

Cross-Linking Treatment of EVA Film To Improve Flavor Preservation

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Surface cross-linking treatment of ethylene–vinyl acetate copolymer (EVA) film was performed by formalization in a moderate condition. This treatment led to a marked depression of flavor sorptions. Maximal sorption depression was observed for 18.8 mmol % formalized film, and the maximal depression ratio of solubility coefficient against the unformalized one was about 54% for decane. To elucidate this phenomenon, sorption depression ratios against molecular size were plotted. The sorption of flavors was linearly depressed with an increase in the molecular sizes of the compounds, and the plots for ethyl esters, aldehydes, and alcohols were on the same line ($r = 0.842$). According to the SEM analysis, which revealed the formation of cross-linkage in the formalized film, the depression effect may be attributed to a restriction of the chain mobility in amorphous regions.

Keywords: Cross-linking; sorption; flavor

INTRODUCTION

In spite of the great influence of flavor deterioration by sorption on food quality, polyolefins having a poor flavor barrier are still predominantly used as an interior lining in food packaging because of their prominent processing properties (Osajima and Matsui, 1993; Shimoda et al., 1984; Charara et al., 1992; Konczal et al., 1992; Nielsen et al., 1992). Some investigators have tried to improve or develop packaging films with less sorption of flavors (Koyama, 1990; Hata, 1993), but their application for interior linings might be restricted due to their poor flexibility.

On the contrary, we have continually researched improvements to commercially available interior linings that cause no loss of processing properties. Primarily, we have introduced the electron beam irradiation treatment with low doses for ethylene–vinyl acetate copolymer (EVA) and low-density polyethylene (LDPE) films, in which more effective sorption depression induced by mild cross-linking was observed. In addition, the depression behaviors of flavors into irradiated films were found to depend on the cohesive energies of film and flavor (compatibility) (Matsui et al., 1992a). On the basis of this finding, surface polarization of EVA film was performed by means of hydrolysis, resulting in a specific sorption depression of volatile compounds; for volatile compounds with a cohesive energy of <19.3 SP value, the sorptions were depressed (Fukamachi et al., 1993). Furthermore, a treatment restricted to the film surface had no influence on the mechanical properties of EVA film. These findings indicated that a sufficient surface modification with more cohesive energy would provide an enhanced flavor-barrier property without any loss of mechanical properties.

Surface hydrolysis of EVA film, however, resulted in a promotion of sorption of polar compounds (especially alcohols) due to their higher affinity with the film. Hence, a surface improvement to depress the sorptions of all volatile compounds was needed for keeping flavor balance of foodstuff. In this paper, an attempt to

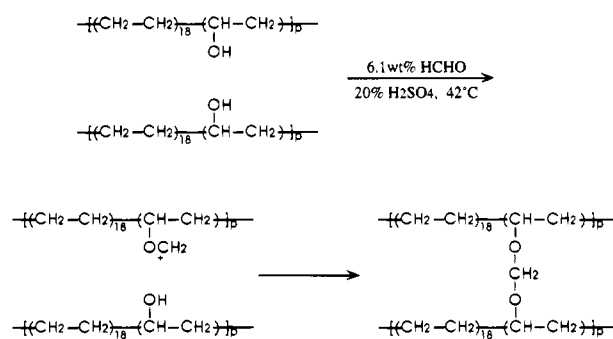


Figure 1. Cross-linking reaction in hydrolyzed EVA film by formalization. The subscript number (mol %) is calculated from the vinyl acetate content (wt %) of EVA film.

achieve the restriction of segmental mobility of polymer chain at the surface is described.

MATERIALS AND METHODS

Material. EVA film of 0.05 mm thickness with vinyl acetate content of 15.0 wt % was manufactured at the Oita Laboratory of Showa Denko K.K., Oita, Japan. The volatile compounds and reagents 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.

