Sorption Depression of Flavors into Modified EVA Film by Lowering Film–Flavor Affinity

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Surface hydrolysis of ethylene–vinyl acetate copolymer (EVA) film resulted in a specific sorption depression behavior of volatile compounds. The sorptions of hydrocarbons, ethyl octanoate, and decanal into hydrolyzed EVA film were depressed, whereas the sorptions for alcohols were all promoted. To elucidate the phenomena, the solubility parameter (SP) concept was introduced. From the plots of sorptions against the SP values of volatile compounds, for all hydrocarbons, ethyl esters, and aldehydes with the cohesive energy of <19.3 SP value, the sorptions were depressed, while for hexanal and all alcohols with the SP value of >19.3 quite the opposite results were obtained. It was considered that the depression effect may be attributed to the lowering of compatibility at the surface between hydrolyzed film and volatile compounds. Sensory evaluation also supported flavor preservation for hydrolyzed EVA film in lemon juice.

INTRODUCTION

The deterioration of flavors is well-known to be partly caused by any interactions between food and food packaging (Mannheim et al., 1987; Letinski and Halek, 1992). Among them, migration (sorption) of flavors would greatly affect the quality of food, because the film has been in direct contact with foodstuffs over a long period of storage (Shimoda et al., 1984; Sadler and Braddock, 1991). Hence, the usage of polyolefin films with flexibility and heat sealability, which have been widely used as interior linings, may be restricted due to their poor gas barrier or greater sorptions of food flavors (Ikegami et al., 1987, 1988; Shimoda et al., 1987).

Recently, some attempts with respect to modification of polyolefin films have been made to improve their physical or chemical properties. With the aim of enhancing gas barrier characteristics, surface alteration of polyethylene (PE) by plasma fluorination (Corbin et al., 1987; Farrell, 1988), grafting of acrylonitrile onto PE by electron beam irradiation (Mori et al., 1991), and casting of unsaturated compounds (Vijayalakshmi and Murthy, 1992) have been performed. There has been, however, less research on sorption depression of flavors by modifying the film property. In our previous papers (Matsui et al., 1990, 1991), electron beam irradiation treatment for ethylene–vinyl acetate copolymer (EVA) film was ascertained to be advantageous for preserving food flavors; when 15.0 wt % EVA film was irradiated at a dose of 10 Mrad, the sorptions of ethyl hexanoate, octane, and d-limonene were depressed about 25, 45, and 60%, respectively, in comparison with the unirradiated film. The depression mechanism could be elucidated thermodynamically by applying the solubility parameter (SP) (Matsui et al., 1992a). In addition, we have induced the affinity concept represented as two-dimensional cohesive energy density distance (δ_c) between film and flavor to estimate the degree of sorption and revealed that the sorption depends on the δ_c value (Matsui et al., 1992b).

These findings led us to a useful suggestion that sorption may be depressed when film–flavor affinity is lowered. In this paper, an attempt at surface polarization of EVA film by chemical modification is described.

MATERIALS AND METHODS

Materials. EVA film of 0.05-mm thickness with vinyl acetate content of 15.0 wt % was manufactured at the Oita Laboratory of Showa Denko Inc., Ltd., Oita, Japan. The volatile compounds used in this study were all guaranteed to be of reagent grade from Nacalai Tesque Inc., Ltd., Kyoto, Japan, and were used without further purification. Commercial one-fifth concentrated lemon (*Citrus limon* Burm. f.) juice was reconstituted with deionized water before use.

Methanolysis of EVA Film. The methanolysis of EVA film was made according to our previous paper (Matsui et al., 1992c); EVA film (110 mm × 120 mm) was reacted with 100 mL of methanol solution containing 4.0 g of sodium hydroxide at 70 °C. Under this reaction, the acetate group was converted into a hydroxyl group as shown in Figure 1.

