食品用プラスチック容器包装における発泡メカニズム

誌名	日本食品工学会誌 = Japan journal of food engineering
ISSN	13457942
著者名	井上,保 塩野,剛 伊與田,浩志
発行元	日本食品工学会
巻/号	19巻3号
掲載ページ	p. 145-151
発行年月	2018年9月

Japan Journal of Food Engineering, Vol. 19, No. 3, pp. 145 – 150, Sep. 2018 DOI : 10.11301/jsfe.17507

◇◇◇ Original Paper ◇◇◇

Characteristics and Mechanism of Bubble Formation in Plastic Packaging for Food

Tamotsu INOUE[1,†], Tsuyoshi SHIONO[1], Hiroyuki IYOTA[2]

[1]*Toyo College of Food Technology, 4-23-2 Minami-Hanayashiki, Kawanishi-shi, Hyogo 666-0026, Japan*
[2]*Department of Mechanical and Physical Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka City 558-8585, Japan*

Heat-sealing technology, which is used for plastic packaging, entails laminating multiple kinds of films together to form a barrier with varying permeability and stiffness. Creating a heat seal consists of heating the heat-seal material and then immediately cooling it down. However, overheating the heat-seal material can introduce defects such as bubble formation. This study examined the effect of the moisture content on bubble formation by using retort pouches as the sample material. The material is composed of polyester, nylon, and polypropylene as the outermost layer, barrier layer, and heat seal material, respectively. A mechanism of bubble formation is proposed on the basis of the moisture adsorption characteristics, viscous elasticity, and barrier characteristics of the sample material.

Keywords: plastic packaging, heat sealing, bubble formation, moisture content, water absorption isotherm

1. Introduction

Heat-sealing technology is used to seal plastic packaging and involves the use of lamination to combine multiple kinds of films to form a barrier with varying permeability and stiffness. Creating a heat seal consists of heating the heat-seal material and then immediately cooling it down.

Mueller *et al.* [1] studied the relationship between melting and inter-diffusion using linear low-density polyethylene (LLDPE). Tsujii *et al.* [2] investigated the crystalline structure of heat-sealed oriented polypropylene (OPP) and cast polypropylene (CPP) films. Poisson *et al.* [3] showed that the introduction of EVA in the PE layer improves the heat-sealing ability and optical properties without degradation of the mechanical and adhesion performance. Yuan *et al.* [4] studied the response of laminated films with LLDPE and LDPE to temperature, time, and pressure using bar sealing.

"Bubble formation" is a defect caused by overheating the heat-sealing material. Hydrophilic materials, such as nylon, contain volatile materials, such as water, within their layers. When these hydrophilic materials are subjected to high temperatures by heat sealing, the volatile materials can evaporate to cause bubbling in the adhesive area. Bubble formation is not only aesthetically displeasing; it can also negatively affect the heat-sealing characteristics of the material.

Hishinuma [5] reported that bubble formation as a result of the evaporation of embedded volatile elements depends on the vapor pressure of the volatile element, and introduced a new method for controlling the formation of bubbles. The method centers on the adjustment of the pressure used in relation to the applied heating temperature.

As for the water adsorption ability of nylon (i.e., polyamides), Fukuda *et al.* [6] examined the effects of varying the aliphatic chain length in the repeating unit of polyamides on the moisture sorption isotherm.

In a previous study, Inoue *et al.* [7] presented a method to prevent bubble formation by focusing on the relationship between the melting surface temperature of the heat-seal material and the boiling temperature of water inside the sample material using an impulse sealer. In addition, they proved that bubbling did not occur once the volatile material had completely evaporated.

This study examined the effect of moisture content on bubble formation using retort pouches as the sample material. In addition, the mechanism of bubble formation was investigated with respect to the moisture adsorption characteristics, viscous elasticity, and barrier characteristics of the sample material.

