed for the pure SMA and SAN copolymers as a function of increasing MA and AN content, respectively. Maleic anhydride and acrylonitrile both partially inhibit positronium formation in the corresponding styrene copolymers.[18] However, it is interesting to note that, in the samples studied here, the intensities of the three miscible blends are somewhat lower than expected as compared with the I_3's of the immiscible samples. The miscible blends also exhibit a negative deviation of I_3 compared with the pure components. For immiscible blends, I_3 seems to follow the rule of additivity.

The series B blends show a clear decrease in τ_3 with increasing AN content, as can be observed in Figure 5. The same SMA copolymer is used in these blends, which implies that the decreasing free volume hole size is a result of the differences in the SAN copolymers. A higher probability for interactions between MA and AN
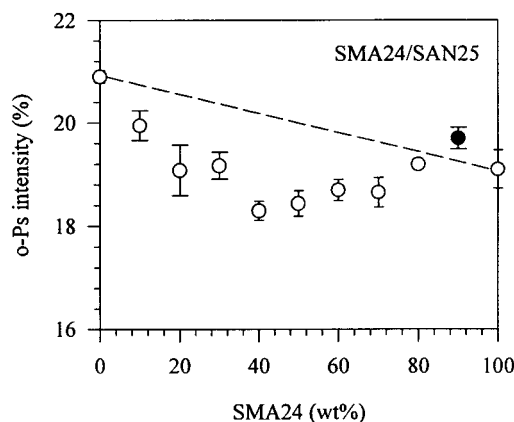
Figure 6. Orthopositronium intensities in series B blends evaluated with POSITRONFIT. Different SAN copolymers melt-mixed with SMA24. The dotted lines are for guidance only.
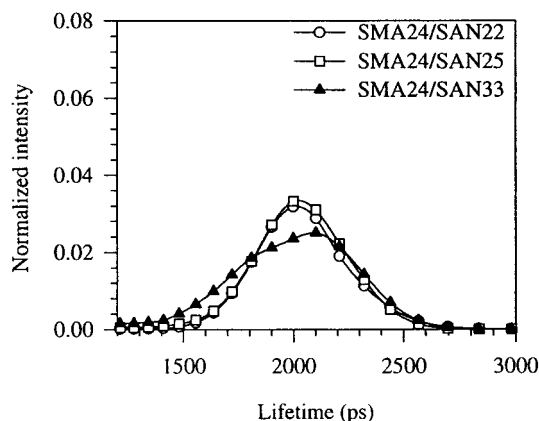

Figure 7. Orthopositronium lifetimes found in series C blends (SMA24/SAN25). Evaluation with POSITRONFIT.


Figure 8. Orthopositronium intensities in series C blends (SMA24/SAN25). Evaluation with POSITRONFIT.

Figure 9. MELT evaluation of series B blends: o-Ps lifetime distributions. Different SAN copolymers melt-mixed with SMA24.

can be expected as the amount of AN units increases in the SAN copolymer. Surprisingly, the o-Ps intensity in the SMA24/SANx blends (Figure 6) increases with increasing concentration of AN. From what is known earlier,[18] a decrease would be expected owing to the stronger inhibiting effect caused by the presence of a larger number of AN units. The two miscible blends have I_3 values that are clearly lower than additive, while the immiscible blend shows a nearly additive intensity compared with the pure components. Miscibility and phase separation seem to have a stronger effect on the o-Ps formation than inhibition by acrylonitrile in this case. The local environment probed by the positrons changes with increasing AN content, leading to a higher probability of o-Ps formation.

Figure 7 shows the mean o-Ps lifetimes measured in the series C blends, including the pure copolymers. All of these blends are miscible according to Figure 2. The average τ_3's of the starting materials are 1.86 ns (SAN25) and 2.01 ns (SMA24), which correspond to hole radii of 2.73 and 2.87 Å, respectively. The blends all show lifetime values between those of the pure constituents. It can be observed that τ_3 of all the blends is clearly lower than that of pure SMA24. The free volume hole size in the blends is lower than what would be expected from a linear relation, but never becomes lower than that of pure SAN25. Figure 8 depicts the o-Ps intensities of the C blends. The I_3 values of the two pure copolymers differ only slightly, 20.9% for SAN25 and 19.1% for SMA24. However, it can once again be

observed that the o-Ps intensities of miscible blends are below a linear relationship, with an exception for the blend containing 90 wt % SMA24, which suggests that this particular blend is partially phase-separated and that PALS is a more sensitive technique than the methods conventionally used to determine miscibility. A large decrease in I_3 was also reported for poly(ethylene oxide)/poly(methyl methacrylate) blends below 25% poly(ethylene oxide) content. In this composition range the blends are miscible and amorphous.[17]