Formalization of EVA Film. The methanolized EVA film (110 mm × 120 mm), which was treated to give a maximal yield of OH groups at the surface (Fukamachi et al., 1993), was formalized by the method as described by Ogata et al. (1956). Briefly, 100 mL of deionized water, 25 mL of 18 M sulfuric acid, and 30 g of anhydrous sodium sulfate were mixed. The mixture was kept at 42 °C. Aqueous formaldehyde solution (25 mL, 35 v/v %), previously kept at 42 °C, was added to the mixture (75 mL) with stirring. The methanolized film was immersed in the mixture (100 mL) for a given time at 42 °C. After immersion, the film was thoroughly rinsed with water until the rinsing water was neutral and dried under reduced pressure. This reaction scheme is 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

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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 sorption equilibrium was established (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. After 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-14A gas chromatograph connected to a Shimadzu Chromatopac C-R4A 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. Amylbenzene was added into the ether eluent as an internal standard (1.0 μL/100 mL) to quantify the sorbed volatile compounds.

Characteristics of Formalized EVA Film. The degree of formalization was determined according to the sodium hydrogen sulfite method (Kimura, 1971): a weighed sample (ca. 1.0 g) of formalized film was steam distilled in 20% H₂SO₄ solution (200 mL). The distillate was diluted to 200 mL with water after HCHO involved in formalization was reacted with NaHSO₃. After excess NaHSO₃ in a 50 mL aliquot of the solution was oxidized with 0.02 M iodine solution, Na₂CO₃ was added to the solution to liberate the NaHSO₃ reacted with HCHO. The free NaHSO₃ was titrated with 0.02 M iodine solution. The degree of formalization was calculated by the equations

$$H = 0.12A/W \quad (1)$$

$$y = 4400H/(1500 - 6H) \quad (2)$$

where y is the degree of formalization (mmol %), H is the hydrogen atom content (wt %) in HCHO involved in formalization, A is the amount of titration (mL), and W is the weight (g) of the sample film.

IR measurement was made on a Shimadzu FT-IR 4000 spectrometer by means of the transmission technique (50 scans and 2.0 cm⁻¹ resolution). The peak assignments adopted were as follows: 1467 (CH₂ scissors band) and 1020 cm⁻¹ (C-O-C stretching band).

Scanning electron micrography (SEM) for the surfaces of methanolized and formalized EVA films was made on TOPCON Model ABT-32 (Tokyo, Japan) under the following conditions: acceleration voltage, 15 kV; pressure, ≤10⁻⁵ Torr; 500× magnification.

The measurements of mechanical properties were done under the same conditions as in our previous papers (Matsui et al., 1990, 1992b).

RESULTS AND DISCUSSION

Essentially, the first step in the sorption of molecules into a film is adsorption and condensation (mixing) at the surface (Macdonald and Huang, 1981). On the basis of this concept, surface polarization treatment for EVA film was performed and was proved to be advantageous for depressing the sorption of flavors except for alcohols, which were promoted due to their higher compatibility with the film (Fukamachi et al., 1993). Hence, a surface improvement that reduces chain mobility must be needed for sorption depression of alcohols. With the aim of restricting chain mobility, the hydroxyl (OH) groups at the surface of methanolized EVA film were cross-linked over formaldehyde (Figure 1). Figure 2 shows the IR spectra of methanolized and formalized EVA films measured by the transmission technique. Comparing the IR spectrum of formalized film with that of a methanolized one, the C-O-C peak (1020 cm⁻¹) was remarkably increased, while the other peaks remained unchanged. Judging from the molecular size of formaldehyde, acting as a cross-linking reagent, a cross-

