

Positron Lifetime Study of Polycarbonate/Poly(Styrene-co-Acrylonitrile) Blends

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Abstract. Positron lifetime spectroscopy was applied to study structure and interphase interaction in partially miscible polycarbonate/poly(styrene-co-acrylonitrile) blends. Orthopositronium (oPs) lifetimes and intensities for blends of different compositions were followed as functions of measurement time. Slight decreases in oPs intensities, caused by irradiation of specimens from positron source during measurement, were observed and oPs parameters, unperturbed by the irradiation, were deduced. These were plotted against the weight ratio of the blend components. In accord with expectations for partially miscible blends, they followed the straight lines of additivity of the free volume of the blend constituents.

Introduction

Polymer blending offers an effective way of tailoring desired macroscopic properties of polymeric materials. Hence, the investigations of miscibility of constituents and blending mechanisms on the microscopic scale are of great importance. Recently, partial miscibility of polycarbonate (PC) with styrene-acrylonitrile copolymer (SAN) has been proved and investigated by means of the dynamic mechanical [1] and dielectric [2] methods. Since the free volume appears to correlate with the macroscopic properties of polymers, positron lifetime spectroscopy (PLS) is a suitable tool for further studies of such systems. Namely, measurement of the orthopositronium (oPs) pick-off annihilation rate turns out to be a direct characteristic of mean free-volume hole size. On the other hand, relating the oPs formation probability to the free-volume holes concentration is not straightforward because irradiation induced changes in the probability during measurement time were observed in a number of polymeric materials and found to depend on chemical composition of the polymers as well as on the positron source strength.

In present contribution, a PLS investigation of the PC and SAN polymers and several PC/SAN blends is described. Dependences of oPs lifetimes and intensities on blend composition and measurement time were followed. The results were discussed from the point of additivity of free volume of blend components.

Experimental

Materials investigated in present study were bisphenol A PC (SINVET 251, $M_n=2.50 \times 10^4$, $M_w=3.60 \times 10^4$ g/mol), SAN (KOSTIL AF 600, $M_n=6.95 \times 10^4$, $M_w=13.5 \times 10^4$ g/mol) and PC/SAN binary blends with the five different SAN percentages, $c_{SAN} = 25, 40, 50, 70$ and 80 wt. %. Acrylonitrile group (AN) represented 24 % of the SAN molecular weight. Neat materials were produced by ENI, Italy, and details of sample preparation were described elsewhere [1]. In order to give a defined thermal history [2] to the materials, samples were annealed in dried nitrogen

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atmosphere for 2 hours and subsequently cooled to room temperature at a rate of 0.5 °C/min. Annealing temperatures were chosen to lie at 115 and 155 °C for neat SAN and PC, respectively, and at ~10 °C above T_g of the PC-rich phase with the higher T_g [1] for the binary systems studied. Positron lifetime spectra were measured by means of a BaF₂ fast-fast lifetime spectrometer with timing resolution of ~220 ps FWHM and coincidence count rate of ~400/s for a ~2.8 MBq ²²Na positron source (carrier-free ²²NaCl, Amersham, sealed between two mylar foils of 2 μm thickness). All measurements were performed at room temperature in air. In order to observe time evolution of oPs lifetimes and intensities during measurement, lifetime spectra were recorded in 0.5-hour steps throughout a ~50 hour total time of data accumulation. Spectra acquired in each individual steps were decomposed into discrete exponential components using a maximum likelihood procedure [3]. Source contribution was determined from lifetime measurements with the well-annealed α-iron reference specimen and recalculated for the particular polymer using method suggested in [4].

Results and Discussion

Three exponential components arising from positron annihilations in the polymer samples were resolved in all the spectra measured for 0.5-hour intervals. We associate the two shortest lifetimes $\tau_1 \sim 190$ and $\tau_2 \sim 420$ ps with annihilations of para-positronium and/or positrons. The third component with lifetime of ~2 ns belongs to oPs pick-off annihilation. In the following, we use its lifetime, τ_{oPs} , and intensity, I_{oPs} , to characterize variations of free volume and oPs yield with blend composition and time t of specimen exposure to irradiation during measurement. In all materials studied, $\tau_{oPs}(t)$ remained constant in time t , however, a slight decrease in $I_{oPs}(t)$ with increasing t , resembling exponential relaxation towards a steady state, was observed (see examples given in Fig. 1). Values of $\tau_{oPs}(t)$ were found to be greater in neat PC than in neat SAN, in agreement with