Evaluations of the positron lifetime spectra were performed using the MELT program that, in addition to average lifetimes and intensities, provides lifetime distributions. Figure 9 shows the o-Ps lifetime distributions of the series B blends. The two miscible blends have very similar Gaussian-like distributions, while the distribution of the immiscible blend is broader and has an unsymmetric appearance. The experimental results agree with the expectations that distributions of immiscible blends are broader than those of miscible blends and are possibly also unsymmetric. Figure 10 shows o-Ps lifetime distributions of the series C blends. These blends are all miscible according to the DSC measurements. Six of the blends have almost exactly identical distributions, while three differ clearly from the others. The latter are the blends containing 20%, 30%, and 90% SMA24. Their distributions appear to be unsymmetric and show slightly broader distributions than do the other blends. These blends are also the ones that show the least positive density deviations, which indicates that they are not completely mixed on a
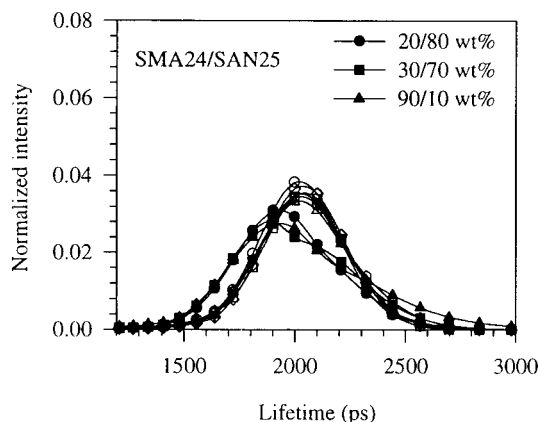
Figure 10. MELT evaluation of series C blends (SMA24/SAN25): o-Ps lifetime distributions.

molecular level. Additional DMA measurements of the blends reveal a small increase in the G'' and the tan δ values in the region between 105 and 130 °C in the 90% SMA24 blend, which is near the T_g of pure SAN25, and give evidence that this blend is not completely molecularly mixed. DMA results of the 20% and 30% SMA24 blends do not give sufficient information on the high-temperature side, where traces of SMA24 would be expected to appear in the case of phase separation. The PALS results are plausibly an indication of phase separation on the molecular level, which can, so far, not be detected by other methods.

It is here appropriate to discuss the reliability of the distributions calculated with MELT. It has been shown that MELT gives reproducible lifetime distributions when simulated lifetime spectra are evaluated, but that the intrinsic broadening increases slightly with increasing lifetime.[26] Evaluation of a large number of positron lifetime spectra collected for PMMA at room temperature showed that the width of the o-Ps lifetime distribution was 360 ± 50 ps.[23] It was also concluded that spectra containing two million counts or more give reliable distributions. All of the MELT evaluations mentioned above resulted in symmetric lifetime distributions, while unsymmetric distributions were only found in some blends of poly(ethylene oxide) and poly-(methyl methacrylate).[17] The spectra were in this study collected using a spectrometer with fwhm equal to 280 ps. A spectrometer with a better time resolution function will probably give spectra that, after a MELT evaluation, show larger differences between lifetime distributions in miscible and immiscible SMA/SAN blends.

Conclusions

Copolymers of styrene–maleic anhydride and styrene–acrylonitrile that are melt-mixed form miscible blends when the styrene contents of the copolymers are sufficiently similar. To determine the miscibility of the blends, several complementary methods must be used. Generally, the o-Ps lifetimes of the blends are found to be between those of the pure constituents. Negative deviations from linearity were found for the probability of o-Ps formation (I_3) in miscible blends. The o-Ps formation probability decreases greatly as the maleic anhydride content in the blend increases, owing to

inhibition of Ps formation by maleic anhydride.[18] The results of this study suggest that immiscible blends of SMA and SAN exhibit broader o-Ps lifetime distributions than do miscible blends. The distributions also seem to have a more unsymmetric appearance. PALS results indicate that three of the SMA24/SAN25 blends are not completely mixed on a molecular scale, which could be confirmed for one of the blends with additional DMA measurements but not for the two others. It is possible that PALS is a more sensitive technique for miscibility studies than conventional methods.

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