Effect of Surface Free Energy of Film Laminated TFS on Content Release Properties†

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Abstract:

Using the film with the wide range of surface free energy values, JFE Steel studied the effect of the surface free energy of the material contacting stuffed content on content release properties. It was found that the properties are closely related to the surface free energy of the material and the materials with surface free energy of less than 23 mN/m or more than 44 mN/m, show excellent properties.

Content release properties can be expressed as the work of adhesion in water between material and protein. Reduction of the work of adhesion leads to a significant improvement in content release properties. Concerning the simulated contents used in this study, the proteins in those contents are primarily absorbed on the surface of the films, followed by adhering fatty acids and carbohydrates, which results in generation of macroscopic adhesives.

1. Introduction

In recent years, the canning industry has increasingly distanced itself from lacquer coating using organic solvents from the viewpoints of preservation of the global environment, improvement of the labor environment during lacquering work, etc., and has switched to water-based lacquer or adopted thermoplastic resin laminates. Cans using PET (polyethylene terephthalate) film laminated steel sheets as the base materials have also been commercialized, with a focus on the beverage can field[1]. As advantages of laminated steel sheets, because the lacquering and baking processes that were necessary with conventional lacquered materials can be omitted, (1) productivity is improved by process omission, (2) organic solvents and other toxic substances can be eliminated from the production process and (3) the product cans have excellent quality performance (formability, corrosion resistance, etc.)[2]. Based on these circumstances, JFE Steel carried out a study in order to develop "Laminated steel sheets for food can use" which are environment-friendly and conform to the property requirements for food cans.

As properties required in materials for food cans, in addition to the basic properties of formability, corrosion resistance, film adhesion, etc., content release properties are also required. Content release properties are evaluated by the ease of release when the contents of the can are removed and the amount of contents remaining on the can inner surface after the contents are removed. Since these properties are closely related to consumers' desire to buy the product, this is an important property which is demanded in food can materials and is also strongly requested by can manufacturers. For example, it is known that processed meat products such as corned beef and luncheon meat easily stick to the inner surface of food cans, the contents (processed meat) cannot be removed easily from the can if conventional PET film laminated steel is used as the can material, and this results in a condition in which content remains on the inner surface of the can,

Photo 1 Appearance of the can inside after taking out the content

† Originally published in *JFE GIHO* No. 39 (Feb. 2017), p. 21–26

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as shown in **Photo 1**.

Because content release properties depend on the detachability between the contents packed in the can and the can inner surface, it can be thought that the surface free energy of the inner film of the can has a large influence on these properties. Therefore, in this study, simulated food cans were prepared using various types of film laminated steel sheets with different surface free energies in a wide range of 19–52 N/m, the cans were packed with contents, and the content release properties were studied. In this paper, the surface free energy range of film laminated steel sheets for satisfactory content release properties is clarified, and the results of a discussion of the mechanism are described.

2. Experimental Method

2.1 Test Materials

The steel material used as the substrate for lamination was electrolytic chromium coated steel (ECCS) with a sheet thickness of 0.21 mm, temper of T-3CA, metallic chromium coating weight of 120 mg/m^2 and hydrated chromium oxide coating weight of 15 mg/m^2 (as Cr weight). Laminated test materials were prepared by thermally bonding the various types of films No. 1 to 8 shown in **Table 1** on the surface of ECCS heated to above the melting point of the film. With test film No. 7, corona treatment was performed on the PET film surface to increase the surface free energy in comparison with the untreated PET film, and with test film No. 8, surface free energy was reduced in comparison with the untreated PET film by forming a resin layer (film thickness: approx. 1 μm) of mixed polyester resin and fatty acid wax on the PET film surface by coating. With both No. 7 and No. 8, the laminated specimens were prepared by thermally bonding the non-treated surface of the film on the ECCS.