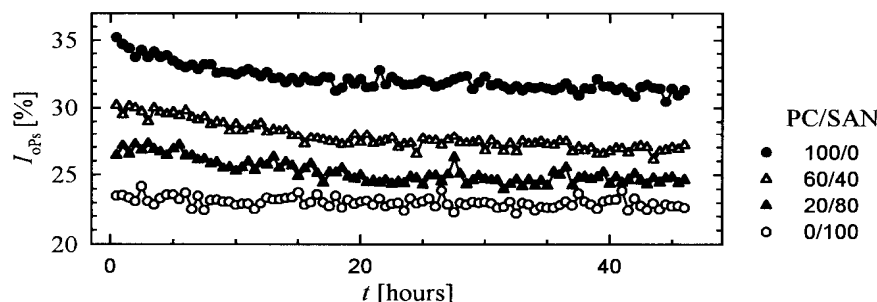


Fig. 1. Examples of observed dependences of I_{oPs} on time t of data accumulation.

literature data [5-8], and monotonically changed with c_{SAN} . Similarly, I_{oPs} and hence oPs yield in PC was found higher than in SAN. The magnitude of the I_{oPs} decrease with time t was found to be ~4 % for neat PC and diminished with increasing SAN content to ~0.6 %, i.e. to about the observation limit, for neat SAN. Since our auxiliary measurements with different positron sources indicated that magnitude of the observed decrease of $I_{oPs}(t)$ in PC depends on the source strength, we assign this decrease to the effect of sample irradiation by positron source rather than to structural changes due to physical ageing of polymer. Relaxation of $I_{oPs}(t)$ towards a steady state can be understood as a result of competition between creation and recombination of the positronium (Ps) inhibitors (free radicals, cations, ionized molecules), produced due to irradiation or positron annihilation in the sample [9]. Polar AN groups absorbing spur electrons are a cause of the lower Ps yield in the neat SAN [5]. They may also diminish the decrease in I_{oPs} during measurement as a consequence of absorption of irradiation induced Ps inhibitors at the polar sites of the SAN chains. A low Ps yield was observed recently for styrene-methacrylate copolymer containing polar groups

in its chains, too [6]. Regarding the decrease in $I_{\text{OPs}}(t)$ with t observed for PC, mutually different experimental results were reported by other authors [7,8]. Our finding of a slight but significantly non-zero decrease of $I_{\text{OPs}}(t)$ is in reasonable agreement with Ref. [7].

By fitting exponential relaxation curves [9] to observed time dependences of I_{OPs} , initial intensities, $I_{\text{OPs}}(0)$, unperturbed by specimen irradiation, were deduced. Quantities $I_{\text{OPs}}(0)$, τ_{OPs} and $(\tau_{\text{OPs}})^3 \times I_{\text{OPs}}(0)$ taken as functions of c_{SAN} were found to follow linear dependency on c_{SAN} close to the line of additivity of components properties in the blends (see Fig. 2). As clearly demonstrated in Ref. [10],

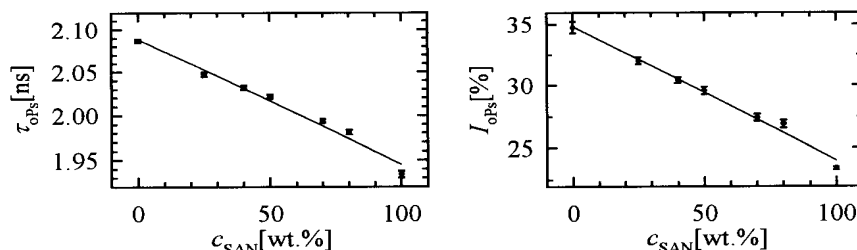


Fig.2. Orthopositronium lifetime and intensity as function of PC/SAN blend composition. Lines of best fit are drawn to guide eyes.

PLS can reflect degree of miscibility of blend components and detect deviations from additivity of free volumes. In partially miscible amorphous blends, additivity of free volumes may be expected if the volume fraction of interphase regions is a very small fraction of the blend [11]. PLS then perceives averaged free volume of the neat constituents in their gross blend compositions. Observed behavior of the PLS parameters in PC/SAN blends is in accordance with this expectation and is similar to that found recently for PC/PMMA partially miscible blends [12]. On the other hand, PLS study [10] revealed a more complicated picture in SMA/SAN blends which appeared to be miscible or phase separated, depending on blend compositions. Finally, it is to be noted that knowledge of the t -dependence of I_{OPs} and use of the unperturbed values $I_{\text{OPs}}(0)$ is important for interpretation of PLS data on polymer blends, especially if the neat constituents exhibit larger effects of irradiation.

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