Sorption and Transport of Water Vapor in an Injection-molded Nylon 6, 6 Sheet

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Solution and diffusion of water vapor in thin films, of 54~85 μm thick, sliced off from injection-molded sheet of nylon 6,6 were studied by the weighing method at 30°C. Among the films, samples sliced off at depths near the surface and the central layer of the sheet were mostly used in the measurements. Integral absorption from, and desorption to, zero concentration were investigated. It was found that the amount of water at absorption equilibrium changed with depth from the surface of the molded sheet, where the sample films were sliced off. The amount of sorbed water decreased gradually with increasing the depth and then leveled off. By assuming that water molecules are absorbed exclusively in the amorphous regions, the depth profile of the degree of crystallinity was estimated from the concentration of water at absorption equilibrium. The profile agreed well with that determined from density measurements. The absorption and desorption curves were of the pseudo-Fickian type. The non-Fickian nature of the processes became less apparent with increasing the final concentration for absorption. An apparent diffusion coefficient D_{app} was calculated from the half-time of the Fickian plots. Values of D_{app} showed concentration dependence, especially in the low concentration region. In the medium and the high concentration regions, the values of D_{app} for the sample film sliced off at a depth close to the surface of the sheet were greater than those for the film sliced off near the central layer of the sheet. The result is ascribed to the fact that the degree of crystallinity is higher for the latter film and that molecular motions of polymer chains in the amorphous regions of the latter film are more restricted.

INTRODUCTION

The injection molding is one of the representative operations of polymer processing. The process consists of filling a cold mold cavity with hot polymer melt. The properties and the microstructures of injection-molded objects are therefore inhomogeneous. If we feed a crystalline polymer in a rectangular mold cavity, the degree of crystallinity, the orientation of crystallites and of polymer chains in the amorphous regions, and physical properties will change according to depth from the surface of a molded sheet. The depth profile of the orientation of polymer chains in a molded plate, for instance, has been determined by measuring the birefringence after having abraded away successive layers from the surface of the plate.[1]

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Usually, the degree of crystallinity of a polymer is determined by measurements of wide-angle X-ray scattering, density, and thermal properties (DSC). With few exceptions, crystalline regions of a polymer at temperatures well below the melting point are generally inaccessible to most penetrants. Under this condition, the solubility of a gas or vapor is directly proportional to the amorphous content of the polymer.[2,3] Therefore, at low sorbed concentrations, it is possible to evaluate the degree of crystallinity from sorption behavior of a given gas or vapor in the polymer, if the perfectly amorphous or crystalline sample is available.

The study of transport behavior of a gas or vapor in polymer has also contributed much to our understanding of the microstructure of the polymer.[3] Furthermore, diffusion behavior of a penetrant in polymer is sensitive to the molecular motions of polymer chains, on a scale comparable to the size of the penetrant molecules. If an amorphous polymer, or the amorphous phase of a crystalline polymer, is in the glassy state, absorption or desorption process of non-Fickian type is observed. This is due to that the diffusional transport is coupled with relaxation mechanism. For a given penetrant-polymer system, the differential absorption curve changes its shape from non-Fickian to nearly Fickian when the system approaches to the glass transition temperature.[4,5] This implies that from the absorption behavior we may get an information about how far the system is located from the glass transition region. In other words, knowledge of local molecular motions in the system may be obtained from differential absorption measurements with a proper probe penetrant, though the knowledge is qualitative in nature. The situation is also the case with the integral absorption experiments for both amorphous and crystalline polymers.[6,7]

In this paper we will describe the sorption and transport behavior of water vapor in nylon 6, 6 films which were prepared by slicing off parallel to the surface of an injection-molded sheet. We will discuss the variation of the microstructures and the molecular motions of polymer chains with depth from the surface of the molded sheet, where the sample films were sliced off.

EXPERIMENTAL

Materials

The injection-molded sheet of nylon 6, 6 (Amilan CM 3001, Toray) was made under the conditions that the injection and the mold temperatures were 280°C and 80°C, respectively. The films of 54~85 μm thick were prepared by slicing off parallel to the surface of the molded sheet. Figure 1 shows schematically the injection-molded sheet and injection direction. The thickness of films used for sorption measurements are also shown in the figure together with the average depths of the films from the surface of the sheet. The films thickness was determined by taking the arithmetic average of numerous readings of a micrometer screw gauge over the area of the film. The sample films 2 and 24, which were sliced off respectively at a depth near the surface and the central layer of the sheet, were mostly used in experiments.

Water vapor used as a penetrant was evolved from deionized water, which
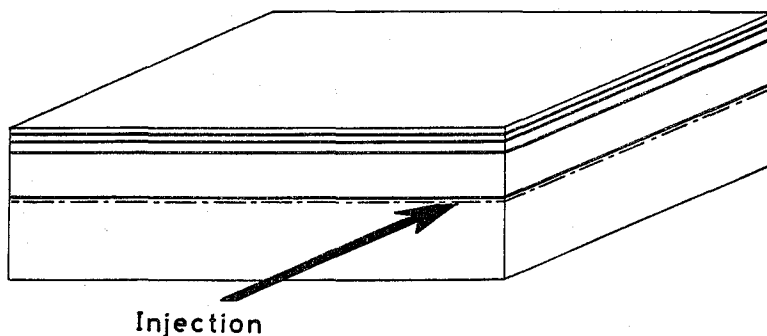
Sample No.	Depth(av.) mm	Thickness μm
2	0.069	85
5	0.193	54
9-1	0.408	55
24	1.246	54

Fig. 1. Nylon 6,6 sample films.

had been degassed at least three times before the experiments.