Preparation of Model Flavor Solution. Volatile compounds were added to a solution (300 mL) of 0.3 w/v % sugar–ester (S-1170, Mitsubishi-Kasei Food Co., Ltd., Tokyo; hydrophilic–lipophilic balance value 11) to make a 10 ppm flavor solution and dispersed homogeneously by an ultrasonic wave generator for 15 min. Treated and untreated films were individually immersed in this model flavor solution and stored at 20 °C until the equilibrium of sorption was achieved (in this experiment, about a 21-day storage).

Recovery of Volatile Compounds. The sorbed film was immersed in 60 mL of diethyl ether and allowed to stand for 2 days. The ether eluents were dehydrated by anhydrous sodium sulfate for 2 h after addition of internal standard (1 μL/100 mL of amylbenzene), followed by concentration on a water bath at 42 °C. The extracts were analyzed by gas–liquid chromatography (GLC). The analysis was performed on a Shimadzu GC-8A gas chromatograph connected to a Shimadzu Chromatopac C-R3A integrator. A fused silica capillary column coated with 10% (cyanopropyl) phenyl polysiloxane (CBP10, 0.25 mm i.d. × 50 m, Shimadzu Co., Ltd., Kyoto, Japan) was used for separation, and the column temperature was programmed from 60 to 240 °C at 2 °C min⁻¹.

Sensory Evaluation. Sensory evaluation was carried out by ranking to determine the difference of flavor quality between three lemon juice samples, when no, untreated, and treated EVA films were immersed in each sample. The ranking was made as follows: 1, bad; 2, good; 3, better. The 10 panelists, who had previous experience in evaluating food flavor, were selected from the Kyushu University. The significance of data obtained was

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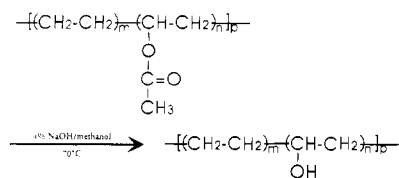
* Author to whom correspondence should be addressed.

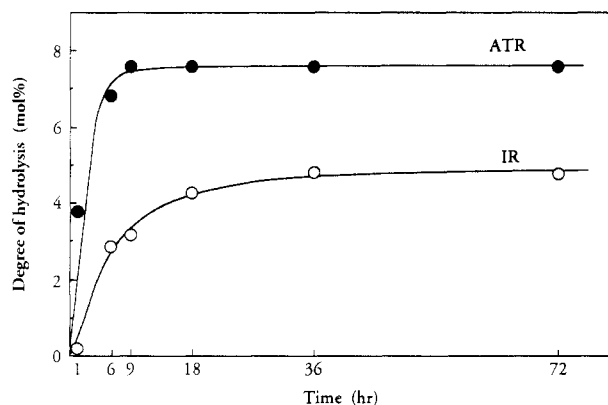**Figure 1.** Hydrolysis of EVA film with methanol.

Figure 2. Yield of OH groups by hydrolysis measured by IR (O) and ATR (●) methods.

judged from the W value, which is the coefficient of concordance. For example, if the rankings by all panelists are the same, the value is 1. In this paper, the data with W value greater than 0.43 are significant ($\alpha < 0.01$).

Characteristics of Modified EVA Film. The degree of hydrolysis was calculated by measuring the decrease in vinyl acetate content. The measurement was made with a Shimadzu FT-IR 4000 spectrometer by transmission technique (50 scans and 2.0-cm^{-1} resolution) and by ATR technique using a KRS-5 prism (100 scans, 2.0-cm^{-1} resolution, and incident angle of 45°). In pre-experiment, a plot of absorbance ratio of the carbonyl peak (1740 cm^{-1}) to the CH$_2$ peak (1467 cm^{-1}) against vinyl acetate content by IR (ATR) measurement was found to be linear

$$y = 0.106(0.116)x \qquad (1)$$

where y is the absorbance ratio (1740 cm^{-1}/1467 cm^{-1}) and x is the vinyl acetate content (wt %). The number in parentheses shows the coefficient for the ATR technique. According to eq 1, the vinyl acetate content in the hydrolyzed EVA film was determined. The degree of hydrolysis (yield of OH groups, mol %) was calculated from the composition determined by the obtained vinyl acetate content.

