

# Desorption Behavior of Sorbed Flavor Compounds from Packaging Films with Ethanol Solution

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Desorption behavior of sorbed flavor compounds such as ethyl esters, *n*-aldehydes, and *n*-alcohols from LDPE and PET films was investigated in 0 to 100% (v/v) ethanol solutions at 20 °C, 50 °C, and 60 °C. In both films, the desorption apparently increased with increasing ethanol concentration and treatment temperature, depending on the compatibility of the flavor compound with the solvent. Namely, the partition coefficient of ethyl esters, *n*-aldehydes, and *n*-alcohols in the LDPE film turned out to be approximately zero at  $\geq 60\%$ ,  $\geq 80\%$ , and  $\geq 40\%$  (v/v) ethanol, respectively (for PET film,  $\geq 80\%$ ,  $\geq 80\%$ , and  $\geq 40\%$  (v/v) ethanol concentrations were required for complete desorption, respectively). As for physical properties (heat of fusion, melting point, and tensile strength and elongation at break) of LDPE and PET films, there were no significant differences between intact film and the treated film with 60% (v/v) ethanol for 30 min at 60 °C. These results suggest that it is possible to apply a desorption solvent such as ethanol solution for desorption of sorbed flavor compounds from packaging films with no physical change in the film properties by this desorption treatment.

**Keywords:** Desorption; flavor compound; packaging film; ethanol solution; recycle

## INTRODUCTION

Under the influence of environmental considerations, recycling of food packaging polymers has to be developed. However, in the case of chemical recycling (reusing), there might be problems, i.e., if sorbed flavor compounds are not properly desorbed from packaging polymers by a washing procedure, they will be re-sorbed into the food that has been refilled into the polymer, causing off-flavors. Several investigations have shown that quality and safety of the food and physical properties of the polymer were affected with the sorption and migration of food flavors, as well as personal hygiene and cleaning agents, into recycled polymers (Nielsen et al., 1992; Leufven et al., 1994; Franz et al., 1996; Miltz et al., 1997; Huber et al., 1997; Tawfik et al., 1998). Moreover, commercial washing with sodium hydroxide solutions was unable to remove some sorbed flavor compounds from the packaging polymers (Nielsen et al., 1994, 1997; Feron et al., 1994; Devlieghere et al., 1997).

In our laboratory, we reported that the sorption of flavor compounds into packaging films from an ethanol solution was maximal at 5–20% (v/v) ethanol concentration and then decreased (Fukamachi et al., 1996). The specific sorption behavior would be brought about by the heterogeneous water–ethanol structure. Therefore, it can be expected that in order to desorb sorbed flavor compounds from different kinds of packaging films, it will be possible to use an ethanol solution as an external desorption solvent.

On the basis of our previous findings for sorption, desorption behavior of sorbed flavor compounds from packaging films was investigated in ethanol solutions, although the solvent would be insufficient due to its economics or restrictions such as flammability. We also determined the changes in physical properties of films by the desorption treatment using an ethanol solution for food packaging applications.

## MATERIALS AND METHODS

**Materials.** Low-density polyethylene (LDPE) film with thickness of 50  $\mu\text{m}$  was supplied by Kuraray Company, Ltd., Osaka, Japan, and poly(ethylene terephthalate) (PET) film with thickness of 100  $\mu\text{m}$  was supplied by Mitsui Chemicals, Nagoya, Japan. The densities of the LDPE and PET films were 0.930  $\text{g}/\text{dm}^3$  and 1.40  $\text{g}/\text{dm}^3$ , respectively. The volatile compounds and other reagents were all guaranteed reagent grade from Nacalai Tesque Inc., Kyoto, Japan, and used without further purification.