(Received 20 Dec. 2017: accepted 21 Jun. 2018)
† Fax: +81-72-758-6959, E-mail: tamotsu_inoue@toshoku.ac.jp

2. Materials and Method

2.1 Materials

The particular pouches studied were composed of vapor-deposited polyester, specifically polyethylene terephthalate (PET), nylon (NY), and polypropylene (PP) as the outermost layer, the barrier layer, and the heat seal material, respectively. The thicknesses of the PET, NY, and PP layers are 12, 15, and 60 μm, respectively. In the case of PET, the oxygen permeation rate is 20 mL/(m^2·d·MPa) at 23℃, 65%RH and the moisture permeation rate is 2 g/(m^2·d) at 40℃, 90%RH, as provided by the supplier (TOYOBO).

2.2 Differential scanning calorimeter measurement

A differential scanning calorimetry (DSC) was used to analyze the material from which the retort pouch is made (PET/NY/PP layers) (DSC-60A; SHIMADZU, Kyoto). The DSC measurement was conducted in the conditions that sample mass: 5.56 mg, sample cell: aluminum (crimp-type), inert gas: nitrogen (50 mL/min) and heating rate: 10℃/min.

2.3 Dynamic viscoelastic measurement

A dynamic viscoelastic measurement was carried out on the PP film using a HAAKE MARS III rheometer (Thermo Fisher Scientific, Tokyo) in the conditions that frequency: 1 Hz and heating rate: 10℃/min.

2.4 Water adsorption isotherm

To vary the moisture contents of sample materials, sample materials and saturated aqueous solution were put into sealed containers and left to stand for approximately 1 week. The relative humidity of saturated aqueous solution at 20℃ is shown in Table 1. A retort pouch (PET/NY/PP, 180 mm×130 mm) and NY film were used as sample materials. The sample weight was measured using an electronic balance (UW620H, SHIMADZU, Kyoto).

Table 1 Relative humidity of saturated aqueous salt solution at 20℃.

Salt (saturated aqueous solution)	Relative humidity at 20℃ (%)
(Silica gel)	(0)
NaOH	8.9
K_2CO_3	43.0
NaCl	75.5
KNO_3	94.0
(Water)	(100)

2.5 Measurements of bubble formation during heat-sealing process

The effect of the moisture content on bubble formation during the heat-sealing process was studied. Figure 1 shows an illustration of the experimental equipment (MTMS kit, Hishinuma Consulting office, Kanagawa). The experimental equipment consist of heating blocks and another non heating blocks. The temperature of heating blocks were controlled at constant using sheathed heaters, temperature sensors and PID controllers. The surface temperature of heating block T_{sf} was monitored using K-type thermocouples (wire-diameter: 0.32 mm). A Teflon cover (50 μm) was placed between the heating blocks and the sample material to control heating rate. The air cylinder was used for pressing the sample material during heating process. The applied pressure was calculated according to the following equation: supplied force divided by the contact area (17 mm× 30 mm) between the sample material and the heating block. In addition, the melting surface temperature was measured using a K-type thermocouple (wire diameter: 50 μm). The sample material was pressed and heated using the heat conduction provided by the heating blocks of the equipment. Subsequently, the sample was moved and cooled down using another non-heating blocks by heat conduction immediately. Table 2 lists the experimental conditions. In these experiments, the surface temperature of both heating blocks T_{sf} was equalized to satisfy the target melting surface temperature T_m.

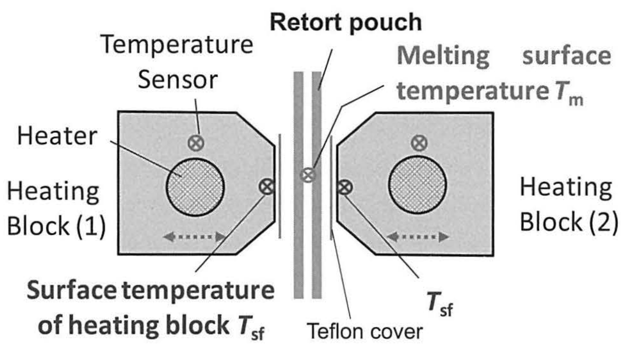

Fig. 1 Experimental equipment of bubble formation during heat-sealing process (MTMS kit).