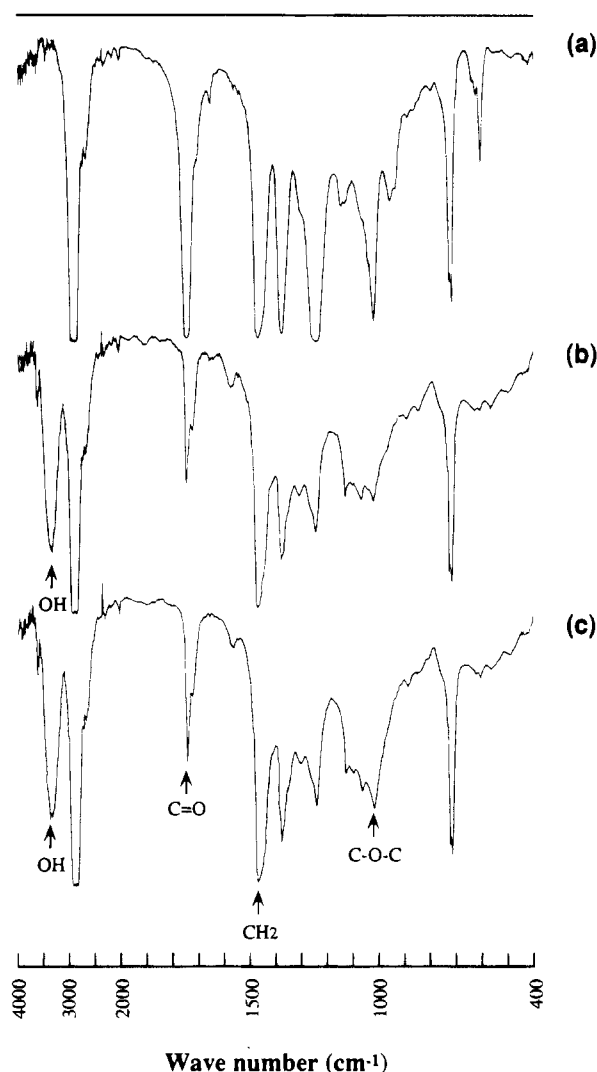


Figure 2. IR spectra of formalized 15 wt % EVA film by transmission technique: (a) untreated and unformalized; (b) methanolized and unformalized; (c) methanolized and formalized film.

linking reaction between neighboring OH groups existing in the same polymer chain could not proceed in this formalization treatment, as depicted in Figure 1. Thus, the increase of the C-O-C peak was attributed to the formation of a hemiacetal structure, cross-linkage, between the OH groups in close polymer chains.

Kuwabara and Obata (1981) adopted the ratio of optical density, $D_{800\text{cm}^{-1}}/D_{850\text{cm}^{-1}}$, for the index of formalization. However, the absorbances of both peaks were so small that one could not calculate the ratio. In this study, the increase of the absorbance ratio of the C-O-C peak (1020 cm⁻¹) to the CH₂ peak (1467 cm⁻¹), $\Delta(A_{1020\text{cm}^{-1}}/A_{1467\text{cm}^{-1}})$, before and after the cross-linking reaction was adopted as an index of the degree of formalization (data not shown). A plot of the degree of formalization determined by the sodium hydrogen sulfite method against $\Delta(A_{1020\text{cm}^{-1}}/A_{1467\text{cm}^{-1}})$ gave a linear relationship ($r = 0.995$)

$$y = 241x \quad (3)$$

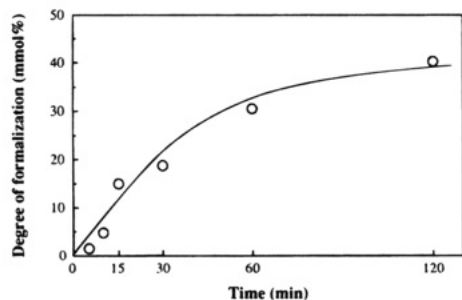
where y is the degree of formalization (mmol %) and x is $\Delta(A_{1020\text{cm}^{-1}}/A_{1467\text{cm}^{-1}})$. On the basis of eq 3, the degree of formalization was calculated by the IR measurement through this study.

Figure 3 shows the effect of reaction time on the yield of the cross-linkage. The degree of formalization remarkably increased with an increase in reaction time

Table 1. Sorption ($\mu\text{gcm}^{-3}/\text{ppm}$) of Volatile Compounds into Formalized EVA Film after Storage for 21 Days at 20 °C

compound	degree of formalization ^a						
	none	0 mmol % ^b	4.8 mmol %	14.9 mmol %	18.8 mmol %	30.6 mmol %	42.7 mmol %
hydrocarbons							
decane	6432	4587 (100)	2686	2307	2088 (46) ^c	2548	2519
<i>d</i> -limonene	2488	1646	1347	1217	1146	1212	1254
ethyl ester							
ethyl octanoate	1377	940 (100)	820	814	766 (81)	785	844
aldehyde							
decanal	1246	1021 (100)	914	902	872 (85)	1001	993
alcohols							
decanol	281	740 (100)	648	638	609 (82)	681	698
nerol	51	93	91	82	76	86	83
α -terpineol	34	56	49	40	36	43	40

^a Calculated by IR measurement. ^b 0, 3.68 mol % methanolized EVA films. ^c The sorption ratio against methanolized EVA film (100%).

