Concentration Distribution of Antioxidant Additive BHT in Polypropylene after Heating

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SYNOPSIS

The concentration distribution of an antioxidant 2,6-di-*tert*-butyl-*p*-cresol (BHT) in the polypropylene (PP) after heating the film containing BHT for a long period of time in succession was studied with use of the rolled film method. The film of 0.003 cm in thickness containing uniformly 710 mg kg^{-1} of BHT was wound tightly around a glass tube. At the beginning, BHT was distributed uniformly in all layers, and after a given time of the heat treatment at 70–100°C, a remarkable alteration of the concentration distribution of BHT in PP took place. The relations between BHT concentration and the distance from the surface were shown by parabolic curves after heating. The BHT concentration was always kept at almost zero concentration at the surface layer of the rolled film. Assuming that the diffusion obeys Fick's law, the diffusion coefficients at 70, 80, 90, and 100°C were estimated to be 1.05, 4.17, 8.69, and 24.7 × 10^{-9} cm^2 s^{-1}, respectively. The activation energy was calculated as 105 kJ mol^{-1}.

INTRODUCTION

For the avoidance of the oxidation and decomposition reactions by molecular oxygen, it is customary to add some aromatic hydroxy compounds into polymers as protective substances.[1] The reaction and the diffusion behavior of these compounds are interesting for polymer chemists. Food chemists and packaging technologists are also interested in the diffusion and the solubility of these compounds because the antioxidants are able to migrate from the package to foods and other products. 2,6-Di-*tert*-butyl-*p*-cresol (BHT), a white powder of MW 220 of relatively high-vapor pressure, has been generally used as an antioxidant for polyolefins under heating. The fact that a very small amount of BHT migrates from the package to some kinds of confectionaries containing a large quantity of fat or oil is well known.[2,3]

At present, polypropylene (PP) is widely used as a material for lunch ware instead of chinaware at the mass lunch facilities in Japan, i.e., schools and hospitals, because they are less expensive, stronger, and of higher work efficiency as compared with chinaware. The studies on the toxicities of BHT and other compounds added to the polymer products have been done by many researchers, but it is necessary to investigate the behavior of these additives in polymers and the ability of migration into many foods and other products. In particular, there are few studies on the behavior of the additive in the polymers used for a long period of time.

Several authors[4-6] have reported the diffusion and solubility of some phenolic antioxidants in LDPE or PP. In these studies, the method consists of analyzing the concentration profile after diffusion of an antioxidant across a stack of polymer sheets, which do not contain antioxidants at the initial stage. However, most hygienic chemists are interested in the mechanisms of the migration of antioxidant additive from polymer to foods and other medical products or the alteration of the concentration distribution of additives in a polymer with the repetition of a long period of time usage.

Therefore, it is better to use the PP stack in which an additive BHT is distributed uniformly in a layer. Only one study, reported by Gondo and Utsunomiya[7] over 20 years ago on the diffusion of

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additive in PP, is considered to be useful to the solution for these problems, although it is still lacking.

One of the authors previously determined the amount of BHT in the PP school lunch wares using a combination of gas chromatography, thin-layer chromatography, and high-performance liquid chromatography.[8] The lunch wares were heated at about 80°C to dry and sterilize them. The behavior of BHT in PP at high temperature therefore still needs to be clarified.

In this paper, the authors report on the alteration of the concentration distribution of BHT from the inner part to the surface of PP after heating for a long period of time at 70–100°C by using a rolled film method.[9] The authors also report the diffusion coefficient and the activation energy of BHT in PP.

EXPERIMENTAL

Reagent

An antioxidant additive BHT as a standard material for the determination of its concentration in PP was purchased from Tokyo Kasei Kogyo Co. and used without further purification. Other reagents were all analytical grade.

Apparatus

The gas chromatograph used in this study was a Yanagimoto Model G3800 gas chromatograph equipped with a flame-ionization detector. The heating oven used was a Sanyo Model MOV heating oven (temperature precision within 1°C).

Preparation of Rolled Films

The commercial PP film used was supplied by TO-NEN FILM Co. This PP film of 0.003 cm in thickness was wound tightly around a glass tube of 1.1 cm in diameter. The film initially contained BHT of 710 mg kg^{-1} and had a crystallinity of 0.54. The X-ray profile of this film did not show any orientation. The rolled film shown in Figure 1 was heated at 70, 80, 90, and 100 ± 1°C in a heating oven. After a given time of heat treatment, the rolled film was drawn off from the heating oven, cut perpendicularly to the diffusion direction, and separated into individual layers.