Table 2 Experimental conditions for bubble formation.

Surface temperature of heating block T_{sf} (℃)	150, 160, 170
Pressure P (MPa)	0.15, 0.30
Moisture content of retort pouch X (%)	0.05, 0.16, 0.44 0.67, 0.97, 1.13

The report pouches, which moisture content were changed as shown in "2.4 water adsorption isotherm section", were used as sample material for these experiments.

3. Results and Discussion

3.1 Characteristics of the multi-layered heat seal film

The DSC result is shown in Fig.2. The PP, NY, and PET layers, which consist of thermoplastic resins, transform from the solid state into a soft, molten (liquid) state as the temperature is increased. The respective polymeric materials exhibited peaks at 124 and 164℃ for the PP layer, 221℃ for the NY layer, and 255℃ for the PET layer because of melting.

Figure 3 shows the results of the dynamic viscoelastic measurement as a function of temperature. The storage elastic modulus G' and the loss elastic modulus G" decreased rapidly at approximately 145–160℃ because of melting. This means that PP film is easy to be deformed by a force at higher temperature condition.

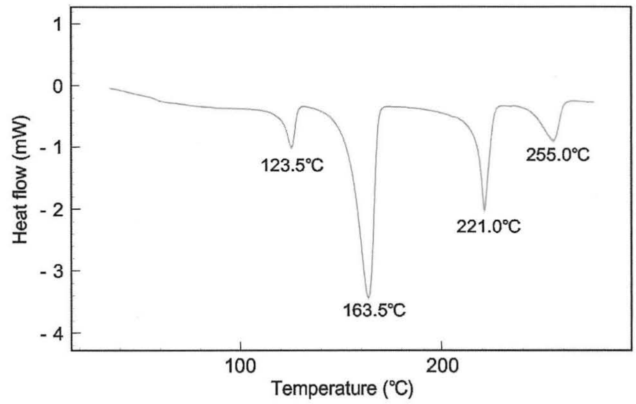

Fig. 2 Differential scanning calorimeter measurement (Retort pouch: PET/NY/PP, heating rate: 10℃/min, sample mass: 5.56 mg).

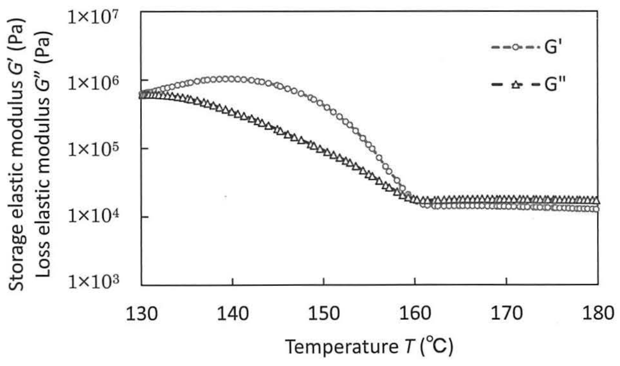

Fig. 3 Dynamic viscoelastic measurement (PP film, heating rate: 10℃/min, Frequency: 1Hz).

Figure 4 shows the water adsorption isotherm of the retort pouch (PET/NY/PP). The moisture content equilibrium increased when the relative humidity was increased.

Figure 5 shows the water adsorption isotherm (NY). The equilibrium moisture content increased as the relative humidity increased, and these values are much higher than those of retort pouch (PET/NY/PP) shown in Fig.4.