Table 2 Surface free energy of liquids used for measuring contact angles

No.	Liquids	Surface free energy (mN/m)		
		γ_l	γ_l^d	γ_l^h
1	Water	71.8	21.5	50.3
2	Glycerol	64.0	34.0	30.0
3	Formamide	58.2	39.5	18.7
4	Ethylene glycol	48.0	32.8	15.2
5	Diethylene glycol	44.8	38.1	6.7

2.2 Measurement of Surface Free Energy

The surface free energy was obtained by measuring the contact angles between the specimens and five types of liquid (water, glycerol, formamide, ethylene glycol, diethylene glycol) shown in **Table 2** with a contact angle meter (Kyowa Interface Science Co., Ltd., model CA-D). γ_l is the surface free energy of the liquid, γ_l^d is the dispersion component of the surface free energy of the liquid and γ_l^h is the polar component of the surface free energy of the liquid.

Based on the obtained measured values, surface free energy was calculated by using the theoretical equation[4)] proposed by Ikada et al. The contact angle measurements were performed by dropping 5 μL of the liquid in an atmosphere with a temperature of 20°C and relative humidity of 50±10%.

2.3 Evaluation of Content Release Properties

Disks with a diameter of 100 mm were punched from the laminated steel sheets prepared in section 2.1, and cylindrical-shaped cups were formed at a drawing ratio of 1.88. Next, these cups were filled with simulated contents (mixture of processed meat and egg) of the composition shown in **Table 3** (a). These simulated contents were adjusted to substantially the same composition as the commercial canned product (content: luncheon meat) shown in Table 3 (b).

Following this, the cups were sealed and retort

Table 1 Test films

No.	Films	Surface treatment	Contact angle of water (deg.)	Surface free energy (mN/m)
1	PVA (Polyvinyl alcohol)	—	20	52
2	EVOH (Ethylene vinyl alcohol)	—	48	44
3	PET	—	73	35
4	PET/PP[a)]	—	89	28
5	PP (Polypropylene)	—	100	23
6	PMP (Polymethylpentene)	—	108	19
7	PET	Corona treatment	59	39
8	PET	Hydrophobic treatment[b)]	102	21

[a)] PET/PP blend film (97/3 weight ratio)
[b)] Polyester resin coating (including fatty acid wax)

Table 3 (a) Composition of the simulated content

Composition of the contents			Nutrient composition			
Egg (g)	Wheat (g)	Meat (g)	Protein (mass%)	Carbohydrate (mass%)	Fat (mass%)	Water (mass%)
22.3	4.1	13.6	16.2	7.1	7.0	69.7

Table 3 (b) Nutrient composition of luncheon meat in the marketplace

Nutrient composition			
Protein (mass%)	Carbohydrate (mass%)	Fat (mass%)	Water (mass%)
16.0	5.0	3.6	75.4

treatment was performed under conditions of 125°C for 90 min. The cups were then opened, and ease of release (whether the content could be removed from the cup by lightly shaking the cup up and down while in an inverted condition) was evaluated. The weight of the contents remaining on the inner side of the cup after removal was also weighed for quantitative evaluation of the content release properties. It can be understood that content release becomes difficult as the weight of the content remaining on the cup inner surface increases. **Figure 1** shows the evaluation standard.

2.4 Analysis of Contents Remaining in Cup

After removal of the contents as described in section 2.3, a qualitative analysis of the contents remaining on the cup inner film surface was performed by analysis of the infrared absorption spectrum by the attenuated total reflection (ATR) method[5] using a microscopic infrared spectrum analysis (microscopic IR) system (JEOL Ltd., WINSPEC-100). Because the

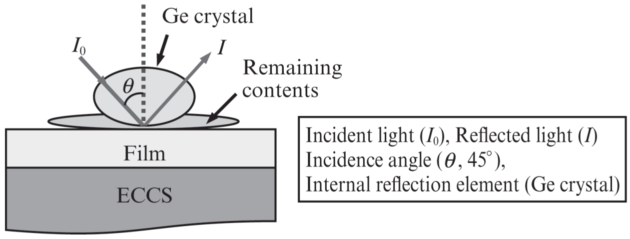


Fig. 2 ATR measurement method

ATR method utilizes an evanescent wave, this method measures the infrared absorption spectrum of the sample surface (approximately 2 μm in the depth direction). Moreover, by adjusting the distance between the internal reflection element (Ge crystal) and the sample, it is possible to obtain information on the remaining contents itself and information on the vicinity of the interface between the contents and the film. **Figure 2** shows an outline of the ATR method. The measurement range was set at 700 cm^{-1} to 4 000 cm^{-1}. Measurement resolution was 4 cm^{-1}, and the cumulative number of measurements was 10.