The measurements of heat seal strength, heat of fusion, melting point, and tensile strength were done at the same conditions as in our previous papers (Matsui et al., 1990, 1992d).

The solubility parameter (SP) value was calculated on the group contributions to cohesive energy according to the method of Fedors (1974).

RESULTS AND DISCUSSION

With the aim of lowering the EVA film–flavor affinity, hydroxyl (OH) groups were induced at the surface by hydrolysis of the acetate group with methanol (Figure 1). Figure 2 shows the effect of reaction time on the yield of OH groups measured by IR and ATR methods. The degree of hydrolysis obtained by the IR method remarkably increased with an increase up to 18 h of hydrolysis and tended to level off afterward. On the other hand, maximal yields at the surface obtained by the ATR method were observed for only 9 h of hydrolysis. This result indicated that the hydrolysis reaction within 1.2 μm of the surface was completed in 9 h. Further hydrolysis would result in undesirable progress farther into the EVA film. Thus, the 9-h hydrolyzation for EVA film to yield maximal OH group at the surface may be suitable for this study.

Table I represents the sorption behaviors of volatile compounds bearing various functional groups into the hydrolyzed EVA films after storage for 21 days. Though data are not shown, sorption equilibrium was achieved for 14 days of storage. Interestingly, the sorptions of hydrocarbons (decane, d-limonene, myrcene), ethyl octanoate, and decanal decreased with increasing degree of hydrolysis obtained by IR method, and maximal sorption depression was observed for 3.46 mol % hydrolyzed EVA film (9-h hydrolysis); the decreasing ratio in solubility coefficient against untreated film was about 62, 52, and 36%, for myrcene, ethyl octanoate, and decanal, respectively. On the contrary, the sorptions for alcohols (decanol, nerol, α-terpineol) were all promoted for the treated film. Hence, the sorption into hydrolyzed EVA film could be primarily depressed for lower polarity compounds, which is consistent with our previous finding (Matsui et al., 1990).

Macdonald and Huang (1981) and Frisch and Stannett (1954) reported that the process of sorption of molecule into film follows three steps: dissolution into film via adsorption and condensation at the surface. Therefore, it is considered that a surface property of hydrolyzed EVA film may be of importance in elucidating the specific sorptions described above. Figure 3 shows the relationship between the degree of hydrolysis obtained by IR technique and the yield of OH groups in 100 carbons within 100 Å of the surface by the ESCA method. The corresponding SP values at the surface were calculated from the surface composition determined by the ESCA method. Apparently, the yield of OH group at the surface gave a maximum at 3.5 mol % (9 h) hydrolysis and decreased afterward, indicating that the polarity or SP value at the surface became maximum at 3.5 mol % hydrolysis treatment. Therefore, the specific sorption behavior for each hydrolyzed EVA film (Table I) was assumed to be brought about by the difference of surface polarity (SP value). To elucidate specific sorption behaviors for hydrolyzed EVA film in more detail, the SP concept was adopted, where the SP value (δ) is an index of compatibility between films and/or volatiles. Also, the enthalpy change in mixing is known to be proportional to $(\delta_p - \delta_v)^2$, where δ_p and δ_v are the SP values of polymer and volatile, respectively (Van Krevelen, 1990). Thus, the greater the $(\delta_p - \delta_v)^2$ value, the less sorption may occur. Figure 4 shows the plot of the solubility coefficient of various volatile compounds against their SP values. In this experiment, untreated and 3.46 mol % hydrolyzed EVA films having SP values of 18.2 and 19.3, respectively, were used. Surprisingly, the sorption behaviors of volatile compounds into 3.46 mol % hydrolyzed EVA film were found to reverse at 19.3 SP value, which corresponded to the SP value for 3.46 mol % hydrolyzed EVA film. That is, the sorptions of hydrocarbons, ethyl esters, and aldehydes composed of more than seven carbon atoms, corresponding to a SP value <19.3, were all depressed in 3.46 mol % hydrolyzed EVA film, whereas for hexanal and all alcohols having SP values >19.3 quite the opposite results were obtained, similar to the behaviors in our previous study (Matsui et al., 1992a). As mentioned above, the first step of sorption of flavor compounds is adsorption and condensation at the surface. The specific sorption behavior, therefore, may be explained as follows: for volatile compounds with a low cohesive energy of <19.3 SP value, which have a low affinity to film or have less energy to reduce the cohesive force between polymer chains, the sorption may be depressed by the increase in the surface cohesive energy of hydrolyzed film. On the other hand, for volatile compounds with high energy of >19.3 SP value, which have enough energy to com-

