Nature of Auto-Oxidations on Plasma-Induced Surface Radicals of Polyethylene Studied by Electron Spin Resonance

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Peroxy radical formation for auto-oxidation process has been extensively studied due to importance of industrial application of a wide variety of irradiated-polymers including those of high density polyethylene (HDPE). All kinds of plasma-irradiated polymers are eventually exposed to air for their practical use, so that the studies of auto-oxidation process are also important for plasma-irradiated polymers. In a previous paper, we reported the special features of the peroxy radicals formed from plasma-irradiated acrylic resins such as polymethacrylic acid (PMAA) and its methy ester (PMMA), and two kinds of copolymers of MAA and MMA commercially known as Eudragit L100 (6:4) and Eudragit S100 (7:3), as studied by electron spin resonance (ESR) including the time- and temperature-dependent spectra.

In this paper, we report the ESR study of peroxy radical formation, as an initial process of auto-oxidation, from Ar-plasma-irradiated polyethylene (PE), both low density polyethylene (LDPE) and HDPE, by its exposure to air (oxygen) immediately after plasma-irradiation.

We have already shown that the observed ESR spectra of plasma-irradiated LDPE were deconvoluted with the aid of the systematic computer simulations invoking three kinds of isotropic component spectra, sextet spectrum (I), septet spectrum (II) and a smeared-out single line spectrum (III). These component spectra were assigned to a mid-chain alkyl radical (1) \( \sim \text{CH}_2\text{CH}-\text{CH}_2 \sim \), an allylic radical (2) \( \sim \text{CH}_2\text{CH} = \text{CH}-\text{CH}_2 \sim \), as discrete radical species, and a dang-

![Fig. 1. Progressive ESR spectral changes on exposure to air of LDPE and HDPE plasma-irradiated for 3min, respectively, together with the simulated spectra shown as dotted lines.](image-url)
ling bond sites (DBS) (3) at the surface cross-linked region, respectively. All these component radicals are essentially identical with those of HDPE reported earlier, but thermally stable DBS (3) is a major component radical in LDPE, instead of a mid-chain alkyl radical in HDPE, indicating the greater formation of highly cross-linked network on plasma-irradiated LDPE surface. The formation of the corresponding peroxy radical was furnished simply by opening the ampule containing the PE samples plasma-irradiated for 3 min to introduce an dry air into the ampule. After agitating the powder samples, the ESR spectra were periodically measured at room temperature.

Figure 1 shows what happened to the ESR spectra when LDPE and HDPE, both Ar-plasma-irradiated for 3 min, was exposed to air. It is seen that the spectrum of LDPE has quickly changed to an unsymmetrical spectral pattern, which is representatively characterized by a sharpening of the central line and its shift to slightly lower magnetic field. The spectral pattern continues to change on standing in air with a decrease in the spectral intensity, and the well-defined sextet-type spectrum was obtained more than 30 min later, which is apparently similar to that of plasma-irradiated HDPE. The simulated spectra shown as dotted lines in Figure 1 disclosed that the change in the spectral pattern in LDPE is caused by a rapid formation and slow dissipation of the peroxy radicals which has a larger g-value than carbon-centered radicals.

The result is in sharp contrast to the nature of spectral changes in HDPE. Exposure of a well-defined sextet-type spectrum of HDPE to air at room temperature does not show a significant change in spectral pattern, but shows only the decrease in the spectral intensity. The computer simulations of these progressive changes, however, have clearly shown the presence of a small amount of peroxy radicals.

