A new bleeding model of additives in a polypropylene film under the atmospheric pressure

***M. Wakabayashi* (a), T. Kohno (b), T. Kimura (b), S. Tamura(b),**

M. Endoh(b), S. Onishi (a), T. Nishioka, Y. Tanaka (b), T. Kanai (a,b)

(a) Idemitsu Kosan Co., Ltd., Japan
(b) Prime Polymer Co., Ltd., Japan

Abstract

A new bleeding model of additives in a polypropylene film under the atmospheric pressure was investigated. Solubility and diffusion are found to be important for explaining this bleeding process. The experimental results were explained more precisely by assuming two transport processes between the amorphous regions and the crystalline ones.

The solubility and diffusion coefficients of higher fatty acid amides and higher fatty acid such as erucamide (13-cis-docosenamide),behenamide (docosanamide), stearamide (octadecanamide) and behenic acid (docosanoic acid) were determined between 40 ℃ and 70 ℃. The difference between the solubilities and the diffusion coefficients was discussed with the size of these additives providing aggregates by hydrogen bonding in the polypropylene film.

The solubility and diffusion coefficients of UV-stabilizers such as 2-(2H-Benzotriazol-2-yl)-4-methylphenol and 2-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol were determined at 40 ℃. The difference between the solubility and the diffusion coefficients was discussed with the solubility parameters and the bulky structures of methyl group and tert-octyl group.

1. Introduction

There are a slip agent, an anti-static additive, etc. which provide performance by bleeding on a film and an antioxidant, a nucleating agent, etc. which act inside a film in the kind of additive. The bleeding process by which the additive in a film comes out on the surface will be considered to be effective in design development of additive prescription, if it can predict. However, clear explanation of the bleeding process of the additive under normal pressure was not completed until now.

Quijada-Garrido and others had reported that the erucamide in PP film under a vacuum passes through the amorphous regions according to a diffusion equation and is released from the globules to the amorphous regions according to first-order kinetics. Then, the amount of desorption of the erucamide at time t (Mt) is described below as the sum of two processes [1].

$$M_t = M_{Fick}\left(1-\frac{8}{\pi^2}\left(\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2\pi^2 Dt}{4l^2}\right)\right)\right)+M_{release}(1-\exp(-kt)) \qquad (1)$$

2. Experimental Procedures

Idemitsu H700 additive-free isotactic polypropylene was used. It has 47% of crystallinity. The blends of additive/PP with small quantity of antioxidant additives (500ppm of IRGANOX1076 (Ciba-Geigy) and 500ppm of IRGAFOS168 (Ciba-Geigy)) were prepared by dry mixing and extruded at 200℃. Next, it was fabricated into the 50-micrometer film in thickness using ϕ 40mm casting machine. The surface was washed with the good solvent after bleeding at predetermined temperature for predetermined time, and the amount of the additive on the film surface was determined by the gas chromatograph or size exclusion chromatograph.

3. Results and Discussion

We considered the bleeding process of the additives under normal pressure as follows. The additive in a PP film dissolves in an amorphous region first, and if it reaches saturation solubility it becomes impossible to dissolve more. The ingredient beyond this saturation

solubility migrates to the film surface. Furthermore, an additive has a certain bleeding speed and migrates to the excess amount beyond saturation solubility to the film surface. Therefore, in order to explain a bleeding process under the atmospheric pressure quantitatively, it is important to find saturation solubility and bleeding speed.

In order to find saturation solubility and bleeding speed under the atmospheric pressure, the following model was proposed in consideration of an amorphous region and a crystalline region.

$$y(t) = (C_0 - C_s)\{\alpha_i + (1-\alpha_i)(1-\exp(-kt))\}\left(1 - \frac{1}{4l}\left(\int_{-l}^{l} c(x,t)dx\right)\right) \quad (2)$$

$$c(x,t) = erf\left(\frac{l-x}{2\sqrt{Dt}}\right) + erf\left(\frac{l+x}{2\sqrt{Dt}}\right) \quad (3)$$

where y(t) is the amount of bleeding additive on the film surface at time t, C_0 is the added amount of an additive, C_s is the saturation solubility, α_i is a diffusion ratio of added amount i, k is the constant of first-order kinetics, l is the half thickness of film, c(x,t) is the concentration at time t and distance x, erf(z) is the error function and D is the diffusion coefficient.

Figure 1 shows the bleeding profiles of erucamide by changing the added amounts of erucamide at 40 ℃. It turned out that a bleeding process can be explained well.

Figure 2 shows the example which applied the modified model to the bleeding process of benzotriazole stabilizer. it also turned out that these bleeding process can be explained well.

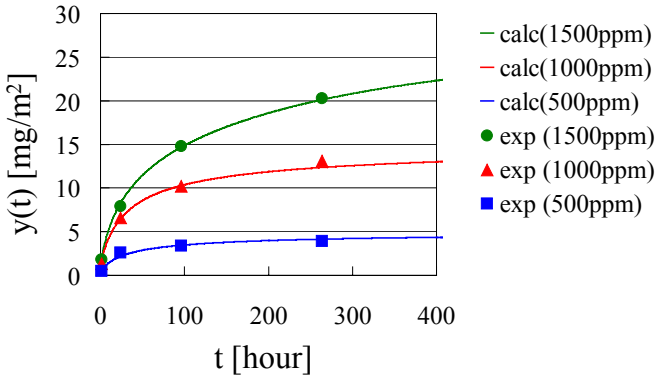

Figure 1: Bleeding profiles of erucamide(13-cis-docosenamide) at 40 ℃ (Saturation solubility C_s:250(ppm), Diffusion coefficient D:5.2x10^{-15} (m^2/s)).

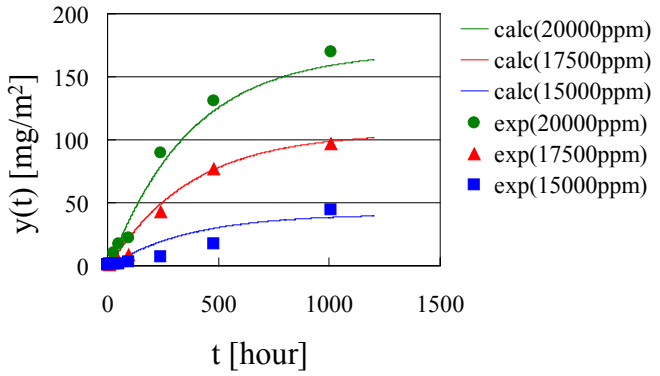

Figure 2: Bleeding profiles of 2-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol at 40 ℃ (Saturation solubility C_s:13,000(ppm), Diffusion coefficient D:2.4x10^{-14} (m^2/s)).

Reference

1. I. Quijada-Garrido, J. M. Barrales-Rienda, L. Alejo Espinoza and J. L. G. fierro, *Desorption of Erucamide Vapor in Vacuum from Erucamide/Isotactic Polypropylene Films*, Macromolecules, 29(27), pp.8791-8797(1996)