Measurement of Antioxidant Additive BHT Content

The method for the preparation of the sample solution was the same as in the previous paper.[10] In particular, the individual layers were refluxed with 100 mL of n-hexane for 2 h at 80°C, and the filtrate was evaporated under the vacuum until just before the solvent completely disappeared and then was dissolved in 2 mL of dichloromethane.

The two columns, 3.4 mm i.d. × 2000 mm, glass tubings packed with 10% SE-30 on Gaschrom Q (60–80 mesh), and 5% silicone OV-17 on Shimalite W (80–100 mesh) were isothermally operated at 160°C. The injector was maintained at 220°C. Nitrogen as a carrier gas was allowed to flow at a flow rate of 50 mL min^{-1}.

RESULTS AND DISCUSSION

Relations between Concentration of BHT and Distance from Surface of Rolled Film

The relations between the concentration of remaining BHT in each PP layer and the distance from the surface after heating at 70, 80, 90, and 100°C are shown in Figures 2–5, respectively.

BHT molecules were distributed uniformly in all layers at the initial stage. However, on heating at 70°C, there took place alteration of the concentra-
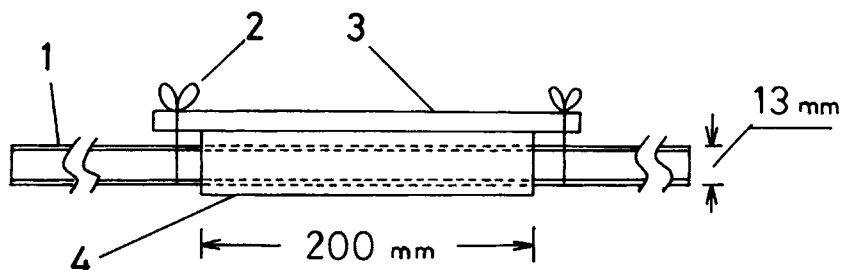
Figure 1 Schematic illustration of reaction apparatus: (1) glass tube; (2) fixed parts; (3) glass rod; (4) rolled film.
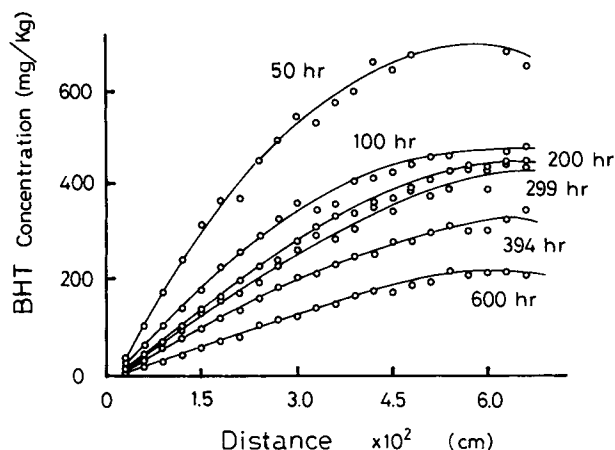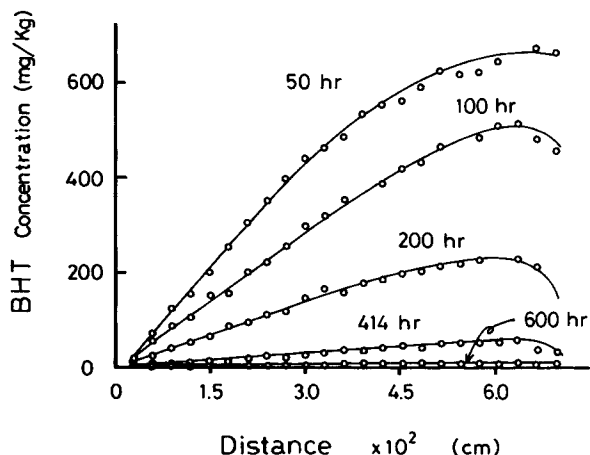
Figure 2 Relations between BHT concentration and distance from surface layer after heating at 70°C.

