Thermodynamic Elucidation of Depression Mechanism on Sorption of Flavor Compounds into Electron Beam Irradiated LDPE and EVA Films

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Electron beam irradiation for low-density polyethylene (LDPE) film up to 20 Mrad resulted in specific sorption depression behaviors of volatile compounds. The sorptions of octane, ethyl hexanoate, and d-limonene into irradiated film were depressed, whereas the opposite behavior was obtained for octanal and octanol. To elucidate these specific phenomena, a thermodynamic attempt of applying the solubility parameter (SP) value was done. As a result, the sorptions of all hydrocarbons and methyl and ethyl esters composed of more than six carbon atoms corresponding to <8.59 SP value were depressed in all, while sorption promotion was observed for all alcohols. A similar result was obtained for irradiated EVA film, for which the sorption depression was observed only for the volatile compound with <8.93 SP value. Calculating the ratio of SP value of volatile compound (δ_F) to that of irradiated film (δ_P), the ratios (δ_F/δ_P) for irradiated LDPE and EVA films gave good agreement at 1.09.

INTRODUCTION

Low-density polyethylene (LDPE) is one of the most extensively used polymers as an interior lining, as is ethylene vinyl acetate (EVA) copolymer, because of its prominent processing properties such as heat sealing characteristics (Hirose et al., 1987). Reports in 1989 on the statistics of shipping value and mass of packaging materials and containers in Japan revealed that the total shipping mass of LDPE for interior linings reached 86% in all (Shimizu, 1990). As is well-known, however, LDPE film has fairly inferior gas barrier properties; the rate of oxygen permeability is roughly 3 orders of magnitude greater compared with that for poly(vinylidene chloride) (PVDC) or ethylene vinyl alcohol (EVOH) copolymer films (Yamazoe, 1989). In addition, the sorptions of flavor compounds into LDPE film were more pronounced than into any other films, as we have already reported (Shimoda et al., 1987). The use of LDPE film as an interior lining, therefore, would result in the marked deterioration of flavors during storage, because of its direct contact with foodstuffs.

In studies on sorption of flavor compounds into films, our interest has been focused on the improvement of commercially available interior linings to provide a high-quality food. The present work is part of a continuing investigation on the depression of sorption by treatment with electron beam irradiation (Matsui et al., 1990, 1991a–c). In previous papers, we have revealed that this treatment for EVA film up to 20 Mrad gave a marked depression effect, being attributable to three-dimensional network structure by mild cross-linking (Matsui et al., 1991c).

The purpose of the present paper is to evaluate the effect of electron beam irradiation on sorption into LDPE and EVA films and to elucidate the mechanism of sorption depression thermodynamically. A new approach based on the interaction between flavor compound and film will be seen.

MATERIALS AND METHODS

Permeation Apparatus. The aqueous-phase permeating apparatus, based on the isobaric method, is described in detail elsewhere (Matsui et al., 1989). Volatile compounds permeating

through a sample film were detected by GC [Shimadzu GC-8A, equipped with a flame ionization detector (FID)]. Experimental runs were carried out at the temperature of the flavor solution of 25 °C, oven temperature of 100 °C, and a carrier gas flow rate of 50 mL/min. The diffusion (D), permeation (P), and solubility (S) coefficients were calculated from the differential permeation curve.

Preparation of Model Flavor Solution. The volatile compound was added to a surfactant solution (300 mL) to make a 200 ppm flavor solution. The concentration of the surfactant, sugar–ester (S-1170, Mitsubishi-Kasei Food Co, Ltd., Tokyo), composed of sucrose mono- and distearate mixture, was 0.3 w/v %.

The volatile compounds and swelling solvents used in these experiments were all guaranteed to be of reagent grade from Nakarai Chemicals Co. Ltd., Kyoto, and were used without further purification.

Preparation of Modified Films. EVA with vinyl acetate content of 15.0 wt % and LDPE (L150 grade) films were manufactured at the Oita Laboratory of Showa Denko KK, Oita, Japan. The characterizations of LDPE film used are summarized in Table I. Both films were of 0.05-mm thickness and were electron beam irradiated with doses of 10 Mrad for EVA film and 5–20 Mrad for LDPE. All other conditions were the same as described in a previous paper (Matsui et al., 1990).

Characteristics of Modified LDPE Film. The measurements of gel fraction, ratio of scission to cross-linking events, degree of crystallinity, melting point, tensile strength, and degree of cross-linking were carried out at the same conditions as already reported (Matsui et al., 1991b).

