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Notes

Spin Label Study of the Free-Volume Relaxation in a Poly(ethylene oxide)/Poly(methyl methacrylate) Blend

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Physical aging of an amorphous polymer gives rise to a progressive change of its properties. Volume relaxation occurs in the glassy state, owing to the nonequilibrium character of this state and the consequent relaxation toward equilibrium. A convenient phenomenological description can be developed within the classical free-volume concept.[1] The rate of the volume relaxation can be related to the time evolution of the free-volume distribution. Aging and annealing experiments involved temperature jumps with subsequent observation of macroscopic quantities such as volume,[1] ethalpy,[2] or mechanical properties such as stress relaxation.[3] Kobayashi et al.[4] and Nakanishi et al.[5] estimated recently the microscopic quantity of free volume by positron annihilation. Some authors have studied also free-volume distribution and physical aging in a glassy polymer by using photochromic, fluorescent, and spin probes.[6] The dynamic properties of polymer blend should depend on the density of the molecular packing, i.e., on the free volume. The physical aging of the blend having a complicated structure should change the amount of the free volume and its distribution. In this paper, we study this topic by ESR spectroscopy using spin labels. Previously we found that ESR spectra of the nitroxide label reflect different environments in a poly(ethylene oxide) (PEO)/poly(methyl methacrylate) (PMMA) blend, with different motional characteristics; two spectral components with different rates of motion—a "fast" and a "slow" component—are observed, with isotropic spectra reflecting fast motion and anisotropic spectra immobilized labels.[7] The composite ESR spectra characterize a heterogeneous medium and a phase separation or concentration fluctuation in the polymer blend. Here, we estimate the fractional amount of the fast component (mobile fraction) of the composite spectra observed at room temperature and study the effect of physical aging on the mobile fraction. We show that formation and annihilation of free-volume sites detected by the spin label method are characteristic of the dynamic behavior of the polymer blend.

Spin-labeled PEO was prepared by the method of Törmälä.[8] Blends were made by mixing the spin-labeled PEO and isotactic PMMA in the ratios of 1:1 and 1:10 by weight. The notation used for these samples is EM1 and EM10, respectively. The number average molecular weight was 6000 for PEO and 5000 for PMMA. ESR measurements were carried out with a JEOL FE3XG spectrometer and a connected MELCOM70/25 computer. Figure 1a shows the ESR spectra of the spin-labeled PEO in the EM10 blend. The spectra were observed at room temperature after the sample was melted at 142 °C for 15 min and stored at ambient temperature for 9 days. In general, the outermost splitting width of the main triplet spectra due to hyperfine coupling caused by the nitrogen nucleus narrows with an increasing mobility of the radicals because of motional averaging of the anisotropic interactions between electron and nuclear spins. The complete averaging gives rise to the isotropic and narrowed spectrum. The outermost splitting is a good measure of the mobility of the spin-labeled PEO. Two components of spectra in the blend with different rates of motion—a "fast" and a "slow" component arising from the radicals—are observed. The fast and slow components can be attributed to radicals in the mobile and rigid regions, respectively. Molecular mobility in the PEO matrices is higher than in the PMMA matrices since the glass–rubber transition temperature (T_g) of PEO (−65 °C) is lower than that of isotactic PMMA (60 °C).[9] As discussed previously,[7] this means that the nitroxide radicals are affected by their environment, for example, the states of aggregation, and the fast and slow component's spectra (the isotropic and anisotropic spectra) are attributed to the spin-labeled PEO trapped in the PEO-rich and PMMA-rich regions of the blend, respectively.

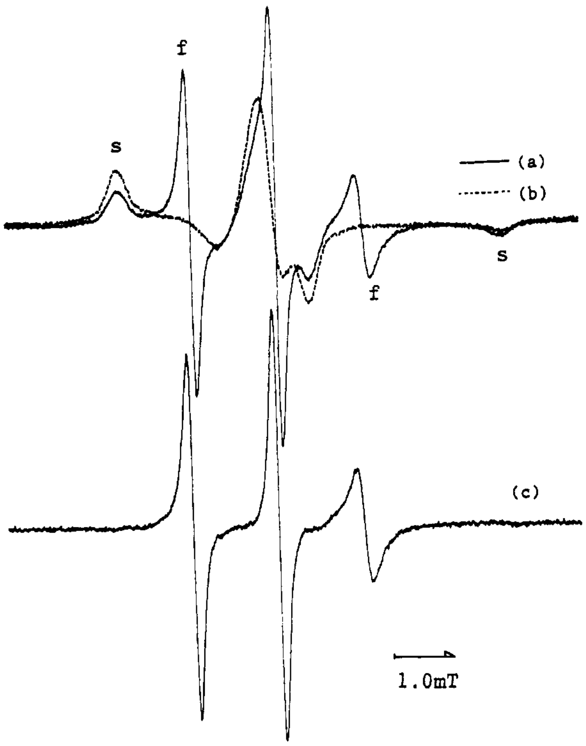

Figure 1. ESR spectra of spin-labeled PEO in PEO/PMMA blend (EM10) before (a, solid line) and after (b, dotted line) aging at −25 °C for 30 min. Spectrum c was obtained by subtracting 0.72 times of spectrum b from spectrum a. Slow and fast components are indicated by "s" and "f", respectively. Measurements were carried out at room temperature.