Figure 4 Relations between BHT concentration and distance from surface layer after heating at 90°C.

tion distribution after a given time of the heat treatment. Six heating times from 50 to 600 h were chosen. The concentration of BHT in the individual layer decreased in accordance with the approach to the surface of the rolled film, and at the surface, it was almost zero.
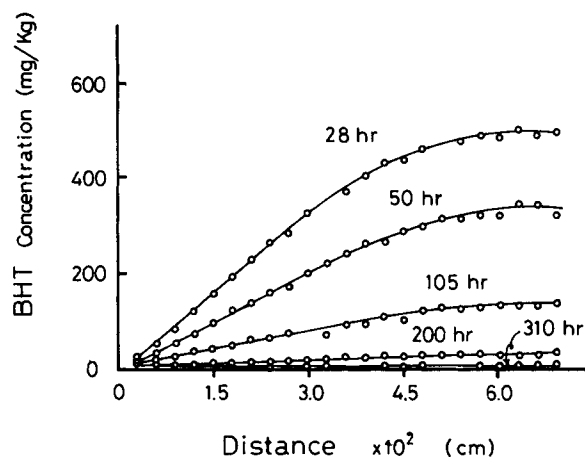
Consequently, these relationships between the BHT concentration and distance are shown by parabolic curves at all heating temperatures. BHT is considered to disappear by vaporization during heating, as Gondo and Utsunomiya[7] pointed out.

Furthermore, the concentration gradient from the inner to the surface of rolled film after 50 h was largest, and after 600 h, there still existed a large quantity of BHT in each PP layer with the exception of the surface.

On heating at 80°C, the applicable optimum tem-

perature for the mass lunch facilities, the tendency of the decrease in the slope of the concentration-distance curve with heating time (50–600 h) was similar to heating at 70°C. The relations between the distance and the BHT concentration also showed parabolic curves at all heating times. BHT in each PP layer disappeared after 600 h. The concentration of BHT at the surface layer of the rolled film was kept at zero concentration in the same manner as mentioned above.

On heating at 90 and 100°C, the decrease in the slope of concentration–distance curve with heating time was similar to that of the other experimental series. In particular, the alteration of BHT concentration in each layer at 100°C was larger than the alteration at the other temperatures and the concentration distribution of BHT after heating for 25

Figure 3 Relations between BHT concentration and distance from surface layer after heating at 80°C.
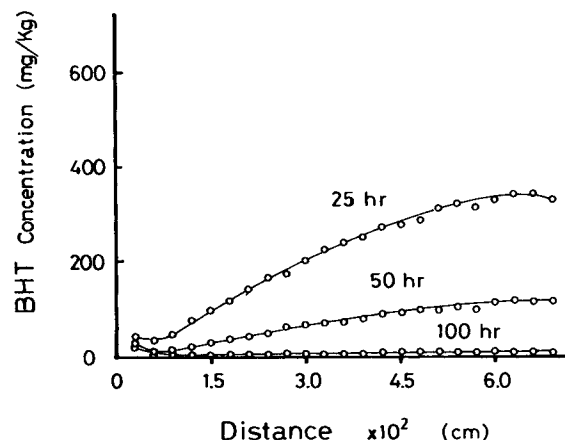
Figure 5 Relations between BHT concentration and distance from surface layer after heating at 100°C.

h seemed to be equal to the one after heating for 50 h at 90°C, and, also, after 50 h, it seemed to be equal to the distribution of BHT after heating for 105 h at 90°C. In addition to this, the concentration of BHT in the surface layer of the rolled film heated at 100°C was somewhat higher than the value obtained at other heating temperatures.

An antioxidant BHT in each PP layer almost disappeared after 600 h at 80°C, 200–300 h at 90°C, and 100 h at 100°C, and, thus, it is considered that the time required for the complete disappearance decreased with a rise in temperature.

Figure 6 shows the relations between distance and BHT concentration in the film heated for 50 h at 70–100°C. The concentration distribution after heating for the same hours was found to depend remarkably on the heating temperature.

As the surface of the rolled film is always kept at almost zero concentration of BHT in all experiments, the decrease of BHT in the rolled film are considered to proceed with the diffusion process. The diffusion velocity of BHT in PP is considered to be influenced by the rate of vaporization of BHT from surface to surrounding; thus, it is influenced by the heating temperature.