The fractional free volume of LDPE film, f_0, was calculated from the derived formula (Asfour et al., 1989)

$$f_0 = [f_g + \alpha(T - T_g)](1 - \phi_c) \tag{1}$$

where T_g is the glass transition temperature of LDPE, taken as −75 °C (Manaresi and Giannella, 1960), f_g (=0.025) is the fractional free volume of LDPE at T_g, α is the difference between the thermal expansion coefficient above and below T_g, taken to be 4.8 × 10⁻⁴ (Asfour et al., 1989), and ϕ_c is the volume fraction crystallinity. Thus, the determination of ϕ_c is allowed to derive the fractional free volume of LDPE.

Estimation of Solubility Parameter. The solubility parameter (SP) value is an index of the compatibility of polymer and solvent, providing helpful information of correlating and predicting the magnitude of solubility of flavor compounds into film from a knowledge of the properties of the individual components alone. The SP value is defined as the square root of cohesive energy density (CED) (Barton, 1985)

Table I. Characteristics of LDPE (L150 Grade) Film

density, g/cm³	molecular weight			structure[a] (per 100 carbons)			
	M_n (×10⁴)	M_w (×10⁴)	M_w/M_n	methyl	ethyl	butyl	short-chain branching
0.928	1.83	16.5	9.0	2.58	4.20	4.49	4.88

[a] IR measurement.

$$SP \text{ value } (\delta) = (CED)^{1/2} = (\Delta E/V)^{1/2} \text{ (MPa}^{1/2}) \qquad (2)$$

where ΔE is the energy of vaporization and V is the molar volume. Relating to the SP value of volatile compounds, the literature data (Burrell and Clifton, 1975) were cited; when there was a lack of data corresponding to a compound in the literature, the value was calculated from the equation defined by Small (1960)

$$\delta = d \sum G/M \qquad (3)$$

where $\sum G$ is the sum of group molar attraction constants derived from measurement of heat of vaporization at 25 °C, d is the density, and M is the molecular weight.

In the case of LDPE and EVA films, the value was estimated from equilibrium swelling measurements with solvents of known SP value suggested by Mangaraj (1963). The solvents used in this experiment were aliphatic hydrocarbons and aliphatic esters with SP values ranging from 7.0 to 10.0. The procedure for swelling measurements was as follows. Specimens weighing 0.01–0.02 g were immersed in a glass tube that contained the solvent under investigation for 24 h at 23 ± 0.5 °C. After the equilibrium swelling was achieved, the film was removed from the solvent, pressed lightly between two sheets of filter paper, placed in a tapered flask, and weighed to calculate the swelling ratio (Q). Hence, a plot of $(1/V \ln (Q_{max}/Q))^{1/2}$ vs δ of the solvents could evaluate a SP value of film from an intercept extrapolated.

RESULTS AND DISCUSSION

Table II summarizes the mechanical changes of LDPE film by electron beam irradiation up to 20 Mrad. The gel, toluene-insoluble fraction, was formed by irradiation, suggesting that any cross-linking reactions must occur in the films; the maximum gel fraction (% gel) was 50.3% at 20 Mrad irradiation. Further, the lowering of melting temperature (T_m) and the increase of elongation (ϵ) indicated the formation of a three-dimensional network structure in amorphous regions by cross-linking. On the contrary, both parameters of degree of crystallinity (χ_c) and stress at yield (σ_Y) significantly decreased with increasing dose, indicating that irradiation for LDPE film may result in the scission of the main chain in crystalline regions as well as for EVA film (Matsui et al., 1991b). This closely agreed with the report of Gal et al. (1986). In addition, the degree of crosslinking (ν) decreased, the free volume (f_0) increased by irradiation, and the ratio of scission to cross-linking events (p_0/q_0) was 1.06. Thus, one may suggest that the LDPE film used in this study is a polymer of scission type, supported by the result that the p_0/q_0 ratio of a polymer of cross-linking type lies between 0.1 and 0.5 (Narkis et al., 1987).