**Preparations of Model Flavor Solution and Film.** The mixture of homologous volatile compounds (ethyl esters, *n*-aldehydes, and *n*-alcohols with carbon numbers 6–12) was added to a solution of 0.3% (w/v) sugar-ester (sucrose mono- and di-stearate mixture, S-1170, Mitsubishi-Kasei Food Co., Ltd., Tokyo; hydrophilic–lipophilic balance value 11) as an emulsifier, to make a 30 ppm flavor solution of each compound. The solution was dispersed homogeneously by an ultrasonic wave generator for 10 min. LDPE and PET films (2.5  $\times$  5 cm) were individually immersed in the model flavor solution and stored until the sorption equilibrium was established (in this experiment: LDPE, 20 °C, 21 days; PET, 37 °C, 28 days).

**Determination of Desorption by Gas Chromatography.** After being washed with deionized water, each film was immediately immersed, on one route, in 60 mL of diethyl ether for 2 days at 5 °C to extract sorbed volatile compounds from the film. Before the extraction, on the other route, the film

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was immersed in ethanol solutions (100 mL) of various concentrations [0, 5, 10, 20, 40, 60, 80, and 100% (v/v)] at 20 °C, 50 °C, and 60 °C, for the desorption treatment. Amylbenzene was individually added into the ether eluent as an internal standard (0.5  $\mu\text{L}/100\text{ mL}$ ) to quantify the volatile compounds. After being concentrated on a water bath at 42 °C, the extracts were analyzed by gas-liquid chromatography (GLC). The analysis was performed on a gas chromatograph (GC-14A, equipped with a flame ionization detector (FID), Shimadzu Company, Ltd., Kyoto, Japan) connected to an integrator (Chromatopac C-R6A, Shimadzu). A fused-silica capillary column (DB WAX, 0.25-mm i.d.  $\times$  60 m, film 0.25  $\mu\text{m}$ ; J&W Scientific) was used for separation, and the column temperature was programmed from 60 °C to 230 °C at 3 °C  $\text{min}^{-1}$ . The data are averages of three replicates. The ratio of remaining amount to desorbed amount in solution was defined as a partition coefficient.

**Measurement of Physical Properties of Films.** *Thermal Analysis.* Heat of fusion ( $\Delta H_f$ ,  $\text{J g}^{-1}$ ) and peak melting temperature ( $T_m$ , °C) of the films were obtained on a differential scanning calorimeter (DSC 100, Seiko Instruments Inc., Tokyo, Japan). The sample for LDPE film, approximately 5.0 mg in weight, was heated at 5.0 °C  $\text{min}^{-1}$  to 200 °C. For PET film, the final temperature was 300 °C. The data obtained from the DSC thermograms were analyzed using a SSC 5000 TA Station (Seiko Instruments Inc., Tokyo, Japan). The data are averages of three replicates, and the reproducibility was  $\pm 2\text{ J g}^{-1}$  for  $\Delta H_f$  and  $\pm 0.3\text{ °C}$  for  $T_m$ .

*Tensile Characteristics.* Tensile strength at break ( $\sigma_B$ ,  $\text{kg cm}^{-2}$ ) and elongation at break ( $\epsilon_B$ , %) were measured by a tensilon (Model UTM-III, Toyo Baldwin Co. Ltd, Tokyo, Japan) with a crosshead speed of 300  $\text{mm min}^{-1}$  and gauge length of 50 mm. Sample films were cut in 15-mm wide strips on the orientation direction. The actual run was performed at 20 °C and 65% relative humidity (RH). The data were obtained from the stress-strain curve, and the coefficient of variation in seven replicates was less than 3.0% as a relative standard deviation.

## RESULTS AND DISCUSSION

Desorption behavior of sorbed volatile compounds with various functional groups from LDPE and PET films were investigated by using various ethanol solutions at 20 °C. Ethanol solution was used as a desorption solvent for sorbed volatile compounds because of the specific sorption behavior of volatile compounds in an ethanol solution (Fukamachi et al., 1996) and the diverse solvent effect by heterogeneous water-ethanol cluster (Yamaguchi, 1998). The partition coefficients of all volatile compounds used in this study from LDPE film before and after immersion in 0 to 100% (v/v) ethanol solutions are summarized in Table 1. In each homologous series, more partition coefficient (namely, larger remaining amounts of compounds in the LDPE film) was observed with increasing carbon chain length, in agreement with the sorption results by Fukamachi et al. (1996). This indicated that desorption of sorbed volatile compounds into an ethanol solution was promoted in less sorbed compounds.

