Note

Sorption Behavior of Flavors with Water Sensitive Ethylene-Vinyl Alcohol Copolymer Film in Aqueous Solution

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Water sorption into ethylene-vinyl alcohol copolymer (EVOH) film largely affected the sorption behavior of flavors in aqueous solution. For EVOH-F (vinyl alcohol content; 68 mol%), the sorptions of flavors increased with temperature up to 20°C (10°C for EVOH-E; vinyl alcohol content; 56 mol%), and afterwards decreased. On the basis of the behavior of the water sorption and the corresponding glass transition temperature (T_g) changes in EVOH films, the signbell-type sorption behavior was considered to result from the flexibility change due to water sorption. Namely, the increase in sorption up to 20°C-storage for EVOH-F (10°C for EVOH-E) would be caused by the increasing free volume in EVOH films with decreasing T_g due to water sorption. On the other hand, at >20°C (EVOH-F)- and 10°C (EVOH-E)-storage, because the EVOH would behave as a rubbery polymer and have a roughly constant T_g , the sorption decreased with temperature.

Keywords: sorption, flavor, water sorption, EVOH film, glass transition temperature

Sorption of flavors into packaging materials is a serious problem related to flavor or quality deterioration during storage of foods (Osajima and Matsui, 1993; Leufvén and Hermansson, 1994). To elucidate this problem, the application of high gas barrier polymers for interior lining has been investigated (Ikegami *et al.*, 1991; Hata, 1993). However, their high gas barrier properties are after known to be affected by humidity or water sorption, especially for polymers containing many hydroxyl groups (Iwasaki and Ogino, 1978). This is due to the formation of hydrogen bonds between water molecules and hydroxyl groups in the polymer chain and to the subsequent loss in cohesive energy or the decrease in chain backbone stiffness (T_g) of the polymer (Salame, 1986; Katsura, 1992). Therefore, water sorption would largely affect the flavor barrier property for packed liquid foods.

In this paper, using ethylene-vinyl alcohol copolymer (EVOH) film with high water sensitivity, the sorption behavior of flavors has been investigated in relation to the chain mobility change due to water sorption.

Materials and Methods

Materials Two grades (F and E) of EVOH film with a thickness of 50 μ m were used (Kuraray Co., Ltd., Kurashiki). EVOH-F and EVOH-E were composed of 68 and 56 mol% vinyl alcohol content, respectively. The volatile compounds used in this study were all guaranteed reagent grade from Nacalai Tesque Inc., Kyoto, and were used without further purification.

Determination of the magnitude of sorption The

sorption determination for EVOH-F and EVOH-E was performed by the immersed method described elsewhere (Fukamachi *et al.*, 1993). Briefly, EVOH film (10×10 cm) was immersed in a model flavor solution (concentration of the volatile compound was set at 10 ppm) and stored at 5, 10, 20, and 30°C until the sorption equilibrium was achieved (in this experiment, 110, 80, 40, and 30 days' storage at 5, 10, 20, and 30°C, respectively).

Characteristics of EVOH film Water sorption in the film was determined by the following procedure. The film (2×2 cm) was immersed in water at 5, 10, 20, 30, and 50°C to achieve swelling equilibrium (about 1 week). After removing water from the surface with filter paper, the film was weighed (W_a). The swelled film was then evaporated to dryness at 104°C, cooled to room temperature and weighed (W_b). The water content was calculated as follows:

$$\text{Water content (\%)} = (W_a - W_b) / W_b \times 100 \quad (1)$$

The calculated value represents the maximal water content at the storage temperature.

The glass transition temperature (T_g) of the prepared swelled films was obtained on a differential scanning calorimeter (DSC) (RDC 220, Seiko Instruments, Inc., Tokyo). The water contents were prepared by immersing EVOH films into several saturated salt solutions at 20°C for 2 weeks. About 10 mg of the swelled film was heated at 10°C/min from -100°C to 150°C. The data obtained from the DSC thermograms were analyzed by an SSC/5200 TA Station (Seiko Instruments, Inc., Tokyo).

Results and Discussion

Primarily, the details of the polymer (EVOH) property change due to water sorption were investigated. Figure 1 shows the water sorption behavior for EVOH-F and EVOH-E at various storage temperatures. The water content remarkably increased with temperature up to 20°C (EVOH-F) and 10°C (EVOH-E), but above these temperatures, the content levelled off (EVOH-F, ca; 11%, EVOH-E, ca. 9%). This behavior indicated that the extent of plasticization due to water was different at different storage temperatures.

Figure 2 shows the relationships between the T_g measured by DSC and the water sorption for EVOH-F and EVOH-E. In both films, T_g decreased with an increase in water content. By fitting their water contents shown in Fig. 1 to the curves, the T_g s of both films at each storage temperature were then estimated (Table 1). As a result, at 5°C-storage the T_g s of both films were in agreement with the storage temperature (5°C). On the contrary, at >10°C-storage the T_g s were lower than the storage temperature. According to van Krevelen (1990), the “thermal distance” of the T_g from the storage temperature is probably connected with the fractional free volume of the polymer. Thus, the increase in “thermal distance” leads to the increase in chain thermal mobility or the free volume in the film due to water sorption.