On the basis of the above findings relating to physical properties of electron beam irradiated LDPE film, an attempt to elucidate sorption behaviors of flavor compounds into the film was made. Table III represents the effect of volatile compounds bearing various functional groups on sorption into irradiated LDPE film in the aqueous phase. The solubility coefficient is measured as the amount of soluble volatile compound in the film, per unit volume and concentration difference across the film, and diffusion coefficient as the rate of transfer in unit thickness of the film. Interestingly, the solubility coefficients in 20-Mrad irradiated LDPE film decreased not

for octanal and octanol but for octane, ethyl hexanoate, and d-limonene, quite similar to the behaviors in our previous paper (Matsui et al., 1990); the maximum decreasing ratio in solubility coefficient in 20-Mrad irradiated LDPE film against the unirradiated one was about 22% for octane, with the smallest polarity among them. Similarly, diffusion coefficients of octane, ethyl hexanoate, and d-limonene significantly increased with irradiation, while the opposite results were obtained for octanal and octanol.

Since these specific sorption phenomena must be brought about by any interaction between treated film and volatile compound, further investigation was performed with attention to the molecular properties of both film and compound. Figure 1 shows the effect of carbon chain length in aliphatic hydrocarbons, ethyl esters, and alcohols on sorption into 20-Mrad irradiated and unirradiated LDPE films. For all hydrocarbons the sorption was depressed in irradiated film, whereas the promotion of sorption by irradiation was found for all alcohols. On the other hand, for ethyl esters a highly specific behavior was obtained in spite of their homologous series; that is, the sorption into irradiated film increased up to six carbon atoms in esters, while in more than six carbon atoms the sorption was significantly depressed. These results revealed that the appearance of this effect must be brought about by the molecular properties of the volatile compound, not by the molecular size.

A similar investigation with regard to diffusion behavior was done. As a result, for hydrocarbons and alcohols the diffusions in irradiated films had the same tendency without affecting the molecular size. As for ethyl esters, the diffusion coefficient decreased in irradiated film up to five carbon atoms, whereas in more than five carbon atoms the opposite results were obtained as well as the sorption behavior. Therefore, the specific behavior of diffusion may also be concerned in another factor, not in molecular size.

Then, to elucidate the specific sorption behaviors in electron beam irradiated LDPE film, the concept of the solubility parameter (SP) value of volatile compound was adopted, which is dealt with as a means of evaluating a film–volatile compound compatibility (Barton, 1985). Figure 2 shows the plot of solubility coefficient of various volatile compounds against their SP values. In general, the SP value decreases with an increase in the number of carbon atoms, except for hydrocarbons. Apparently, sorption behaviors of volatile compounds in irradiated LDPE film were found to reverse at a point of 8.59 of SP value. That is, the sorptions of all hydrocarbons and methyl and ethyl esters composed of more than six carbon atoms corresponding to less than 8.59 SP value were depressed in irradiated film in all, whereas for compounds having an SP value >8.59 quite the opposite results were obtained. Essentially, the process of sorption of molecule into film follows three steps: dissolution into film via adsorption and condensation (mixing) at the surface (Macdonald et al., 1981; Frisch et al., 1954). Thus, sorption (solubility) is brought about in breaking loose from the neighbor polymer chains by condensation of volatile compound. The specific sorption behavior, therefore, may be explained as follows. The volatile compound with high cohesive energy of >8.59 SP value, which has enough energy to compensate for the forces between polymer chains, increases the chain mobility, resulting in an increase in the solubility with the increase in free volume by irradiation (Table II). On the other hand, for the volatile compound with low energy of <8.59 SP value, which cannot reduce

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Table II. Characteristic Change of Irradiated LDPE Film

dose, Mrad	% gel[a]	$\chi_c,$[b] %	$T_m,$[c] °C	σ_Y[d] (×10⁵), N/m²	$\epsilon,$[e] %	P_0/q_0[f]	Q[g]	ν[h]	f_0[i] × 10⁻²
0	0	52.8	104.4	102.8	157.1				3.45
10	41.8	49.3	103.9	94.3	167.4	1.06	1.14	0.86	3.70
20	50.3	49.2	103.3	89.4	179.6		1.15	0.85	3.71

[a] Soxhlet extraction with toluene for 10 h at 140 °C. [b] Degree of crystallinity. [c] Melting temperature. [d] Stress at yield. [e] Elongation at break. [f] Scission to cross-linking ratio. [g] Degree of swelling. [h] Degree of cross-linking. [i] Fractional free volume.