Table I. Sorption of Volatile Compounds into Hydrolyzed EVA Films after Storage for 21 Days at 20 °C

compound	sorption, $\mu g \cdot cm^{-3}$/ppm (degree of hydrolysis,[a] mol %)						
	0	1.05	1.37	3.00	3.46	4.23	4.51
hydrocarbons							
decane	894 (100)[b]	719	633	468	399 (45)	572	681
d-limonene	1260 (100)	1060	777	678	558 (44)	789	944
myrcene	1480 (100)	1210	824	680	557 (38)	844	1030
ethyl ester							
ethyl octanoate	823 (100)	670	554	461	394 (48)	487	521
aldehyde							
decanal	830 (100)	726	725	624	537 (65)	619	665
alcohols							
decanol	203	264	364	369	406	353	346
nerol	44.2	54.6	75.3	79.4	92.7	67.4	69.4
α-terpineol	25.6	29.3	35.0	36.1	38.0	32.1	32.8

[a] Calculated by IR measurement. [b] The sorption ratio against untreated EVA film (100%).
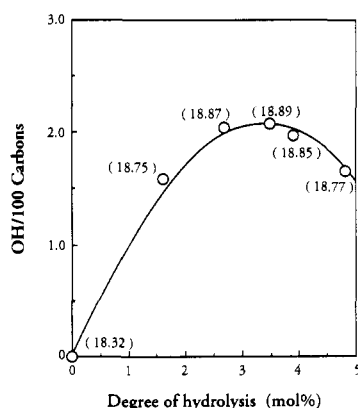

Figure 3. Relationship between the degree of hydrolysis and amount of OH group in 100 carbons for EVA film obtained by ESCA spectra. Numbers in parentheses show the SP value ($MPa^{1/2}$) at the surface of EVA film.

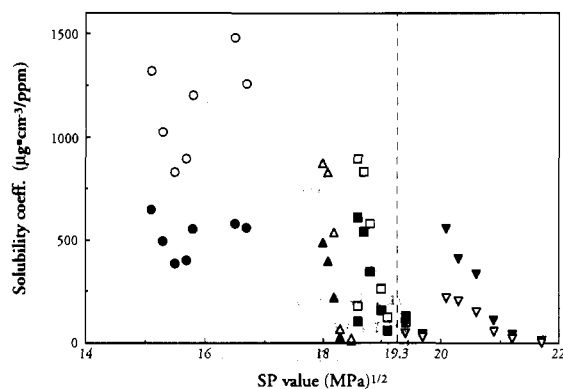**Figure 4.** Relationship between the sorption of volatile compounds into untreated (O, Δ, □, ▽) and hydrolyzed (●, ▲, ■, ▼) EVA films and their SP values. Volatile compounds: hydrocarbons (O, ●), ethyl esters, (Δ, ▲), aldehydes (□, ■), alcohols (▽, ▼). The value of 19.3 corresponds to the SP value for 3.46 mol % hydrolyzed EVA film surface.