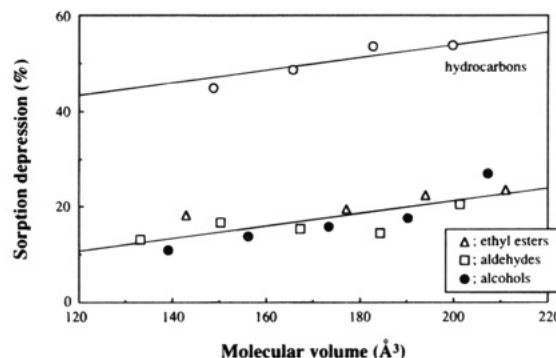
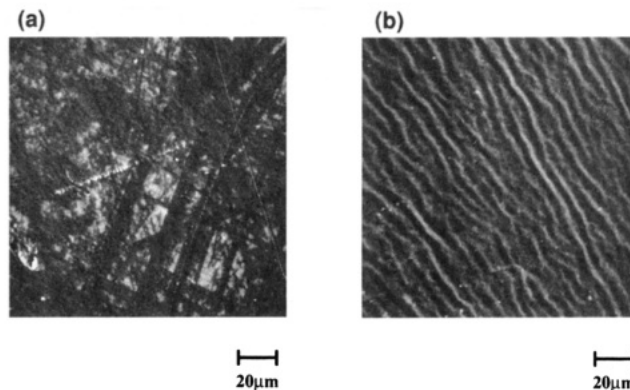
**Figure 3.** Effect of reaction time on yield of cross-linkage.

up to 120 min and tended to be constant afterward. Taking into account the fact that OH groups existed in the film surface restrictively, this result indicated that the surface formalization was complete in 120 min.

Table 1 represents the sorption behaviors of volatile compounds bearing various functional groups into the formalized EVA films after storage for 21 days to achieve sorption equilibrium. The formalization was carried out within 120 min: 5, 10, 30, 60, and 120 min of reaction. Interestingly, the sorption of volatile compounds decreased with increasing degree of formalization regardless of the functional groups (polarity) of the volatile compounds. The maximal sorption depression was observed for 18.8 mmol % formalized EVA film (30 min formalization). The depression ratios in solubility coefficients against methanolized film were about 54%, 19%, 15%, and 18% for decane, ethyl octanoate, decanal, and decanol, respectively.

In previous papers (Matsui et al., 1992a,c; Fukamachi et al., 1993), it was demonstrated that film-flavor affinity is a very important factor with respect to the sorption of flavors; the lower the affinity between film and flavor, the less sorption was observed. Contrary to the finding, the sorptions of all compounds were depressed remarkably in spite of the consistency of the film polarity (SP value for a methanolized film, 19.5; for an 18.8 mmol % formalized one, 19.5) and the compatibility between film and volatile compounds by formalization. This result suggested that other factors were involved in the sorption depression of flavors.

According to Frisch et al. (1954), the process of sorption of molecule into film follows three steps: dissolution into film via adsorption and condensation at the surface. Then, sorption (solubility) is brought about by the breaking loose of the neighboring polymer chains during the condensation of volatile compound. Therefore, a marked depression of sorption in formalized EVA film would be caused by a restriction of the chain mobility in amorphous regions. Figure 4 shows the effect of the molecular size of volatile compounds on the reduction of sorption by formalization. The calculation of the

**Figure 4.** Effect of molecular size on sorption depression of volatile compounds into 18.8 mmol % formalized EVA film. Volatile compounds: hydrocarbons (○); ethyl esters (△); aldehydes (□); alcohols (●).**Figure 5.** Scanning electron micrographs of (a) methanolized and unformalized and (b) methanolized and formalized EVA films; 500 \times magnification. The former was treated under the same condition without HCHO as formalized one. (The figure is reproduced here at 50% of the original.)

molecular size was made according to the volume increment method (Slonimskii et al., 1970). Reduction in the sorption of volatile compounds was linearly dependent on the molecular sizes of the compounds. As shown in Figure 4, the plots for volatile compounds gave a straight line with a slope of *ca.* 0.15, although for hydrocarbons on another line. This result indicated that sorption was depressed by about 1.5% for each molecular volume of 10 Å³.