The dry basis moisture content of the retort pouch X_{pouch} was estimated by equations (1) and (2), using the dry basis moisture content of NY, X_{NY}, and assuming that the moisture content of the PET and PP layers is almost zero.

$$X_{pouch} = X_{NY} \frac{\rho_{NY} W_{NY}}{\rho_{pouch} W_{pouch}} \quad (1)$$

$$\rho_{pouch} = \rho_{PET} \frac{W_{PET}}{W_{pouch}} + \rho_{NY} \frac{W_{NY}}{W_{pouch}} + \rho_{PP} \frac{W_{PP}}{W_{pouch}} \quad (2)$$

where ρ and W are the density and thickness of each material at dry condition, respectively. The calculated result in Fig. 4 is in general agreement with the experimental result, which indicated moisture mainly exists at the NY layer.

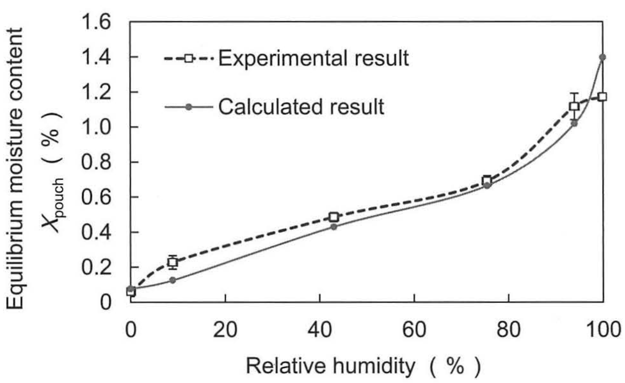

Fig. 4 Water adsorption isotherm (PET/NY/PP, temperature: 20℃).

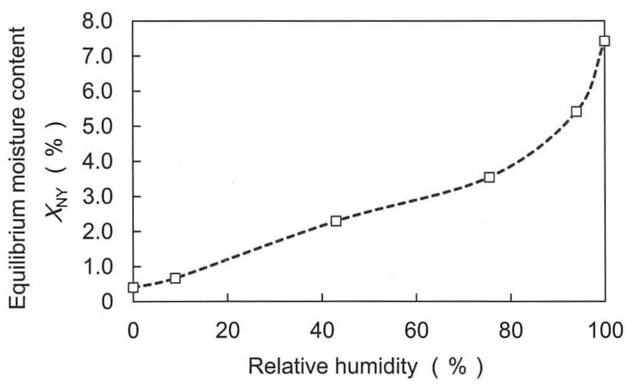

Fig. 5 Water adsorption isotherm (NY film, 20℃).

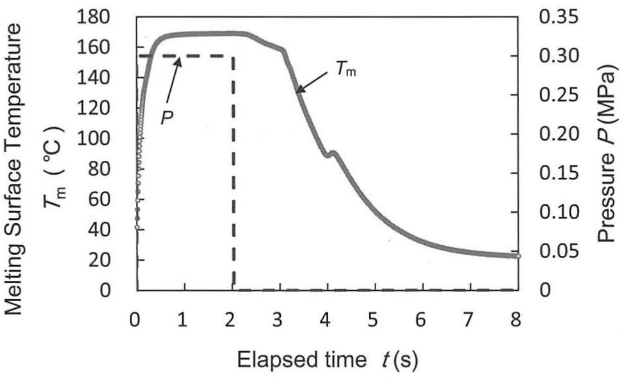

Fig. 6 Changes of melting surface temperature and pressure (T_{sf}=170℃, heating time: 2 s, sample width: 87 μm, Teflon cover: 50 μm, P=0.3MPa).

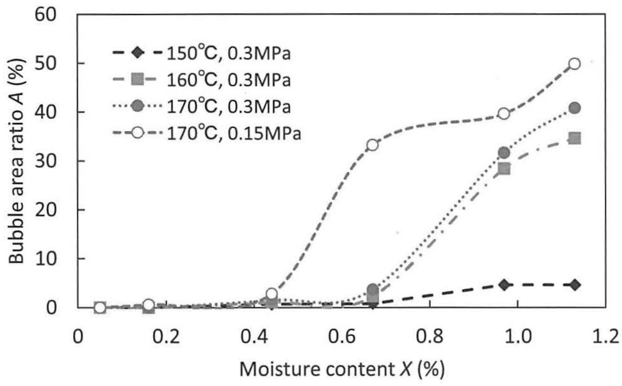

Fig. 8 Effects of moisture content, temperature and pressure on bubble area ratio (Retort pouches).