Methods

The absorption and desorption experiments were carried out by the weighing method. The amount of water at absorption equilibrium and the rates of absorption and desorption were measured using a high-vacuum apparatus equipped with an electromagnetic microbalance (Model GAB-1, Chyo Balance Corp.). The pressure of water vapor was measured with Baratron® pressure transducer (Type 221A, MKS). Integral absorption from, and desorption to, zero concentration were investigated at 30°C.

Density of the sample films was measured by the density gradient column method at 30°C. The mixture of carbon tetrachloride and acetone was used to establish a gradient in a column.

RESULTS AND DISCUSSION

Sorption Isotherms

Figure 2 shows the sorption isotherms of water vapor in the nylon 6,6 films at 30°C. C is the concentration of water absorbed by the polymer at equilibrium and p and p_0 are the pressure and the saturated pressure of water vapor, respectively. Unfilled and filled circles represent the data points of sample film 2 and 24, respectively. For the sample films, no substantial change in dry weight was observed within the experimental error after repeated absorption and desorption cycles; that is, there was no absorption-desorption hysteresis. Furthermore, the order of measurements using the same sample film had no effect on the values of C. The results indicate that crystallites in the molded sheet are stable for the
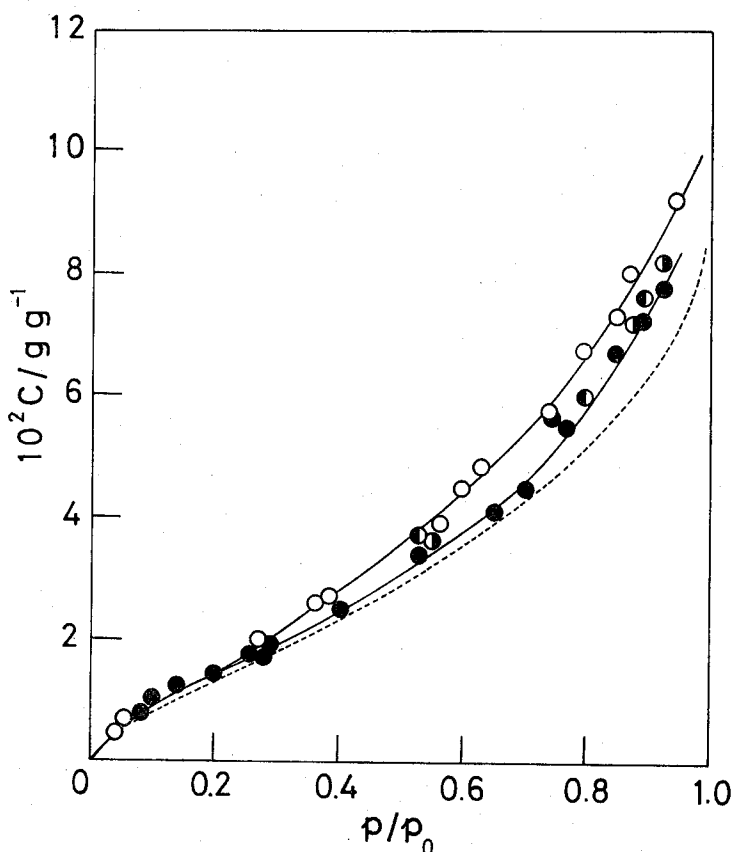
Fig. 2. Sorption isotherms of water vapor in nylon 6,6 at 30°C.
○: No. 2, ●: No. 24, ◑: No. 5, ◐: No. 9-1, ·········:
nylon 6,6 drawn yarn.[8]

aggression of absorbed water molecules and that conformation of the polymer chains in the amorphous regions is in rather stable state.

In Fig. 2, it is seen that, if a comparison is made at a certain relative vapor pressure, C for the sample film 2 of the smallest depth from the suuface of the molded sheet is higher than that for the sample film 24 of the largest depth and that data points for the films 5 and 9-1 locate between those of these two films. Thus a tendency to decrease C with increasing depth, where a sample film was sliced off, is noticed in the figure. Generally, solution of penetrant molecules in crystalline regions of polymer is not to be expected.[2,3,5] The solubility coefficients of the simple gas and crystalline polymer systems, for which Henry's law is obeyed, decrease linearly with increasing volume fraction of the crystalline regions. Therefore, if inaccessible nature of the crystalline regions in our sample films to water molecules is assumed, the tendency seen in Fig. 2 suggests that the degree of crystallinity in the molded sheet increases from the surface toward the central layer of the sheet. A measure of the degree of crystallinity of the sample film, ϕ_a, was evaluated from the sorption behavior by comparing the values of C at

relative humidities 0.550 and 0.890. Since neither amorphous nor perfectly crystalline sample is available with our sliced-off films, the relation between ϕ_a and depth thus evaluated was superposed to the dependence on depth of the degree of crystallinity ϕ_d which is calculated from density data. For the superposition the sample film 2 was chosen as a reference, because ϕ_a and ϕ_d had been obtained with this film.

