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FREE-RADICAL DECAY IN A POLYMER BLEND PMMA/PEO STUDIED BY THE EPR METHOD

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Abstract—The EPR method was used for studying decay of free radicals in a blend of poly(methyl methacrylate) (PMMA) with poly(ethylene oxide) (PEO). The influence of the composition of the blend (up to 70 vol% PEO) and of the time of mixing on the transfer of a radical centre was determined. The time of mixing for a blend affects molecular motions as a result of specific interactions between dissimilar PMMA and PEO chains. These molecular motions control the transfer of the radical centre so that free radicals decay more rapidly in the blend mixed for 6 min than in that mixed for 12 min. A slower decrease in the concentration of free radicals in a sample of a PMMA/PEO blend containing 50 vol% PEO compared with samples with 10, 30 and 70 vol% is also observed.

INTRODUCTION

A mixture of thermodynamically miscible polymers poly(methyl methacrylate) and poly(ethylene oxide) (PMMA/PEO) is a material with useful properties.

The miscibility of the components of the blend is caused by specific interactions between components [1] and leads to homogeneity at a macroscopic level. The method of vibrational spectroscopy showed [2] that atactic PMMA can be regarded as a copolymer of isotactic and syndiotactic structure. PEO, usually in the stable helical structure, is transformed on contact with PMMA into the trans planar structure. It is not known how the conformationally irregular atactic PMMA can affect formation of the planar structure of PEO [3]. It is assumed that two PEO units may be bonded with three PMMA units. PEO easily crystallizes in the form of crystalline lamellae built in the amorphous PMMA matrix in various ways [4]. In a search for interactions and for investigation of the effects of microcharacteristics of a blend, the ESR method is useful. The method was used for determining the influences of blend composition and of the time of mixing the blend on molecular motions that control the motion of the radical centre.

EXPERIMENTAL PROCEDURES

PMMA (Röhm G.m.b.H., Darmstadt; trade mark Plexiglas 233) ($\bar{M}_w = 3 \cdot 10^6$) and a PEO sample (BDH Chemicals Ltd, Poole, England) ($\bar{M}_w = 5 \cdot 10^6$, $T_m = 65 \pm 2°$) were used.

Blends were prepared by mixing on a Brabender plastograph for 12 min at maximum 65 r.p.m. at 195° in proportions vol% PEO 90:10, 70:30, 50:50, 30:70. The predicted miscibility [5] of a blend PMMA/PEO was actually observed in several studies [6–9]. Blends of PMMA/PEO (50:50 vol%), for which the effect of the degree of mixing was investigated, were prepared by mixing for 6 and 12 min at 65 r.p.m. and at 195°. The samples were irradiated at liquid N_2 temperature by gamma-irradiation with a total dosage of 1 Mrad. The spectrum was measured on an X-band Varian E-4 EPR spectrometer at temperatures from −150° to +150°.

Mechanical destruction was performed on samples shaped into cylinders (7 mm dia; 7 mm length) with a special drill under vacuum at liquid N_2 temperature. The method has been described [10].

RESULTS AND DISCUSSION

The EPR method was used for evaluating temperature relations (from −150° to +150°) for the decrease of concentration of free radicals in a polymer matrix from the spectrum of a blend.

Figure 1 shows the EPR spectrum for gamma-irradiated blend PMMA/PEO (50:50 vol%) at −40°. The character of the spectrum corresponds to the nine-line spectrum of PMMA end $—CH_2—C(CH_3)COOCH_3$ radical [11], where decay of radicals was followed.

Figure 2 shows a comparison of the effect of the degree of mixing of a blend on free radical decay. The sample was gamma-irradiated PMMA/PEO (50:50 vol%). The samples were mixed for 12 and 6 min respectively at 195°. The duration of mixing was shown to affect the decay of free radicals. Free radicals decay more rapidly in the PMMA/PEO sample (50:50 vol%) mixed for the shorter period. The effect is probably connected with the interchain specific interaction tending to reduce the entanglement between dissimilar chains. Interchain specific interaction may locally align the chain segments,

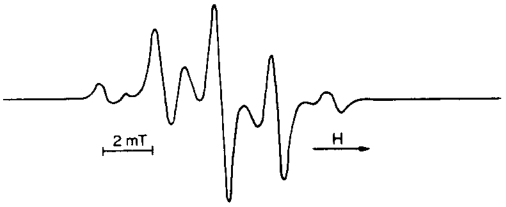

Fig. 1. EPR spectrum of gamma-irradiated blend (1 Mrad) PMMA/PEO containing 50 vol% PEO at −40°.