3. Results and Discussion

3.1 Results of Evaluation of Content Release Properties

Eight types of test materials (laminated steel sheets) with different surface free energy values were formed into a cylindrical cup shape, and the cups were filled with simulated contents. After performing retort treatment, the ease of release when the contents were removed from the cup was evaluated, and the weight of the remaining contents on the cup inner surface was measured. The results are shown in **Fig. 3**. The results

Score	4	3	2	1	Before the content is taken out
Appearance after content was taken out					
Content release properties	The content was easily taken out.	The content was taken out.	The content was slightly difficult to be taken out.	The content was difficult to be taken out.	
Amount of the remaining content in the cup (mass%)	<1.0	1.0-5.0	5.0-10.0	>10.0	

Fig. 1 Evaluation method for content release properties

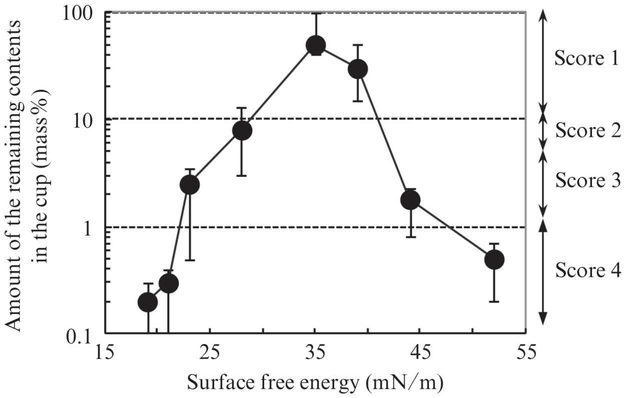
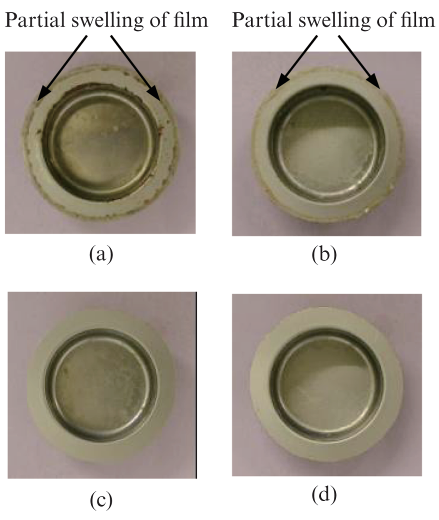


Fig. 3 Effect of surface free energy on content release properties

of five repeated measurements are shown by the error bars. From these results, content release properties are greatly influenced by the surface free energy of the test material. It was found that the contents could be removed easily in the high surface free energy region of more than 44 mN/m and, conversely, in the low surface free energy region of 23 mN/n or less, and virtually no contents remained in the can under these conditions. On the other hand, in the surface free energy range of 28–39 mN/m, the contents adhered firmly to the cup inner surface and removal from the cup was difficult. Thus, content release properties show excellent performance under a surface condition of high surface free energy (hydrophilicity) and under a surface condition of low surface free energy (hydrophobicity), but performance is not adequate in the range between those two conditions.

Photo 2 shows the results of observation of the inner side of the cups after removal of the contents.



(a) No. 1 PVA laminated ECCS
(b) No. 2 EVOH laminated ECCS
(c) No. 5 PMP laminated ECCS
(d) No. 7 Hydrophobized PET laminated ECCS

Photo 2 Appearance after contents were taken out.

Although the materials with surface free energy 44 mN/m or more displayed good release of the contents, it was found that swelling of the films (polyvinyl alcohol (PVA) and ethylene vinyl alcohol copolymer (EVOH)) occurred due to the water contained in the contents. Because these films have a low contact angle with water, as shown in Table 1, and are highly hydrophilic, they dissolve easily in water. In order to use these films in food can materials, a resin design that suppresses dissolution in water while maintaining high surface free energy appears to be necessary.