Figure 2 shows the progressive changes of the component spectra of LDPE and HDPE as a function of standing time in air for the simulated spectra shown in Figure 1. It can be seen that all the component spectra, (I), (II) and (III) in LDPE, decay in intensity on exposure to air, but among these, II and III quite rapidly disappeared. Likewise, the component spectrum (III) in HDPE almost instantly disappeared, but the spectrum (II) in HDPE behaved differently from that in LDPE, which decays only gradually with standing time. The rate of decay of sextet spectrum (I) of LDPE is similar to that of HDPE ($\tau_{0.5} = 0.34$ for LDPE and ca. 0.32 for HDPE). On the other hand, the formation of peroxy radical (dashed lines in Figure 2) shows a maximum in intensity about 10 min later and then decreases gradually with prolongation of standing time in air in both PE, which apparently underwent the chain termination reactions through the hydroperoxide consuming several moles of oxygens. Further, it was deduced from Figure 2 that the ratio of
peroxy radical quantity against a total amount of radicals in HDPE is only ca. 16% at the stage showing a maximum amount of peroxide radical formation, while it is ca. 54% in LDPE. Thus, it became clear that only a slight change in spectral pattern on exposure of plasma-irradiated HDPE to air is caused by peroxide radical formation in much lower ratio and then concealed from its clear observation in the spectra.

Figure 3 shows the peroxide radical spectra in the simulated spectra shown in Figure 1. It is apparent that both spectral features in LDPE and HDPE change gradually with time indicating that the spectra are composed of more than two components, and can be deconvoluted into two kinds of representative component spectra shown as two types of dotted lines in both LDPE and HDPE. One spectrum (1P) has shown to be a typical powder anisotropic spectral pattern of peroxide radical with a partial g-averaging (rough dotted line) and the other (2P) gave a nearly isotropic single line with nearly complete averaging of g-anisotropy (fine dotted line), probably due to the rapid C-O bond rotation of peroxide radical. Thus, it was shown that 2P decayed with a higher rate than 1P due to more rigorous molecular motion. It can be considered that the presence of two kinds of spectra of peroxide radicals is due to the difference in the polymer surface morphology at the site of the peroxide radical formation.

All these results strongly indicated that a mid-chain alkyl radical of sextet spectrum (I) is of much lower reactivity with oxygen, and the formation of peroxide radicals stems mainly from septet spectrum (II) and a smeared-out broad line (III) in both cases.

It is a well-known fact that peroxide radical formation of HDPE occurs mostly at amorphous region due to high capability of oxygen diffusion. In fact, the rate of oxygen diffusion into crystalline region was reported to be about one tenth relative to that to amorphous region. Thus, the difference in the nature of peroxide radical formation between LDPE and HDPE can be rationalized in terms of the fact that a large amount of DBS (3) were formed at the amorphous cross-linked layer at the surface of plasma-irradiated LDPE, and was very sensitive to oxygen, whereas the mid-chain alkyl radicals (1) mainly formed in plasma-irradiated HDPE were unimportant in the formation of peroxide radical, since most of such radicals are located at the crystalline region. Part of allylic radicals (2) is considered to be located at crystalline region especially in the case of HDPE. In fact, as was shown in Figure 2, part of septet spectra (II) as well as sextet spectrum (I) remained even after standing for a long period of time in air.

From these reasons, the ESR spectra of peroxide radicals (Figure 3) were similar in pattern between LDPE and HDPE, and much less amount of peroxide radicals were formed in HDPE than LDPE, although the ESR spectra of plasma-induced radicals are quite different in pattern from each other.

The ESR spectrum of peroxide radicals does not give any information of the original radical structures due to the absence of any hyperfine splitting constants in the spectra, although it does give the information of the molecular motion where the peroxide radicals are located. It is difficult, therefore, to elucidate the spectral feature of peroxide radicals derived from each of three original carbon-centered radicals, unlike the case of plasma-irradiated polytetrafluoroethylene (PTFE) where three component radicals formed were able to be obtained separately so that the ESR spectrum of each peroxide radical was elucidated. However, the present result in PE can be most
reasonably explained by invoking that 1P could be formed from DBS (3), where the molecular motional freedom at the cross-linked layer must be highly restricted, while 2P was formed from the other radicals, (1) and (2), since 1P was present in a larger quantity than 2P in the simulated spectra of peroxy radicals in both LDPE and HDPE.

We believe this is the first detailed spectral analysis of peroxy radicals of PE, and of the nature of progressive changes of its formation produced by any kind of radiation method.

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References