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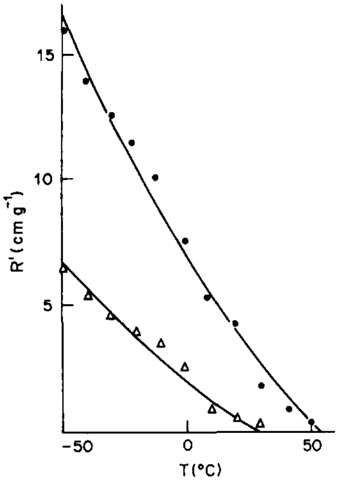

Fig. 2. Dependence on the time of mixing of the concentration of free radicals in gamma-irradiated blend (1 Mrad) PMMA/PEO containing 50 vol% PEO. ●, PMMA/PEO sample (50:50) mixed for 12 min; △, PMMA/PEO sample (50:50) mixed for 6 min.

reduce local chain convolution, and thus reduce the entanglement between dissimilar chains [12]. With stronger interactions, the dissimilar chains are less entangled in a blend. This view explains why, in a sample mixed for 12 min, the local convolution of a chain is reduced because of stronger interactions so that the free-radical decay is slower than that for a sample mixed for 6 min. PEO chains in the blends are preferentially in a planar zig-zag conformation [13].

Figure 3 shows the dependence of free radical decay on the temperature for gamma-irradiated blends (1 Mrad) with various proportions of PEO. The sample containing 50 vol% PEO, with the largest contact area of PMMA and PEO, exhibits slowest reduction of the free radical concentration. Specific interactions of these two types of chains result then in retardation of the transfer of the radical centre in a particular sample with respect to the sample with compositions PMMA/PEO 90:10 and 70:30.

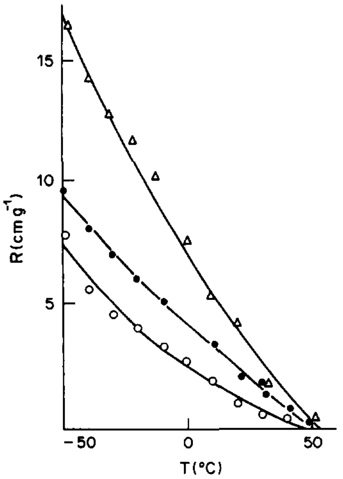

Fig. 3. A plot of the concentration of free radicals in gamma-irradiated blend (1 Mrad) PMMA/PEO for various blend compositions. ●, 30 vol% PEO; △, 50 vol% PEO; ○, 70 vol% PEO.

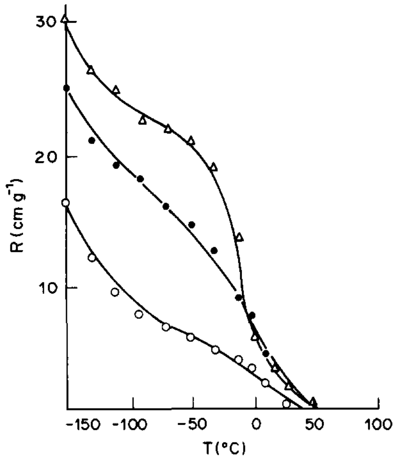

Fig. 4. A plot of the concentration of free radicals generated by mechanical destruction for various blends of PMMA/PEO. ●, 10 vol% PEO; ○, 30 vol% PEO; △, 50 vol% PEO.

In other experiments, free radicals in the samples were generated by mechanical destruction. Figure 4 shows the radical decay in these blends. The results for samples with radicals generated by mechanical destruction agree with those obtained for samples containing radicals generated by gamma-irradiation. A slower decrease of the concentration of free radicals has also been observed for a blend containing 50 vol% PEO than for samples containing 10 and 30 vol% PEO.

We see that, by lengthening the time of mixing up to 12 min and by increasing the contact area between PMMA and PEO, the rate of decay of free radicals is reduced.

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