The test materials with surface free energy 23 mN/n or lower are promising food can materials, as they did not display swelling or damage of the film or the surface film, and content release properties were excellent. However, the polypropylene (PP) and polymethylpentene (PMP) films have high gas permeability in comparison with PET films[6]. Therefore, if these films are used in food can materials for contents that contain a high amount of proteins, such as fish and meat, discoloration (sulfide stain) of the steel sheet will occur because the film cannot shield the steel from the hydrogen sulfide that evolves in the retort treatment process[7]. Accordingly, within the range of study in this report, test material No 8, in which a resin consisting of a mixture of polyester and fatty acid wax was coated on the PET film surface, is considered the most promising material for food can materials.

3.2 Results of Analysis of Contents Remaining in Cup

With test material No. 3, which was laminated with an untreated PET film, it was not possible to remove the simulated contents from the cup, and contents remained on the cup inner surface. A qualitative analysis of the region where these contents remained was performed by the FT-IR-ATR method.

In the ATR method, the internal reflection element (Ge crystal) is placed in contact with the specimen, and total reflection measurement is performed. In this report, changes in the composition of the adhering material in the depth direction were investigated by moving the internal reflection element from the position in contact with the surface of the remaining contents to a position in contact with the PET film.

The result of measurement of the IR spectrum with the internal reflection element in contact with the surface of the contents is shown in **Fig. 4** (a). **Table 4** summarizes the band assignments of the various IR spectra. An aliphatic C = O stretching peak can be observed at 1 745 cm^{-1}, and aliphatic (fatty acid) C-H stretching peaks can be observed at 2 852 cm^{-1} and 2 924 cm^{-1}. Furthermore, a peak that seems to originate from the peak of C = O stretching of the amide bond can be

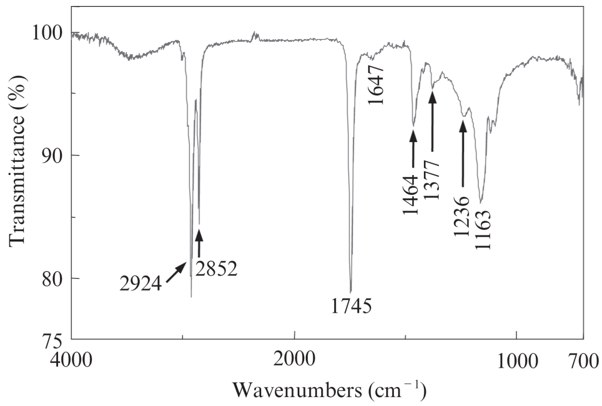
Table 4 Band assignments for the infrared spectrum.

Wave numbers (cm^{-1})	Assignment[11, 12]
3 286	N-H stretching
2 951-2 960	C-H stretching
2 920-2 924	C-H stretching
2 838-2 868	Aliphatic C-H stretching
1 746-1 749	Aliphatic C = O stretching
1 716	Aromatic C = O stretching
1 647	C = O stretching of amide bond
1 541	C-N stretching, N-H bending
1 454-1 465 1 375-1 380	C-H bending

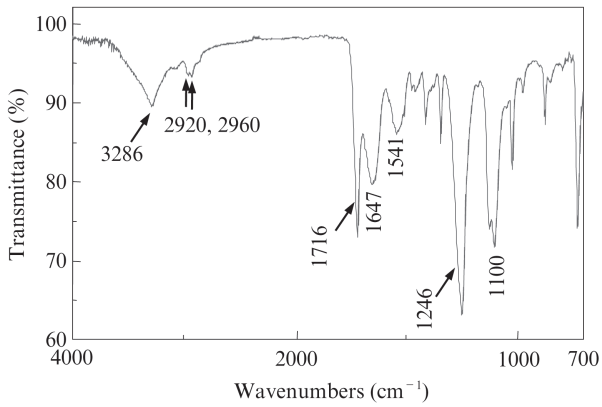
observed at 1 647 cm^{-1}.