Figure 5 shows the surface states of formalized and unformalized-methanolized EVA films analyzed by SEM. The latter was treated under the same condition without HCHO as for the formalized one. By comparing both SEM analyses, the observed "wave" structure for the formalized film would result from any cross-linking reactions. Thus, the reduction of sorption was assumed to be due to chain restriction by cross-linking.

Table 2. Sorption of Flavors in Lemon Juice into Untreated, Methanolized, and Formalized EVA Films after Storage for 21 Days at 20 °C

compound	sorption, $\mu\text{g}\cdot\text{cm}^{-3}/\text{ppm}$		
	untreated	methanolized ^a	formalized ^b
β -pinene	3526	2512 (100)	1812 (72) ^f
<i>p</i> -cymene	273	223 (100)	202 (91)
<i>d</i> -limonene	891	724 (100)	612 (84)
β -myrcene	885	701 (100)	533 (76)
linalool	47.3	46.7 (100)	36.5 (78)
α -terpineol	26.4	49.3 (100)	45.5 (92)

^a Methanolized, 3.5 mol % methanolized EVA film. ^b Formalized, 3.5 mol % methanolized–21.2 mmol % formalized EVA film. ^c The sorption ratio against methanolized EVA film (100%).

Table 3. Characteristic Change of Formalized EVA Film

	degree of formalization				
	EVA	0 mmol % ^f	4.3 mmol %	18.3 mmol %	27.5 mmol %
ΔH_f , ^a mJ/mg	72.0	99.5	98.2	97.7	99.4
T_m , ^b °C	87.9	107.2	107.0	107.1	107.0
σ_B ^c ($\times 10^5$), N/m ²	266.0	298.5	278.4	270.1	275.9
σ_Y ^d ($\times 10^5$), N/m ²	159.2	124.6	119.0	119.2	111.8
ϵ , ^e %	233.6	207.8	208.0	201.1	209.1

^a Heat of fusion. ^b Melting temperature. ^c Tensile strength at break. ^d Stress at yield. ^e Elongation at break. ^f 3.5 mol % methanolized EVA film.

A practical investigation for formalized EVA film was performed using commercial lemon juice. Table 2 summarizes the sorptions of flavor compounds in lemon juice into untreated, methanolized, and 21.2 mmol % formalized EVA films. As shown in the table, reduction of sorption in formalized EVA film was observed for all compounds. The decreasing ratios in solubility coefficients for β -pinene, *d*-limonene, β -myrcene, and linalool were 28%, 16%, 24%, and 22%, respectively, consistent with the model system (Table 1). Therefore, a practical use of the formalized film on foodstuff would be very effective in preserving the flavor.

Mechanical property is the most important factor when films are used as an interior lining. Table 3 summarizes the mechanical changes of EVA film by formalization up to 30 mmol %. As shown in the table, the mechanical properties (tensile strength at break, stress at yield, and elongation at break) were barely affected by the cross-linking treatment. Furthermore, small changes in heat of fusion and melting temperature would lead to a retainment of heat seal strength of the formalized EVA film. Thus, the formalized one would be sufficiently used as an interior lining.

In conclusion, it was found that reduction of sorption of flavors into EVA film can be achieved by a formaldehyde cross-linking reaction. The reduction was assumed to be apparently brought about by a chain restriction (cross-linking). Consequently, the surface cross-linking improvement of EVA film would be very effective in depressing the sorption of flavors with sufficient mechanical (processing) properties.

ABBREVIATIONS USED

EVA, ethylene–vinyl acetate copolymer; SP, solubility parameter; GLC, gas–liquid chromatography, IR, infrared; SEM, scanning electron micrography.

Registry No. Supplied by the Author: Formaldehyde, 50-00-0; methanol, 67-56-1; decane, 124-18-5; 1-decanol, 112-

30-1; 1-decanol, 112-31-2; ethyl octanoate, 106-32-1; β -pinene, 18172-67-3; *d*-limonene, 138-86-3; β -myrcene, 123-35-3; *p*-cymene, 99-87-6; α -terpineol, 98-55-5; linalool, 78-70-6; amylbenzene, 538-68-1; ethylene–vinyl acetate copolymer, 24937-78-8.

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Received for review February 17, 1994. Accepted June 28, 1994.*

* Abstract published in *Advance ACS Abstracts*, August 1, 1994.