Treatment as a Diffusion Process

Theory

We assume that the process obeys Fick's law, as described below:

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \tag{1}$$
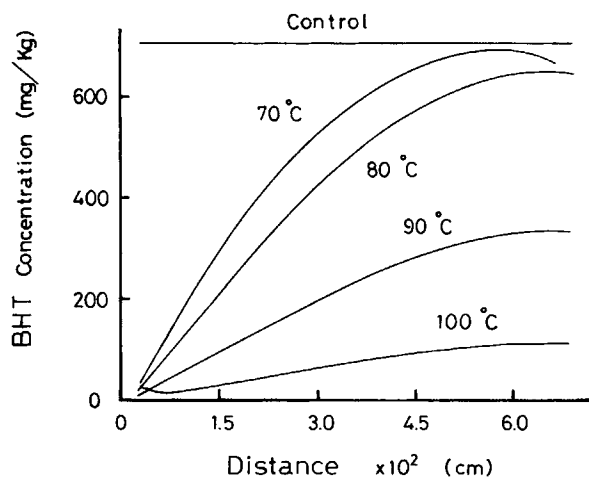
Figure 6   Concentration of BHT in PP after heating for 50 h at several temperatures plotted against distance from surface.

where c is the concentration of diffusing material; t, time; x, distance; and D, diffusion coefficient.

If we are interested in diffusion out of a plane sheet of thickness L, in which the diffusing substance is initially uniformly distributed and the surface of which is kept at zero concentration, the conditions are given in eqs. (2) and (3):

$$C = C_0; \quad 0 < x < L; \quad t = 0 \tag{2}$$

$$C = 0; \quad x = 0; \quad x = L; \quad t = 0 \tag{3}$$

The solution of eq. (1) satisfying the initial condition (2) and boundary condition (3) is given in eq. (4):

$$C = \frac{4C_0}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} e^{-D(2n+1)^2\pi^2t/L^2} \sin \frac{(2n+1)\pi x}{L} \tag{4}$$

where n takes value $0, 1, 2, \ldots$. This trigonometrical-series-type solution converges satisfactorily for moderate and long times.

By developing and multiplying the right side of eq. (4) about $n = 0, 1, 2, \ldots$, eq. (5) is obtained:

$$C = \frac{4C_0}{\pi} \left(e^{-D\pi^2t/L^2} \sin \frac{\pi x}{L} + \frac{1}{3} e^{-D \cdot 9 \cdot \pi^2t/L^2} \sin \frac{3\pi x}{L} \right.$$
$$\left. + \frac{1}{5} e^{-D \cdot 25 \cdot \pi^2t/L^2} \sin \frac{5\pi x}{L} + \cdots \right) \tag{5}$$

Taking the logarithm of eq. (5), it leads to the approximate eq. (6):

$$\text{Log} \frac{C\pi}{4C_0} = \text{Log} \sin \frac{\pi x}{L} - \frac{1}{2.303} \cdot \frac{D \cdot \pi^2 \cdot t}{L^2} \tag{6}$$

If a diffusion coefficient is independent on the concentration, the plot of $\log c\pi/4C_0$ to t must produce a straight line and the diffusion coefficient can be determined from the slope of the straight line. In this experiment, c is considered to be the concentration of BHT in a PP stack at each temperature and time.

The activation energy in diffusion (E) and D is usually combined by eq. (7):

$$D = D_0 e^{-E/RT} \tag{7}$$

where D is the diffusion coefficient; D_0, a constant; E, the activation energy; R, the gas constant, and T, the absolute temperature.
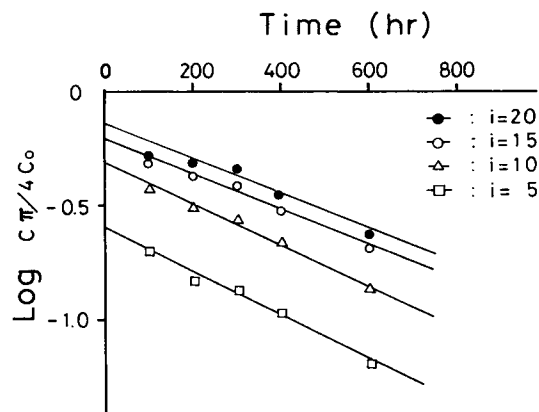
Application to Experimental Data

Now we wish to describe the application of eq. (6) to the experimental data. To obtain diffusion coefficients from the experimental results, the data at the 5th, 10th, 15th and 20th layers from the surface of the rolled film were chosen. Figures 7–10 show the relationships between log $c\pi/4C_0$ and heating times at 70, 80, 90, and 100°C. The term i in these figures means the ith layer from the surface; therefore, as the thickness of the film used is 0.003 cm, in i = 20, 15, 10, and 5, the distances to each layer from the surface layer are 0.06, 0.045, 0.03, and 0.015 cm, respectively.