Fig. 1. Changes in water content in EVOH-F (○) and EVOH-E (△) films as a function of storage temperature.

Fig. 2. Changes in T_g s of EVOH-F and EVOH-E films due to water sorption.

Table 1. Changes in T_g s in EVOH films due to water sorption.

EVOH-F		EVOH-E	
Water content (%)	T_g (°C)	Water content (%)	T_g (°C)
9.0 (5°C) ^{a)}	5.2	7.3 (5°C)	5.8
9.5 (10°C)	3.5	8.6 (10°C)	−0.1
10.9 (20°C)	−0.1	8.7 (20°C)	−0.2
11.0 (30°C)	−0.4	8.8 (30°C)	−0.3
11.2 (50°C)	−0.9	8.9 (50°C)	−0.4

^{a)} The number in parentheses shows the storage temperature in water.

Table 2. Sorption of volatile compounds into EVOH-F at various storage temperatures.

Compounds	Sorption ($\mu\text{g}\cdot\text{cm}^{-3}/\text{ppm}$)			
	Storage temperature (°C)			
	5	10	20	30
Hydrocarbons				
Octane	0.37	0.47	0.45	0.18
Nonane	0.38	0.56	0.54	0.24
Decane	0.70	0.80	1.30	0.86
Undecane	1.52	1.93	2.93	2.67
<i>d</i> -Limonene	0.55	0.68	0.49	0.42
Esters				
Ethyl heptanoate	0.44	0.60	1.51	0.79
Ethyl octanoate	1.14	1.58	1.64	1.37
Ethyl nonanoate	1.28	1.95	2.32	2.10
Aldehydes				
Octanal	1.39	3.29	4.38	3.76
Nonanal	1.93	3.23	5.43	4.53
Decanal	3.88	4.99	8.40	6.26
Undecanal	6.28	9.06	12.59	11.70
Alcohols				
Octanol	0.73	0.89	1.32	1.14
Nonanol	1.24	1.57	3.15	1.35
Decanol	1.61	1.75	2.81	1.23
Undecanol	1.58	2.97	3.60	1.32
Nerol	0.84	0.91	1.70	0.85
α -Terpineol	0.42	0.51	0.94	0.57

Table 3. Sorption of volatile compounds into EVOH-E at various storage temperatures.

Compounds	Sorption ($\mu\text{g}\cdot\text{cm}^{-3}/\text{ppm}$)			
	Storage temperature (°C)			
	5	10	20	30
Hydrocarbons				
Octane	0.26	0.29	0.74	0.28
Nonane	0.38	0.64	0.74	0.49
Decane	0.81	2.02	1.80	1.73
Undecane	1.95	4.83	3.79	3.66
<i>d</i> -Limonene	0.42	1.12	1.03	0.48
Esters				
Ethyl heptanoate	0.44	1.06	1.04	0.77
Ethyl octanoate	0.98	2.41	1.83	1.28
Ethyl nonanoate	1.81	3.90	3.50	1.94
Aldehydes				
Octanal	6.64	10.23	9.60	6.07
Nonanal	4.03	9.22	7.32	6.22
Decanal	5.84	11.90	10.76	9.31
Undecanal	8.74	18.25	19.18	17.14
Alcohols				
Octanol	0.70	0.92	0.95	1.05
Nonanol	1.12	1.58	1.75	1.21
Decanol	1.36	2.30	2.57	1.11
Undecanol	1.39	2.88	3.27	1.05
Nerol	0.64	0.91	1.37	0.67
α -Terpineol	0.27	0.40	0.65	0.39

Tables 2 and 3 show the sorption of volatile compounds into EVOH films at various storage temperatures in aqueous solution. The sorptions into EVOH-F were maximal at 20°C-storage for all volatile compounds, similarly to EVOH-E at 10–20°C. In general, if the T_g of a polymer is unchanged, sorption obeys the Arrhenius-type relationship $S=S_0 \times \exp(-\Delta H_s/RT)$ (van Krevelen, 1990); sorption decreased with storage temperature. However, the behavior for EVOH films did not depend on the storage temperature. Interestingly, the storage temperatures which gave the maximal sorptions were in good agreement with the temperatures at the turning points in Fig. 1. Therefore, the appearance of the specific sorption behavior for EVOH was considered to depend on the chain thermal mobility at the storage temperature. Namely, at up to 20°C-storage for EVOH-F (10°C for EVOH-E), EVOH would behave as a semi-rubbery polymer, and the free volume would increase due to the increasing “thermal distance” from the corresponding T_g , resulting in the increase in sorption. On the other hand, at >20°C (EVOH-F)- and 10°C (EVOH-E)-storage, because the EVOH would behave as a rubbery polymer and have a roughly constant T_g (Table 1), the sorption decreased with temperature according to the Arrhenius-type relationship.

Consequently, for water sensitive polymers such as EVOH film, the sorption behavior of volatile compounds was largely affected by the water sorption. This was attributed to the

polymer chain mobility (i.e., glassy, semi-rubbery or rubbery states). Thus, in the usage of a water sensitive polymer as a food packaging film, understanding of the T_g in relation to storage temperature would be needed for providing a food with less flavor deterioration due to sorption.

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