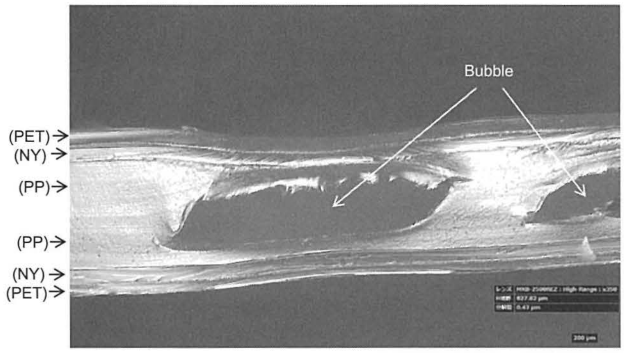

Fig. 9 Cross section of a bubble in retort pouch (T_{sf}=170℃, P= 0.15 MPa, heating time: 2 s, X=1.13%)

3.2 Bubble formation during heat-sealing process

Figure 6 shows a plot of the changes in the melting surface temperature and pressure (T_{sf}=170℃, heating time: 2 s) as a function of time. Initially, the temperature of the melting surface rapidly increased, after which it stabilized and approached a constant value (170℃) within 1 second, which value was same as surface temperature of heating blocks.

Figure 7 shows the effects of varying the moisture content, temperature, and pressure on bubble formation. These images were captured using a digital camera (DMS1000, LEICA Microsystems, Tokyo). The bubble area ratio A was measured using a digital microscope system (KH-8700, HiROX, Tokyo). The bubble was judged by contrast and the bubble area ratio A was calculated as average of a captured area (5mm×8mm) around center of each images. Figure 8 shows the effects of moisture content, temperature and pressure on bubble area ratio. The number of bubbles is smaller when the moisture content of sample material X is lower. In addition, the number of bubbles is smaller when the temperature T_{sf} is lower and the pressure is higher. Our results showed that retort pouches (PET/NY/PP) should be stored in rooms with lower humidity to prevent bubble formation during heat sealing.

3.3 Mechanism of bubble formation in plastic packaging

Figure 9 shows a cross section of a bubble in the PP layer of the sample material. This image was acquired using a microscope system (KH-8700, HiROX, Tokyo). The cross section of sample material was made using a sharp blade. The PP layer transforms from the solid state into the soft, liquid state as the temperature increases during the heat sealing process. This means that the coefficient of viscosity and the coefficient of elasticity are lower at higher temperatures. The high temperature caused the water on the boundary between the PP and NY layers to evaporate. This evaporated water vapor transfers into the PP layer because the PET layer has high barrier characteristics for moisture. In short, we propose the following mechanism of bubble formation: as the temperature of the material increases during heat-sealing, the water adsorbed in the nylon (confirmed by the adsorption isotherm of NY) transfers to the polypropylene layer (confirmed by the dynamic viscoelastic of PP) because the water vapor is prevented from escaping through the polyester layer (confirmed by the barrier characteristics of PET).

4. Conclusions

This study examined the effect of moisture content on bubble formation in retort pouches as the sample material. The experimental results showed that the ratio of the area occupied by bubbles to that of the sample material is smaller when the moisture content of the sample is lower.