**Effect of Ethanol Concentration.** Partition coefficient is the index of the remaining amount ( $\mu\text{g}\cdot\text{cm}^{-3}$ ) of the volatile compound in the film after immersion in a desorption solvent. Hence, a low partition coefficient means that the volatile compound has a higher solubility for the solvent than for the film, and larger amounts are desorbed in the solvent. From the data shown in Table 1, the coefficients of all volatile compounds decreased with increasing ethanol concentration, although the decreasing behavior was different for each homologous series. The complete desorptions of ethyl

**Table 1. Partition Coefficients of Volatile Compounds in LDPE Film Before and After Immersed in Ethanol Solutions for 2 Days at 20 °C**

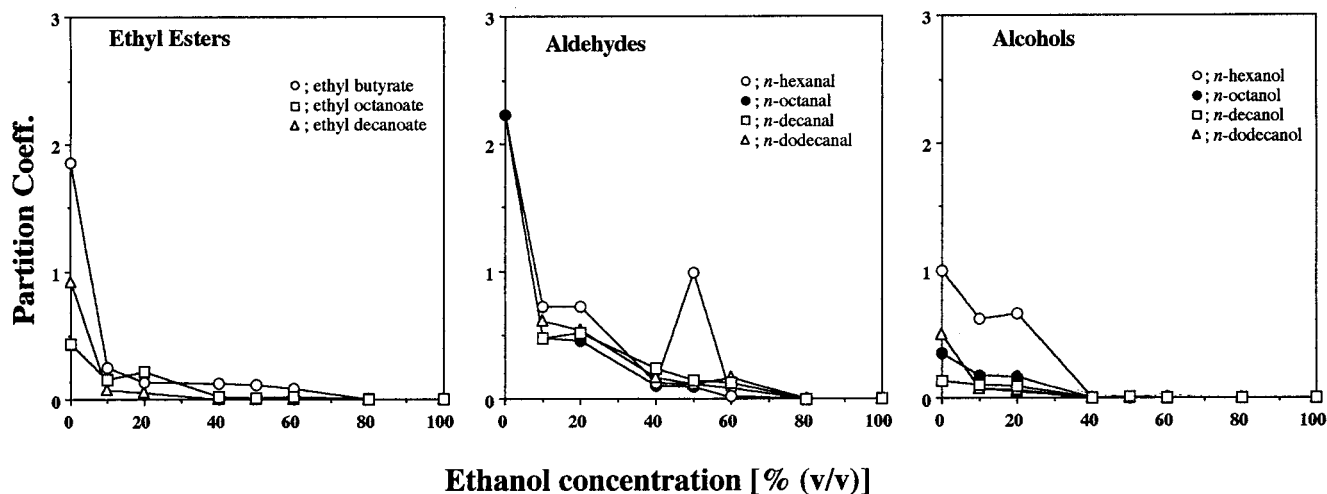
compound	partition coefficient <sup>a</sup>							
	ethanol concentration [% (v/v)]							
	0	5	10	20	40	60	80	100
<b>ethyl esters</b>								
ethyl butyrate	2.76	0.16	0	0	0	0	0	0
ethyl hexanoate	0.15	0.17	0.12	0.11	0	0	0	0
ethyl octanoate	1.76	1.66	1.28	0.70	0.04	0	0	0
ethyl decanoate	>100	>100	>100	>100	0.10	tr <sup>b</sup>	tr	tr
<b>aldehydes</b>								
<i>n</i> -hexanal	>100	>100	>100	>100	0.19	0.16	0.07	0
<i>n</i> -octanal	>100	>100	>100	>100	1.02	0	0	0
<i>n</i> -decanal	>100	>100	>100	>100	8.41	0.45	tr	0
<i>n</i> -dodecanal	>100	>100	>100	>100	1.61	0.80	0.03	0.03
<b>alcohols</b>								
<i>n</i> -hexanol	3.61	0	0	0	0	0	0	0
<i>n</i> -octanol	0.10	0.07	0	0	0	0	0	0
<i>n</i> -decanol	0.14	0.17	0.10	0.07	0.02	0.01	0	0
<i>n</i> -dodecanol	1.58	2.67	1.80	0.67	0.07	0.03	0.02	0.03

<sup>a</sup> Partition coefficient indicates the ratio of remaining amount of volatile in film to absorbed amount of volatile into solvent. <sup>b</sup> tr, <0.01.