After the blend was stored at ambient temperature for more than 1 week and phase separated, it was aged at temperatures below 23 °C. The sample was stored at a desired temperature for 30 min and subsequently heated to room temperature, and the ESR measurements were

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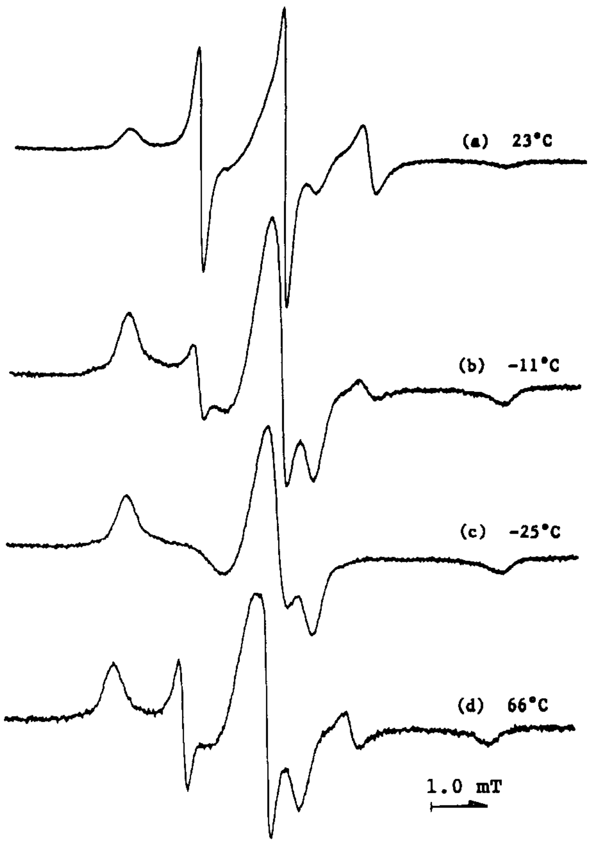

Figure 2. Variation of ESR spectra of spin-labeled PEO in a PEO/PMMA blend (EM10) with aging and annealing temperatures (a) 23 °C, (b) -11 °C, (c) -25 °C, and (d) 66 °C. ESR spectra were observed at room temperature.

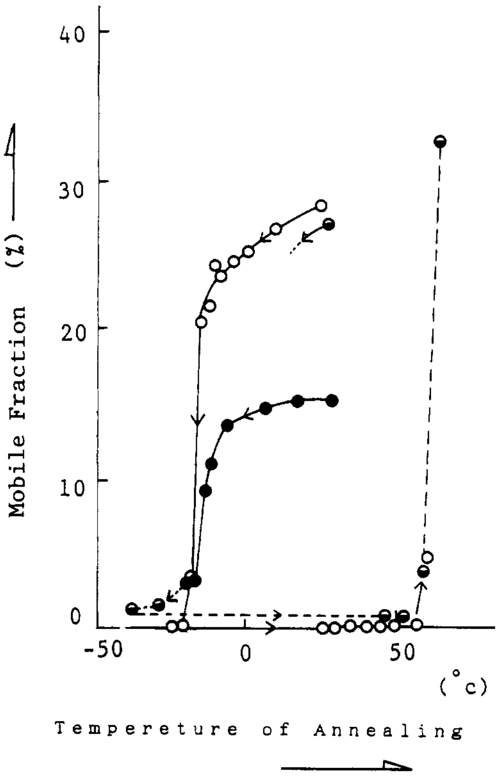

Figure 3. Change in mobile fraction in PEO/PMMA blend with aging and annealing temperatures. EM10 blend (○) was stored for 9 days at ambient temperature after molecular mixing for 15 min at 142 °C. EM1 blend was stored for ca. 1 h (●) and for 36 days (◒) at the ambient temperature after the molecular mixing. The arrows indicate the routes on which the changes of the mobile fractions were observed.

carried out at the same temperature. Figure 2 shows the variations of the ESR spectra of the spin-labeled PEO in the EM10 blend with aging temperature. One of the main changes is a reduction of the narrow triplet of the fast component and a growth of the outermost peaks of the slow component as the aging temperature was lowered. Surprisingly, the narrow triplet disappears on aging at -25 °C. Cameron et al.[10] interpreted the double-peak feature of ESR spectrum of a nitroxide spin probe as reflecting tumbling with a distribution of correlation times arising from a distribution of free volume within a polymer matrix. Sohma et al.[11] and Tsay et al.[12] also interpreted the double peaks of the ESR spectra of spin-labeled and spin-probed poly(methyl methacrylate) in terms of a "freezing in" of free volume.

In our case, the variation of the ESR spectra shown in Figure 2 can be also interpreted in terms of a "freezing" of free volume. The effect of crystallization in PEO can be ruled out because the aging effect is observed even with a small amount of PEO in the blend. The fractional amount of the fast component (mobile fraction) should be a good measure of the distribution of free volume. In order to estimate the mobile fraction, one must decompose the experimental spectrum into two components.