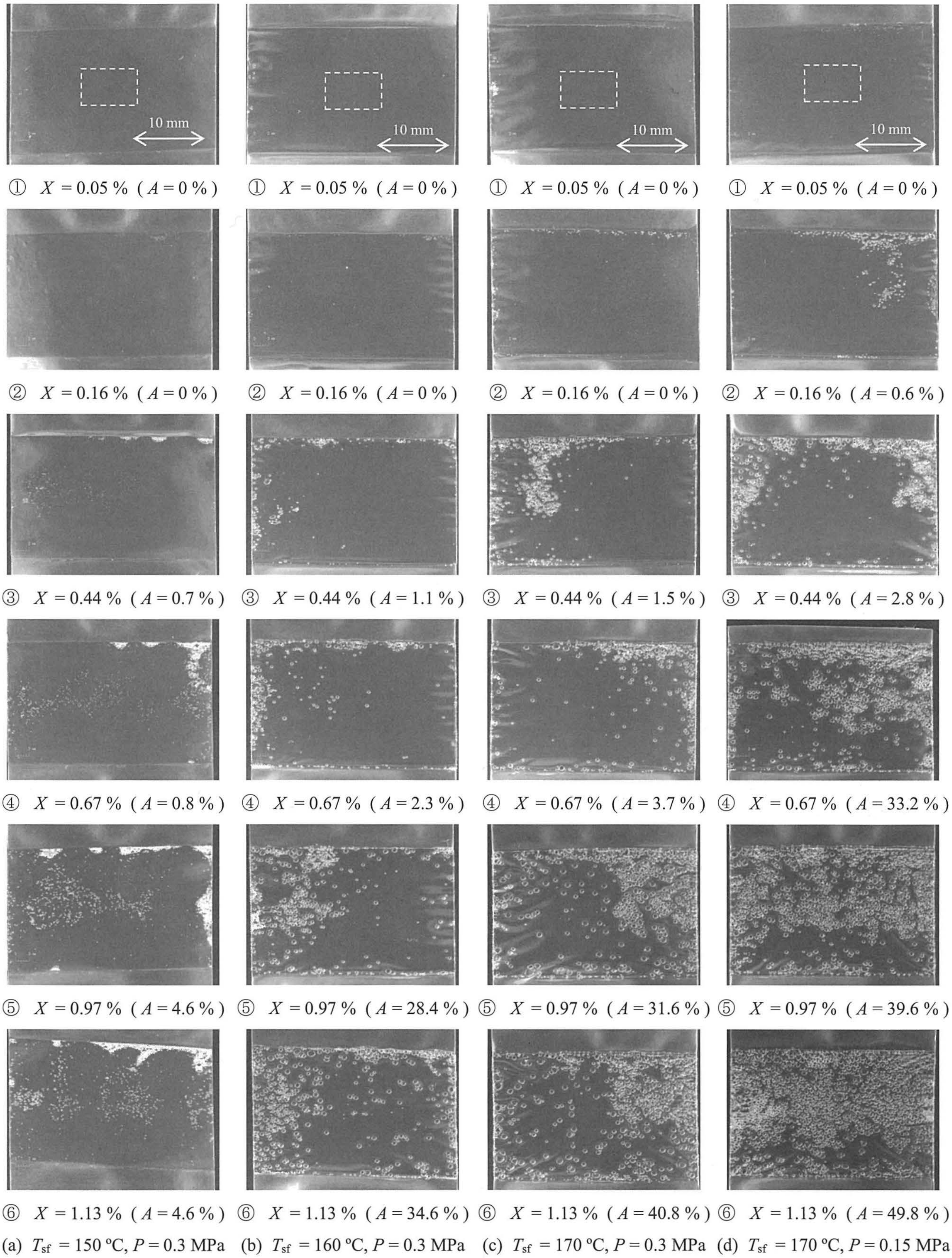

Fig. 7 Effects of moisture content, temperature and pressure on bubble formation (Retort pouches).

Our results enabled us to propose the following mechanism of bubble formation: water adsorption isotherm of nylon, dynamic viscoelastic of polypropylene, and barrier characteristics of polyester. We therefore concluded that the problem caused by bubble formation in retort pouches containing a nylon layer can be solved by storing the pouches in rooms with lower humidity.