On heating at 70°C, the plots for four kinds of layers lie on straight lines, respectively, though log $C\pi/4C_0$ for 100 h at i = 20 deviates slightly below the straight line. The slope of the straight line increased gradually with the approach to the surface.
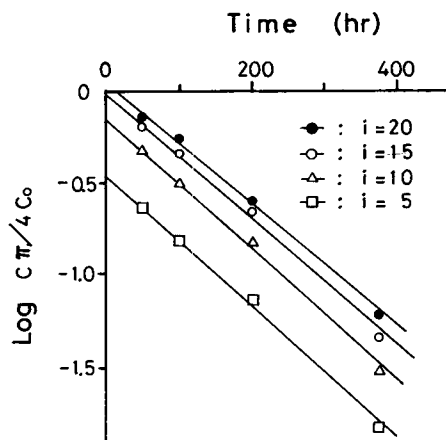
On heating at 80°C, the plots lie clearly on a straight line in all layers, and also the slope of these straight lines increased gradually with the approach to the surface layer.

On heating at 90 and 100°C, the plots also lie on straight lines. As the velocity of diffusion of BHT in PP at 100°C is larger than that at the other temperatures, log $c\pi/4C_0$ was plotted only for three heating times t, i.e., 25, 50, and 104 h. In this case, the slope of the straight line at the 5th layer seemed to be slightly lower than that of the other three.

The values of the diffusion coefficients determined from the slope were described in Table I. The standard deviations of the D values obtained in the different distances from surface at the same temperature were found to be very low, and the D value was found to increase remarkably with a rise in temperature. The activation energy of diffusion was estimated using eq. (7).
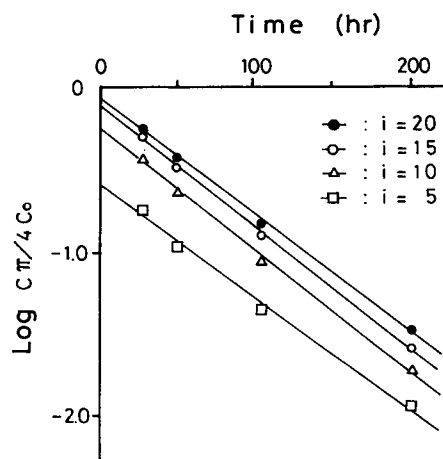
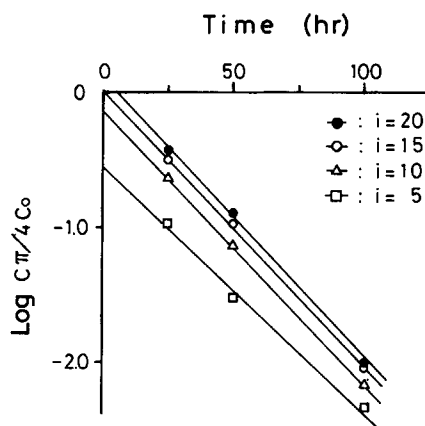**Figure 8**   Relations between log $C\pi/4C_0$ and t at 80°C.

The relations between ln D and $1/T$ are shown in Figure 11. The plots lie on a straight line and thus the value of the activation energy was calculated as 105 kJ mol^{-1} from the slope of a straight line.

Gondo and Utsunomiya[7] investigated the diffusion of BHT into a PP stack without antioxidants by placing the sheets containing 1 wt % BHT as a reservoir of antioxidant above and below the stack and observed the diffusion through the PP stack. The values of the diffusion coefficient found according to Sekido's method were 1.1, 2.6, 8.1, and 16.5 × 10^{-9} cm^2 s^{-1} at 70, 80, 90, and 100°C, respectively, and the activation energy was 98 kJ mol^{-1} at a higher temperature (70–100°C) than the melting point of BHT. Furthermore, these values indicated that an additive BHT in PP was vaporized from the surface by heating.