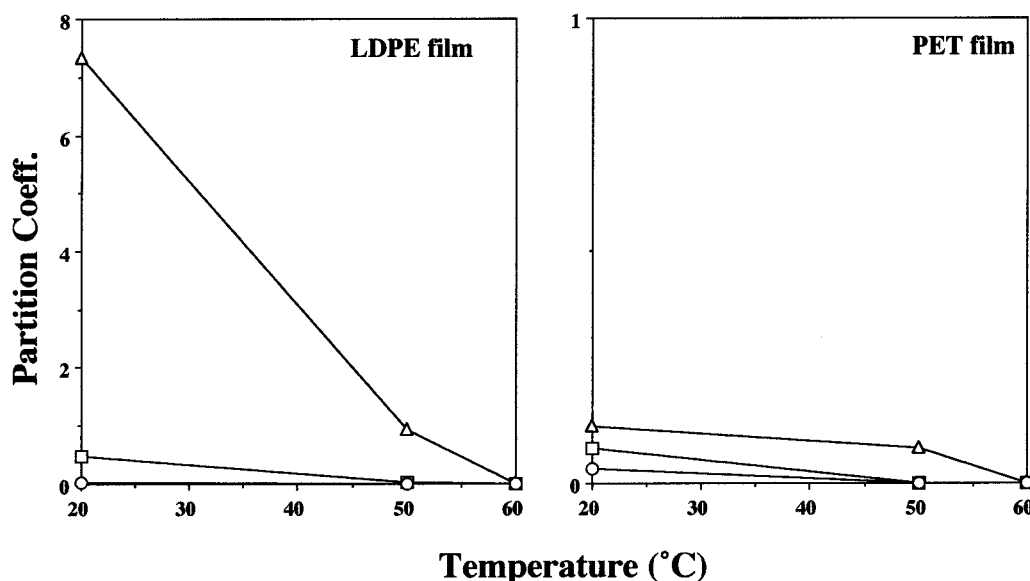
esters, *n*-aldehydes, and *n*-alcohols were observed at  $\geq 60\%$ ,  $\geq 80\%$ , and  $\geq 40\%$  (v/v) ethanol, respectively. These results indicate that the desorption behavior was dependent on the concentration of the desorption solvent and on the compatibility of volatile compounds with the solvent.

Other investigations have found that the sorption amounts of volatile compounds into PET films were much lower than their sorption into LDPE films because of minimal interaction between volatile compounds and the PET film (Leufven et al., 1994; Nielsen, 1994). For PET films, we obtained desorption behavior similar to that of LDPE films, with increasing ethanol concentration (Figure 1). The complete desorptions of ethyl esters, *n*-aldehydes, and *n*-alcohols were also observed at  $\geq 80\%$ ,  $\geq 80\%$ , and  $\geq 40\%$  (v/v) ethanol, respectively. Therefore, the desorption of a volatile compound from film by this solvent method would largely depend on the compatibility between the compound and the solvent rather than compatibility between the compound and the film.