Acknowledgments

We are grateful to HiROX, Shimazu, and the Technology Research Institute of Osaka Prefecture for analysis support. In addition, we would like to thank Editage (www.editage.jp) for English language editing.

NOMENCLATURE

A : bubble area ratio,%
t : time, s
T : temperature, ℃
P : pressure, Pa
X : moisture content (dry-basis),%
Subscripts
m : melting surface
sf : surface of heating block

References

1) C. Mueller, G. Capaccio, A. Hiltner, E. Baer; Heat sealing of LLDPE: Relationships to melting and inter diffusion. J. Appl. Polymer Sci., **70**, 2021–2030 (1998).
2) T. Tsujii, Y. Hashimoto, U. S. Ishiaku, M. Mizoguchi, Y. W. Leong, H. Hamada; Effect of heat-sealing temperature on the properties of OPP/CPP Heat Seals. Part II. crystallinity and thermomechanical properties. J. Appl. Polymer Sci., **99**, 513–519 (2006).
3) C. Poisson, M. Hervais, M. F. Lacrampe, P. Krawczak; Optimization of PE/Binder/PA extrusion blow-molded films. I. Heat sealing ability improvement using PE/EVA blends. J. Appl. Polymer Sci., **99**, 974–985 (2006).
4) C. S. Yuan, A. Hassan, M. I. H. Ghazali, A. F. Ismail; Heat sealability of laminated films with LLDPE and LDPE as the sealant materials in bar sealing application. J. Appl. Polymer Sci., **104**, 3736–3745 (2007).
5) K. Hishinuma; "Heat sealing technology and engineering for packaging," DEStech Publications, Inc. U.S.A., 2007, pp. 157–161.
6) M. Fukuda, M. Miyagawa; "Relation between moisture uptake and concentration of amid group in Nylon" (in Japanese). HEART Hyokyo Institutional Repository 15, 125–135 (1995).
7) T. Inoue, Y. Nakajima, T. Tanaka, H. Fukushima; "Prevention of bubble formation using simultaneous pressure and temperature in heat sealing" (in Japanese). Bull. Toyo College of Food Technol., **2**, 15–21 (2013).

「日本食品工学会誌」, Vol. 19, No. 3, pp. 151, Sep. 2018

◇◇◇ **和文要約** ◇◇◇

食品用プラスチック容器包装における発泡メカニズム

井上　保[1,†]，塩野　剛[1]，伊與田浩志[2]

[1]東洋食品工業短期大学，[2]大阪市立大学大学院　工学研究科

プラスチックの包装には，加熱と冷却で接着が完成できるヒートシール技術が適用されている．プラスチックのフィルムやシートを使った包装材料では，透過成分のバリア性や剛性の調節のために数種のフィルムを貼り合わせるラミネーションが行われる．ナイロンなどの親水性の材料では水分のような揮発成分を層内に保有するものもあり，ヒートシールによって高温下に曝されると気化し，溶着層で発泡を起こす．発泡はヒートシール面の美観を損ねるばかりでなく，ヒートシール性にも影響を及ぼすことが知られている．

本研究では，レトルトパウチを試料とし，発泡に与える水分の影響について実験的に調べた．フィルムの材料構成は，透明蒸着 PET12 μm/ONY15 μm/CPP60 μm とした．その結果，発泡は，含水率が低いほど起こりにくいこと示した．低湿度の環境下で保管することが有効であることが示唆される．加えて，水分吸着等温線，粘弾性，バリア性を考慮し，発泡のメカニズムについて解析を行った．

（受付 2017 年 12 月 20 日，受理 2018 年 6 月 21 日）
〒666-0026　兵庫県川西市南花屋敷 4 丁目 23 番 2 号
† Fax: 072-758-6959, E-mail: tamotsu_inoue@toshoku.ac.jp