The diffusion coefficients reported by them agreed with our results at corresponding temperatures, and,

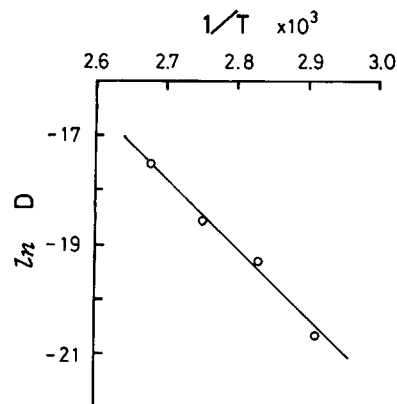**Figure 7**   Relations between log $C\pi/4C_0$ and t at 70°C.

Figure 9   Relations between log $C\pi/4C_0$ and t at 90°C.

Figure 10 Relations between log $C\pi/4C_0$ and t at 100°C.

Figure 11 Relations between ln D and reciprocal of absolute temperature $1/T$.

also, the value 105 kJ mol^{-1} of activation energy obtained by the present study agreed with the value 98 kJ mol^{-1} mentioned above.

Since the polymer segments vibrate thermally with a large amplitude depending on heating temperature, voids are produced in amorphous regions into which are able to pass BHT molecules. The number of the voids will increase with a rise in temperature. Moreover, the mobility of BHT in the polymer may also be affected by the proportion of amorphous regions to crystals because priority is given to the amorphous regions for the moving of the BHT molecule.

Since BHT molecules are more volatile and of lower molecular weight as compared with the other phenolic antioxidants, they are expected to have high mobility in PP at a given temperature. It is very interesting to compare the diffusion behavior of BHT in PP with BHT revealed in this study with that into PP without BHT as reported by Gondo and Utsunomiya.[7] Both PP films used showed little difference in the crystallinity and showed no ori-

entation by X-ray measurement. There were no evident differences between diffusion coefficients and activation energies obtained by those two methods at the same temperature. It seemed that the mobility of BHT in PP is not influenced by the initial state of whether additives were distributed uniformly in PP or not. Immediately after heating, the BHT molecules at the surface and in its vicinity are allowed to vaporize quickly toward the outside and they obtained zero concentration in a short time. Consequently, there would be a considerable large concentration distribution between the surface and the inside of the film. The BHT molecules existing in the polymer are thus vaporized to migrate and to diffuse toward the surface. We believe that the rolled film method is useful to understand the migration mechanism of additives in polymers.

CONCLUSION

The concentration distribution of an antioxidant 2,6-di-*tert*-butyl-*p*-cresol (BHT) in polypropylene

Table I Diffusion Coefficients D for Four Temperatures

| Temperature (°C) | n | Diffusion Coefficient ($D \times 10^9$ cm^2 s^{-1}) | | | | | |
| | | ith Layer from Surface | | | | | |
		$i = 5$	$i = 10$	$i = 15$	$i = 20$	Mean	SD[a]
70	4	1.18	1.12	0.95	0.94	1.05	0.10
80	4	4.31	4.33	4.20	3.82	4.17	0.21
90	4	8.30	8.98	8.95	8.55	8.69	0.28
100	4	22.8	25.3	25.2	25.5	24.7	1.10

[a] SD: standard deviation.

(PP) film after heating the PP film containing BHT was studied with use of the rolled film method.

When the PP film containing BHT ($710 \ mg \ kg^{-1}$) distributed homogeneously was heated at 70–100°C, the concentration distribution of BHT occurred. The relationships between BHT concentration and the distance from the surface were shown as parabolic curves, and just at the surface, the BHT concentration was kept almost zero. The diffusion velocity of BHT in PP was considered to be influenced by the rate of the vaporization of BHT from the surface to outer layer.

Assuming that the diffusion obeys Fick's law, the diffusion coefficients at 70, 80, 90, and 100°C were estimated to be 1.05, 4.17, 8.69, and $24.7 \times 10^{-9} \ cm^2 \ s^{-1}$, respectively. These values agreed well with the values obtained by Gondo and Utsunomiya[2] with the use of a PP stack without antioxidants. The activation energy also agreed well with the value they reported. The rolled film method was considered to be useful to investigate the behavior of additive in polymers.

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