Only one narrow spectrum is obtained when subtracting an appropriate intensity of the spectrum after aging from the spectrum before aging. Figure 1c shows the spectrum obtained by subtracting 0.72 times the spectrum after aging at -25 °C (1b) from the spectrum before aging (1a). Thus, the spectrum (1a) should be composed of 28% of the "fast" and 72% of the "slow" components. For simplicity, the mobile fraction is estimated from the ratio of the intensity of the outermost peaks of the slow component's spectrum to those of a spectrum obtaining only the slow component such as Figure 1b. The mobile fraction obtained by this method is represented as open circles in Figure 3. It decreases gradually with decreasing aging temperature in a range of 23 °C to -10 °C and drops abruptly around -13 °C. This suggests that the volume in the PEO-rich phase of the phase-separated system contracts and the spin-labeled PEO becomes immobile. The PEO/PMMA blend is estimated to contain a mobile fraction of more than 28% at the equilibrium state at room temperature. Volume relaxation occurs in the glassy state of the blend, owing to its nonequilibrium character and the consequent relaxation toward equilibrium. The mobile fraction detected by ESR should disappear in the glassy equilibrium state at -13 °C. It was also found that the intensity of the fast component of the spectrum decreases with storage time at -13 °C. This reflects a relaxational phenomenon. It is mainly noted that the structure developed below room temperature is stable at the same temperature. The formation of free-volume sites, i.e., the volume expansion in the PEO-rich phase cannot be observed within a few hours at room temperature, i.e., the relaxation time for the recovery of the structure is too long to be observed by the ESR method. After the aging experiments, the sample was annealed at a temperature above 23 °C for 30 min, subsequently cooled at room temperature and the ESR measurements were carried out at the same temperature. The open circles in Figure 3 also show variations of the mobile fraction in the EM10 blend with annealing temperature above 23 °C. The spectrum did not change during annealing at temperatures below 60 °C, but the intensity of the fast component of the spectrum increased at 60 °C as shown in Figure 3. The variation of the spectrum is shown in Figure 2d. The fast component disappeared above 68 °C because of molecular mixing of the PEO and

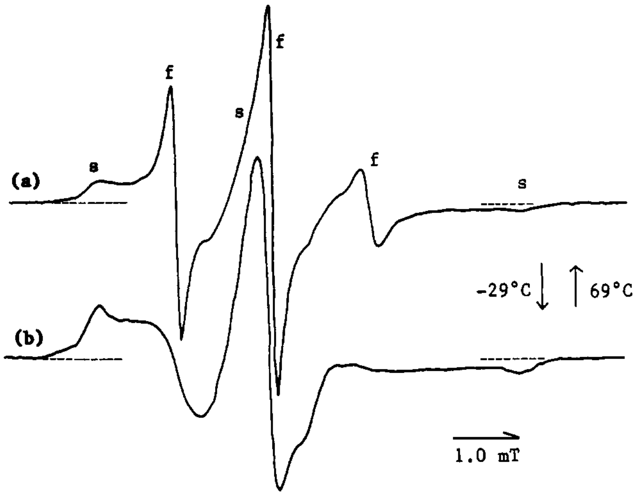

Figure 4. ESR spectra of spin-labeled PEO in PEO/PMMA blend (EM1) after annealing at 69 °C (a) and after aging at −29 °C. Slow and fast components are indicated by "s" and "f", respectively. Measurements were carried out at room temperature.

PMMA chains, e.g., the molecular motion of the PEO chain is disturbed by the PMMA chain in the molecular mixed system.

Figure 4 shows ESR spectra of the spin-labeled PEO in the EM1 blend, observed at room temperature. It is found that aging below room temperature decreases the intensity of the fast component and annealing above the temperature increases its intensity. The mobile fraction is also plotted against annealing temperature in Figure 3. Mobile labels appear abruptly at 69 °C in the EM1 blend. This drastic change in comparison with that in the EM10 blend can be interpreted in terms of the higher transition temperature of the molecular mixing in the EM1 blend. The characteristic temperatures at which the mobile fraction decreased and increased drastically do not seem to be composition dependent. The temperatures should be related to the glass–rubber transition temperatures of PEO (−65 °C) and PMMA (60 °C). The contraction and the stretching of PMMA chains in the blend may play an important role in the structural change in the PEO-rich phase.

The formation of free volume is observed at 60 °C above room temperature by the ESR method. The experiments concerning free volume involved temperature jumps with subsequent observation of macroscopic quantities such as contraction and expansion of volume. The macroscopic quantities in general reflect the whole properties of the complicated system. However, the microscopic quantity, i.e., the mobile fraction estimated by the ESR method, is focused on a particular region: the PEO-rich phase in the phase-separated system.

Some authors have studied the blends of PEO and isotactic PMMA by such techniques as differential scanning calorimetry, X-ray diffraction, and optical polarizing microscope.[13] The spin label technique is a simple and effective way of studying the structural change in a particular region.

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Registry No. PEO, 25322-68-3; PMMA (isotactic homopolymer), 25188-98-1.