Fig. 4 (b) shows the result of measurement of the IR spectrum when the internal reflection element was pushed into the contents so that it was in contact with the PET film surface. The peak of C = O stretching of the amide bond can be observed at 1 647 cm^{-1}, peaks of C-N stretching and N-H bending can be observed at 1 541 cm^{-1}, and the peak of N-H stretching can be observed at 3 286 cm^{-1}. Thus, absorption peaks that are considered to originate from proteins appear clearly. On the other hand, because the peak of C = O stretching of fatty acids (1 745 cm^{-1}) was not observed, it can be understood that the fatty acid component does not exist near the film surface. From these results, it can be thought that a large amount of proteins exist near the PET film surface, and other contents in the part separated from the PET film surface contain a large amount fatty acids. The inside cup surface of material No. 4 (material laminated with PP film), which had satisfactory content release properties, were also measured by the ATR method. The results are shown in Fig. 4 (c). Although a slight peak of C = O stretching of fatty acid (1 749 cm^{-1}) was observed, peaks originating from proteins were not detected.

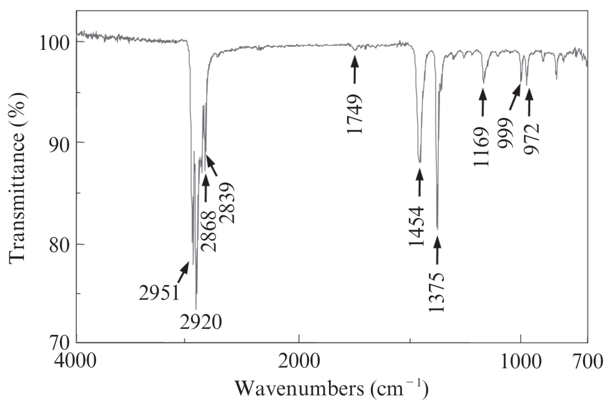
In general, it is widely thought that the first reaction that occurs when body tissues are in contact with a material is adsorption of proteins (it is thought that the initially-adsorbed proteins undergo repeated desorption and adsorption and finally reach equilibrium adsorption), and adhesion of fats and cells occurs following the reaction[8]. Likewise, in the case of the content release properties investigated in this report, it is thought that proteins in the contents initially adsorb on the film surface, and followed by adhesion of other components of the contents such as fats, carbohydrates, etc., and this leads to the formation of macroscopic adhesions.



(a) Surface of the remaining contents (No.3 PET laminated ECCS)



(b) Surface of the film (No.3 PET laminated ECCS)



(c) Surface of the film (No.4 PP laminated ECCS)

Fig. 4 ATR measurement results of the remaining contents in the cup

3.3 Effect of Surface Free Energy of Test Material on Content Release Properties

As shown in Fig. 3, the results of the evaluation of the release properties of the simulated contents clarified the fact that content release properties are excellent in the region where surface free energy is low and hydrophobicity is large and in the region where surface free energy is high and hydrophilicity is large. The following will discuss the reason for the excellent content release properties in both of these test materials, in spite of their mutually contradictory properties.

Although much theoretical research has been done on the work of adhesion between materials and adhering substances, virtually all of those studies treated cases in which the medium was a vacuum or air. However, the simulated contents used in this report have a water content of approximately 70 mass%, as shown in Table 3. Therefore, when studying the adhesion (=work of adhesion) between the test materials and the contents, it is considered necessary to treat water as the medium.

The following theoretical equation has been proposed for the work of adhesion $W_{12,W}$ in water[9]. Here, γ is surface free energy.

$$W_{12,W}=\gamma_{1W}+\gamma_{2W}-[\gamma_{12}]_W \quad \cdots\cdots (1)$$

where, the subscripts 1 and 2 indicate the material surface and the adhering material, respectively. In this report, the material is the test material (film laminated steel sheet) and the adhering material consists of proteins. In Eq. (1), $[\gamma_{12}]_W$ shows the interfacial free energy between the surface of the test material and the proteins in water, and the interfacial free energy of the test material and the proteins is the sum of the dispersion component (shown by superscript d) and the polar component (superscript P). Because it is thought that the interaction between water molecules does not contribute to the work of adhesion $W_{12,W}$ in water, interfacial free energy in water is treated in the same manner as in a vacuum, and the work of adhesion $W_{12,W}$ in water is expressed by the following equation.