Table II. Sorption of Flavors in Lemon Juice into Untreated and Hydrolyzed EVA Films after Storage for 20 Days at 20 °C

compound	sorption, $\mu g \cdot cm^{-3}$/ppm	
	untreated	hydrolyzed
d-limonene	425 (100%)[a]	318 (74.8%)
myrcene	352 (100%)	266 (61.9%)
p-cymene	352 (100%)	226 (75.6%)
linalool	8.1	ND[b]
α-terpineol	22.7	31.6

[a] The sorption ratio against untreated EVA film (100%). [b] ND, not detected.
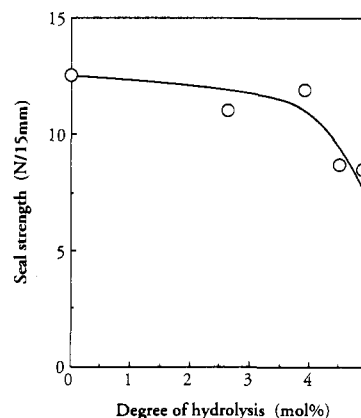
Figure 5. Change in heat seal strength for hydrolyzed EVA films at sealing temperature of 140 °C.

pensate for the forces, the adsorption onto the film surface was promoted by an increase in affinity, resulting in the increase of sorption into treated film.

A practical investigation for hydrolyzed EVA film was performed using commercial lemon juice. Table II summarizes the sorptions of flavor compounds in lemon juice into untreated and 3.46 mol % hydrolyzed EVA films. As shown in the table, sorption depression in hydrolyzed EVA film was observed for terpene hydrocarbons (d-limonene,

myrcene, and p-cymene) except for α-terpineol; the decreasing ratios in solubility coefficient were 25.2, 37.1, and 24.4%, respectively. These behaviors were consistent with the model system (Table I). Also, sensory evaluation supported the advantage of using the hydrolyzed film: the preservation of flavors in hydrolyzed EVA film was significantly superior to that in untreated film [W = 0.79; S (sum of squares deviation) = 158, α < 0.01].

Heat seal strength is the most important factor when using films as an interior lining. Figure 5 shows the change in heat seal strength for hydrolyzed EVA films at a sealing temperature of 140 °C. As a result, the heat seal strength of EVA film was slightly affected by hydrolysis; the strength gradually decreased with increasing degree of hydrolysis, and for >4.0 mol % films the decrease was remarkable. Taking into account the sorption behaviors, 3.5 mol % hydrolyzed EVA film was the most useful and
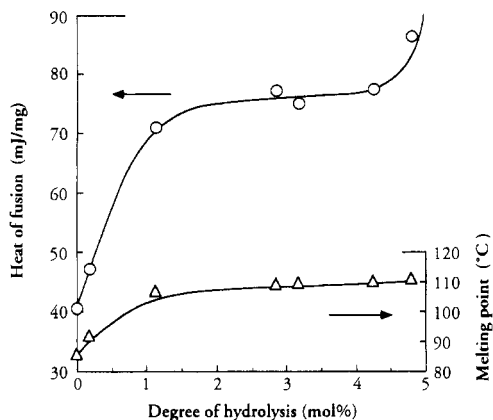
Figure 6. Changes in heat of fusion (O) and melting point (△) for hydrolyzed EVA films.

practical with respect to highest depression and sufficient seal strength.

Figure 6 shows the change in the heat of fusion and melting point as a function of the degree of hydrolysis. As shown in the figure, melting point increased with increasing degree of hydrolysis and reached a constant value at an OH amount of 3.0 mol %, while heat of fusion tended to further increase at more than 4.0 mol % OH amount.

Although tensile strength and elongation at break decreased slightly with increasing degree of hydrolysis (data not shown), the mechanical property would be little affected by hydrolysis treatment.

In conclusion, it was found that sorption depression of flavors into EVA film can be achieved by hydrolysis with methanol. The depression effect which depended on the SP value was assumed to be apparently brought about by lowering the compatibility between film surface and volatile compound. Consequently, the surface-polarized improvement of EVA film will be very effective in depressing the sorption of flavor compounds without any mechanical property changes.

ABBREVIATIONS USED

EVA, ethylene–vinyl acetate copolymer; PE, polyethylene; SP, solubility parameter; GLC, gas–liquid chromatography; IR, infrared; ATR, attenuated total reflection; ESCA, electron spectroscopy for chemical analysis.

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