Table III. Sorption Behavior of Volatile Compounds Bearing Various Functional Groups into Irradiated LDPE Film at 25 °C in the Aqueous Phase

	octane		ethyl hexanoate		octanal		octanol		d-limonene	
	0 Mrad	20 Mrad	0 Mrad	20 Mrad	0 Mrad	20 Mrad	0 Mrad	20 Mrad	0 Mrad	20 Mrad
D^a × 10⁹	21.6	27.2	11.3	13.1	6.1	5.2	5.2	4.6	5.8	6.1
P^b × 10⁷	37.2	36.6	5.8	6.0	1.7	1.6	0.9	1.0	11.5	10.7
S^c	172.5	134.6	50.9	45.6	28.7	31.1	17.7	22.1	198.9	177.5

[a] Diffusion coefficient (cm² s⁻¹). [b] Permeation coefficient (μg cm⁻¹ s⁻¹ per mg L⁻¹). [c] Solubility coefficient (μg cm⁻³ per mg L⁻¹). The CV of four replications was less than 3.0%.
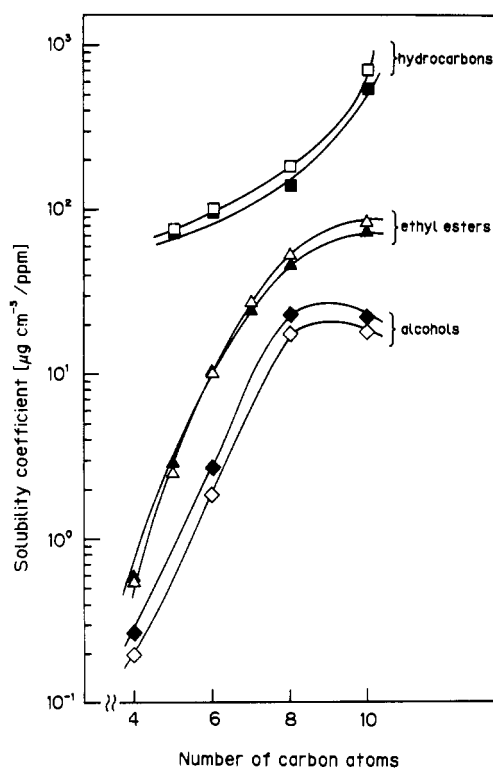

Figure 1. Effect of carbon chain length in aliphatic hydrocarbons, ethyl esters, and alcohols on sorption into irradiated LDPE film at 25 °C. Irradiated dose: 0 Mrad ($\square$, $\triangle$, $\diamond$); 20 Mrad ($\blacksquare$, $\blacktriangle$, $\blacklozenge$).

Figure 2. Relationship between SP value and solubility coefficients of volatile compounds in irradiated LDPE film at 25 °C. Volatile compound: n-hydrocarbons, 0 Mrad ($\square$), 20 Mrad ($\blacksquare$); methyl esters, 0 Mrad ($\triangledown$), 20 Mrad ($\blacktriangledown$); ethyl esters, 0 Mrad ($\triangle$), 20 Mrad ($\blacktriangle$); n-aldehydes, 0 Mrad ($\bigcirc$), 20 Mrad ($\bullet$); n-alcohols, 0 Mrad ($\diamond$), 20 Mrad ($\blacklozenge$).

the forces, the sorption may be depressed by the chain restriction due to mild cross-linking.

In a similar plot of diffusion coefficient vs SP value, the diffusions in irradiated LDPE film were promoted only for compounds with SP value <8.72. The detailed explanation is as follows. The volatile compound with low SP value <8.72 is thought to diffuse in the form of "monomer" within the film due to its low cohesive energy, so that the diffusion increased with the increment of free volume of film or amorphous region by chain scission in the irradiated film. On the contrary, the compound with high SP value >8.72 is assumed to diffuse in the form of "macropenetrant" with large molar volume apparently due to its high cohesive energy (Orofino et al., 1969). Hence, the restriction of chain segment mobility by mild cross-linking may lead to the depression of diffusion of this volatile compound as a macropenetrant.

