

Study of Deformation of Crystalline Polymer by ESR Method

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INTRODUCTION

The deformation mechanism of crystalline polymers recently has interested many investigators. The aim of this paper is to study the mechanism of deformation of linear polyethylene by the electron spin resonance (ESR) method. The ESR method used by the authors has supplementary methods to detect polymer matrix and accompanying special features: (1) Paramagnetic probes are dispersed into specimens before or after deformation. Informations about polymer matrix is obtained through motions of the probe, which is detected by the ESR method. Since the size of the probe is larger than that of crystalline lattice, selective informations on an amorphous phase can be obtained. (2) Paramagnetic sites (free radical, alkyl type radical $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ in the case of polyethylene) are introduced into polymer matrix by γ -ray irradiation, and then detected by the ESR method. The paramagnetic site has been found to form mainly in non-crystalline phase including crystal defects^{1, 2}. Its recombination reaction is very sensitive to change in a crystalline texture.

EXPERIMENTAL

Linear polyethylene Hizex 1200J(Mitsui Petrochemical Co.) was used as a material. Samples were prepared by stretching sheets of polyethylene, immersed in xylene solution of paramagnetic probes(2,2,6,6-tetramethyl-4-piperidinol-1-oxyl) at room temperature, and then dried in reduced pressure.

Meanwhile, original and stretched sheets were irradiated with γ -rays of Co 60 to the total dose of about 10^7 rad in vacuum at liquid nitrogen temperature, and then ESR was measured to estimate radical concentration. Further, radical decay was measured by heating the samples above liquid nitrogen temperature.

RESULTS AND DISCUSSION

Figure 1 shows the variation of the hyperfine separation of ESR spectra (distance between outermost peaks of a three-line pattern) with temperature for the sample in which

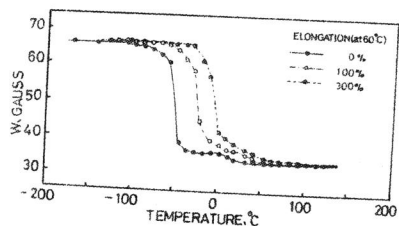


Figure 1 Hyperfine separation (W) vs. temperature

the probes were dispersed after stretching. Rapid narrowing of the separation is found in the figure. This could be arisen when the probe begins to rotate rapidly and averaging out the anisotropic hyperfine interaction of nitrogen atom with an unpaired electron. This narrowing is believed to be due to glass transition. The narrowing temperature is shifted to high temperature side by stretching reflecting the increased tension of amorphous chains. This shift of narrowing temperature of the

sample in which the probe had been dispersed before stretching (Case I) was smaller than the case where the probe had been dispersed after stretching(Case II). The hyperfine separation at room temperature was found to show saturating tendency with increasing stretching ratio at about 100 - 200 % in Case I. But, the separation linearly increased in Case II. The orientation function of amorphous chains also showed a similar saturating tendency. In Case I the probe was difficult to be extracted above stretching of 100 - 200 %. In Case II penetration of the probe into the sample was much delayed by stretching. These facts may indicate that molecular chains at the surface of samples was specially strained compared with the interior.

It was found for the γ -irradiated samples radical concentration was changed with stretching ratio of the sample. Further, stepwise radical decay was found when the samples were heated above liquid nitrogen temperature. The first step was below -110 °C and the second was above -80 °C. The height of the first step changed with stretching ratio. These facts may be related to the deformation of crystalline domain. The second step was shifted to high temperature side by stretching corresponding the fact mentioned in Figure 1.

REFERENCES

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