$$\begin{aligned} W_{12,W}=2\,[\,&\gamma_1^d\,\{1-2\,(\gamma_1^d\gamma_W^d)^{1/2}/\,(\gamma_1^d\cdot\gamma_W^d)\}] \\ &\cdot\,[\,\gamma_2^d\,\{1-2\,(\gamma_2^d\gamma_W^d)^{1/2}/\,(\gamma_2^d\cdot\gamma_W^d)\}]^{1/2} \\ &+2[\,\gamma_1^P\,\{1-2\,(\gamma_1^P\gamma_W^P)^{1/2}/\,(\gamma_1^P\cdot\gamma_W^P)\}] \\ &\cdot\,[\,\gamma_2^P\,\{1-2\,(\gamma_2^P\gamma_W^P)^{1/2}/\,(\gamma_2^P\cdot\gamma_W^P)\}]^{1/2} \quad \cdots\cdots (2)\end{aligned}$$

In this report, albumin, which is contained in the simulated contents (mainly egg white), was selected as the protein, and $\gamma_2^d=31.4$ mN/m and $\gamma_2^P=33.6$ mN/m[10] were used as the values of its surface free energy. As the surface free energy of water, from Table 2, $\gamma_W^d=21.5$ mN/m and $\gamma_W^P=50.3$ mN/m were used.

If the surface free energies of the test materials (film laminated steel sheets) are inserted in Eq. (2), the results shown in **Fig. 5** are obtained. The surface free energy of the test material and the work of adhesion $W_{12,W}$ between the test material and the protein (albumin) show their maximum values when the surface free energy of the test material is 35 mN/m. It can be understood that a test material with surface free energy of around 35 mN/m adheres strongly with the protein (albumin).

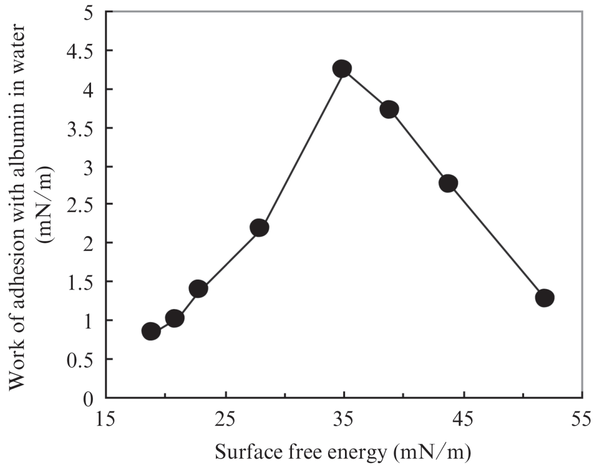


Fig. 5 Relation between surface free energy and work of adhesion with albumin in water

Because this result is approximately the same as the relationship between the content release properties and surface free energy shown in Fig. 3, it is thought that the release properties of processed meat can be expressed as the work of adhesion between the test material and proteins in water, and release properties improve with materials having smaller work of adhesion in water. Furthermore, the results shown in Fig. 5 are not limited to the test materials used in this report, but also hold for other materials with similar surface free energy values. Thus, when the medium is water, it is thought that these results will generally hold for the adhesion phenomena of substances with strong adhesion.

4. Conclusion

The results of an evaluation of the content release properties of various types of film laminated steel sheets and an investigation of the influence of surface free energy on release performance have been described. The key points are as follows.

(1) Content (processed meat) release properties are greatly influenced by the surface free energy of the test material. In the region where the energy value is high (in this report, 44 mN/m or more) and the region where the energy value is low (here, 23 mN/m or less), release properties are excellent, as the contents do not adhere to the inner surface of the can (protein is not adsorbed).

(2) Mainly proteins were found on the material surface after the contents were removed. It is thought that this is caused by initial adsorption of proteins on the test material surface, which invites adhesion of fatty acids, etc. and this develops into the forma-

tion of macroscopic adhesions.

(3) Content (processed meat) release properties can be expressed as the work of adhesion between the test material and proteins in water. Release properties improve with materials having smaller work of adhesion in water.

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