The concept of SP value was applied for terpenes (Table IV). As shown in the table, sorption depression in
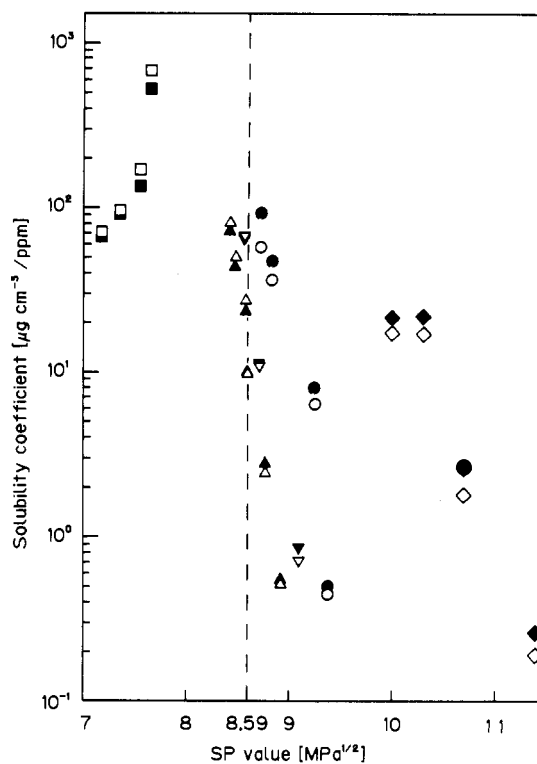
Table IV. Application of the Concept of SP Value for Sorption of Terpenes in Irradiated LDPE Film at 25 °C

	d-limonene (7.36)[a]		myrcene (7.78)		citral (8.95)	
	0 Mrad	20 Mrad	0 Mrad	20 Mrad	0 Mrad	20 Mrad
D^b × 10⁹	5.8	6.1	6.2	7.2	3.3	3.2
P^c × 10⁷	11.5	10.7	10.9	11.8	1.6	1.7
S^d	198.9	177.5	175.6	163.5	48.8	54.4

[a] SP value (M Pa¹ᐟ²). [b] Diffusion coefficient (cm² s⁻¹). [c] Permeation coefficient (μg cm⁻¹ s⁻¹ per mg L⁻¹). [d] Solubility coefficient (μg cm⁻³ per mg L⁻¹).

irradiated LDPE film was observed for d-limonene (7.36 SP value) and myrcene (7.78), but not for citral (8.95). This result demonstrated that the sorption may be depressed only for the compound with <8.59 SP value. In conclusion, the mechanism of sorption depression could
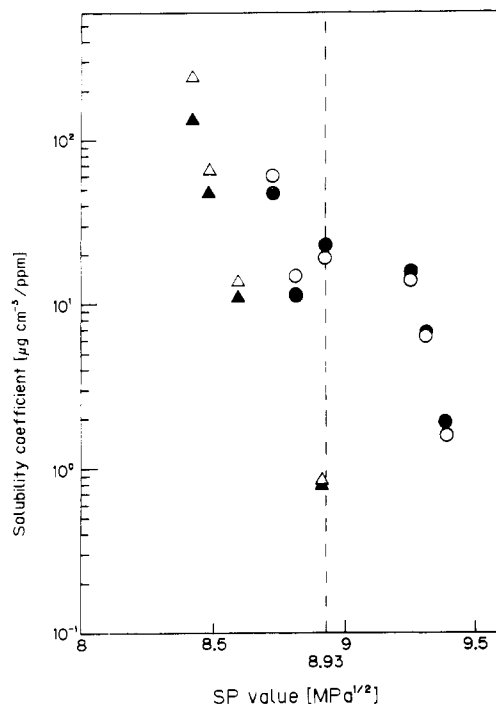
Figure 3. Relationship between SP value and solubility coefficients of volatile compounds in irradiated EVA film at 25 °C. Vinyl acetate content is 15.0 wt %. Volatile compound: ethyl esters, 0 Mrad (△), 10 Mrad (▲); n-aldehydes, 0 Mrad (O), 10 Mrad (●).

be elucidated by application of SP value (in other words, compatibility) for the first time.

The same application was made for electron beam irradiated EVA film into which the sorption was markedly depressed as already reported (Matsui et al., 1990). Figure 3 shows the plots of solubility coefficient of aliphatic ethyl esters and aldehydes in unirradiated and 10-Mrad irradiated 15.0 wt % EVA films as a function of their SP value. For irradiated EVA film, the reverse phenomenon of sorption from that for LDPE film was recognized and the sorption was depressed for the volatile compound with <8.93 SP value. Therefore, it was clear that a close relationship between this depression effect and the cohesive energy of volatile compound may exist. The distinction of SP values at a point of reversing the sorption behaviors for LDPE or EVA film is considered to be attributable to the difference of cohesive energy of each film. Thus, the concept of SP value was applied for volatile compound and irradiated film, further investigation being performed upon the compatibility with film.

With regard to the diffusion behaviors, for ethyl esters the diffusion coefficient increased in irradiated EVA film, whereas for aldehydes the coefficient decreased up to seven carbon atoms. That is, the decrease in diffusion coefficient for irradiated EVA film was observed only for the volatile compound with >8.93 SP value in a similar manner for LDPE film, although the values were distinct.