**Effect of Treatment Temperature.** Temperature is an important environmental variable affecting the transport process. In general, acceleration of sorption and desorption can be expected with increase in temperature (Nielsen et al., 1992). Franz et al. (1996) demonstrated that the migration of a volatile compound from a polymer was dependent on its volatility, which was under the control of temperature and time. We studied the effect of temperature on the desorption of *n*-decanal from LDPE and PET films. These experiments were carried out with 40%, 60%, and 80% (v/v) ethanol solutions for 6 h at 20 °C, 50 °C, and 60 °C. As shown in Figure 2, the partition coefficients of *n*-decanal in each ethanol solution in both films apparently decreased with increasing temperature. For instance, the partition coefficient of *n*-decanal in 40% (v/v) ethanol turned out to be approximately zero at 60 °C, whereas at the lower temperature, the complete desorptions could not be established. An explanation for the increasing desorption at higher temperatures might be that the compatibility of the volatile compound with the film decreases at a fast rate.



**Figure 1.** Desorption behavior of volatile compounds with ethanol concentration from PET film for 2 days at 20 °C.



**Figure 2.** Effects of temperature on desorption of *n*-decanal from LDPE and PET films. Symbols are the remaining ratios of *n*-decanal in 40% ( $\Delta$ ), 60% ( $\square$ ), and 80% ( $\circ$ ) (v/v) ethanol solutions.

**Table 2.** Changes in Physical Properties of LDPE and PET Films by Desorption Treatment

property	LDPE film (mean <sup>a</sup> $\pm$ SD)		PET film (mean $\pm$ SD)	
	intact	after desorption <sup>b</sup>	intact	after desorption
$\Delta H_f$ (J/g) <sup>c</sup>	54.9 $\pm$ 0.4	53.5 $\pm$ 0.5	32.3 $\pm$ 0.7	28.8 $\pm$ 0.8
$T_m$ (°C) <sup>d</sup>	109.9 $\pm$ 0.2	108.9 $\pm$ 0.1	258.1 $\pm$ 0.3	258.3 $\pm$ 0.1
$\sigma_B$ (kg/cm) <sup>e</sup>	240.0 $\pm$ 7.1	244.7 $\pm$ 3.4	1683.3 $\pm$ 48.2	1674.2 $\pm$ 50.2
$\epsilon_B$ (%) <sup>f</sup>	342.5 $\pm$ 6.0	340.9 $\pm$ 9.9	207.3 $\pm$ 5.3	206.0 $\pm$ 6.0

<sup>a</sup> Means of three replications. <sup>b</sup> Desorption corresponds to immersing in 60% (v/v) ethanol solution for 30 min at 60 °C. <sup>c</sup>  $\Delta H_f$ , heat of fusion. <sup>d</sup>  $T_m$ , melting point. <sup>e</sup>  $\sigma_B$ , tensile strength at break. <sup>f</sup>  $\epsilon_B$ , elongation at break.

**Effect of Desorption Treatment on the Physical Properties of LDPE and PET Films.** To determine the physical properties such as heat of fusion, melting point, tensile strength at break, and elongation at break, the intact film and the film after desorption treatment were assayed. The mean values are presented in Table 2. In these experiments, the desorption treatments for LDPE and PET films were performed by immersing the films in 60% (v/v) ethanol solution for 30 min at 60 °C. There were no significant differences in melting point or elongation at break, but heat of fusion and tensile strength at break changed slightly after the desorption treatment. As these results show, the physical properties of films would be little affected by the desorption

treatment. Tawfik (1998) showed that tensile strength and modulus of elasticity properties of PET were significantly affected with the level of absorption of *d*-limonene, while elongation was not influenced. These differences could be explained by the differences in the chemical species and the initial concentration of the volatile compound used, as well as the thickness of the films.

Consequently, the desorption behavior of the sorbed volatile compounds from the films varied with the type of volatile compound and the type of film, the concentration of desorption solvent, and treatment temperature, depending on the compatibility of the sorbed volatile compound with the film or solvent. Therefore,

with the optimal combination of desorption parameters, it would be possible to achieve the complete desorption of sorbed flavors from packaging films. Of course, it should be noted that further study is needed for the solvent-desorption of odor-active aroma compounds such as pyrazines (Matsui et al., 1999) below their threshold level.

#### ABBREVIATIONS USED

LDPE, low-density polyethylene; PET, poly(ethylene terephthalate); GC, gas chromatography; DSC, differential scanning calorimeter.

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