Figures 4 and 5 represent the plots of $(1/V \ln (Q_{max}/Q))^{1/2}$ against the SP value of swelling solvent used to determine the SP values of both EVA and LDPE films. From Figure 4, the SP values of unirradiated and irradiated EVA films were 8.13 and 8.20, respectively. For LDPE film, the SP value was determined to be 7.90 and 7.92 for unirradiated and 20-Mrad irradiated films, respectively (Figure 5). These data revealed that the cohesive energy of polymer is little affected by electron beam irradiation. The higher value of EVA film compared to that of LDPE film indicates that the polarity of EVA film is higher, because it possesses
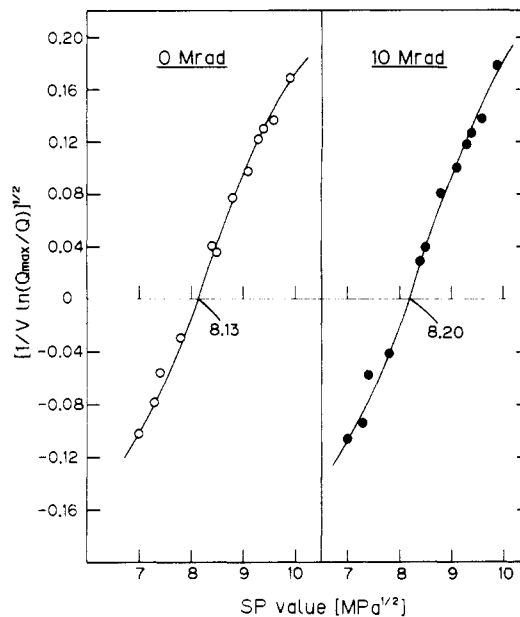

Figure 4. Plots of $(1/V \ln (Q_{max}/Q))^{1/2}$ against SP value for EVA film. Vinyl acetate content is 15.0 wt %. Irradiation dose: 0 Mrad (O); 10 Mrad (●).
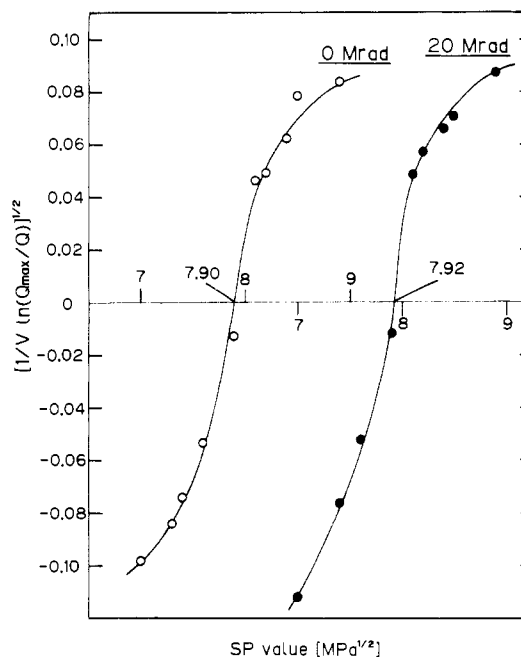

Figure 5. Plots of $(1/V \ln (Q_{max}/Q))^{1/2}$ against SP value for LDPE film. Irradiation dose: 0 Mrad (O); 20 Mrad (●).

acetate groups. As mentioned earlier, the SP value is an index of compatibility of foreign substances, and thus the closer the value, the better mixing is obtained. Hence, to evaluate the compatibility of volatile compound with irradiated film, the ratio of the SP value of volatile compound (δ_F) to that of irradiated film (δ_P) at a point of reversing the sorption behavior was calculated; the ratio for LDPE (δ_F/δ_P) was 8.59/7.92 = 1.085 and for EVA (δ_F/δ_P) was 8.93/8.20 = 1.089, giving nearly agreement at ca. 1.09, despite the different SP values for each film. This agreement demonstrated that the appearance of sorption depression in EVA and LDPE films by electron beam irradiation depends on the "mutual interaction" power between cohesive energies of volatile compound and film. Stated another way, values of δ_F/δ_P of less than 1.09 could indicate depressed sorption of flavor compounds.

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ABBREVIATIONS USED

LDPE, low-density polyethylene; EVA, ethylene vinyl acetate copolymer; SP, solubility parameter.

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