The depth profile of the degree of crystallinity is shown in Fig. 3. Circles and squares refer to ϕ_a and ϕ_d, respectively. There is no substantial difference between the depth dependence at the two relative humidities. The depth profiles evaluated relatively using the sorption data coincide well with that determined from density measurements in the whole region. Thus it can be concluded that difference in the concentration of water at absorption equilibrium is mainly due to the difference in the degree of crystallinity of the sample films. Stated in another way, the result suggests that change of the degree of crystallinity of a molded sheet of crystalline polymer can be estimated from the amount of inactive penetrant at absorption equilibrium by employing sliced-films of the sheet, though the estimation remains a relative measure unless the reference film with perfectly amorphous or crystalline nature is available.

The degree of crystallinity increases gradually with increasing the depth and levels off in deeper parts of the molded sheet. This is a reflection of the fact that the surface, which is in contact with the cavity wall of mold during injection-molding process, is cooled faster than the central layer of the sheet. The gradual increase of the degree of crystallinity with the depth implies that the rate of
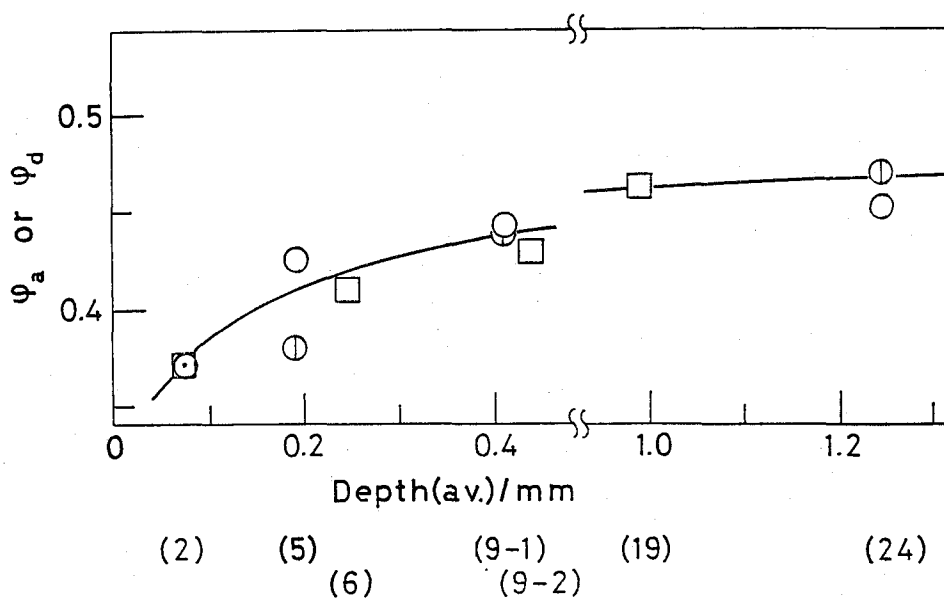

Fig. 3. Depth profile of the degree of crystallinity. ⊕: ϕ_a at p/p_0=0.550, ○: ϕ_a at p/p_0=0.890, □: ϕ_d. The sample film 2 is chosen to superpose the depth profile of ϕ_a to that of ϕ_d and indicated by a circle and a square with center dot.

crystallization of nylon 6, 6 is moderate. Similar depth dependence was seen in results of measurements of wide-angle X-ray scattering and thermal properties (DSC), and also those of polarized microscopic observations.

Sorption isotherm of water vapor in nylon 6, 6 drawn yarn[8] is also shown in Fig. 2 by a dotted line. The amounts of sorbed water for films are slightly greater than those for yarn. This may also result from the difference in the degree of crystallinity of these samples.

Absorption and Desorption Behavior

Figures 4 and 5 show the results of integral absorption and desorption measurements at low and high equilibrium concentrations, respectively. The results are given by the form of the Fickian plots, M_t/M_∞ against $t^{1/2}/X$. Here M_t is the amount of water absorbed by the polymer film or desorbed from the film at time t, M_∞ the final uptake or loss at infinite time, X the thickness of the film. Solid lines refer to absorption curves and broken lines to desorption curves. The sample numbers are indicated in the figures.

For the Fickian diffusion process, absorption curve exhibits a straight line up to 0.6~0.7 of M_t/M_∞. Also, a straight line can be seen up to 0.2~0.3, or more, of M_t/M_∞ for desorption curve.[4,5,9] All of absorption and desorption curves shown in these figures, therefore, are not true Fickian type. Furthermore, the initial slopes increase with increasing films thickness. This is called the "thickness anomaly"[10] which is observed in step-change sorption experiments by changing the thickness of the samples.[11] The non-Fickian behavior has been ascribed to slow relaxation motions of polymer chains which occur within a time scale comparable to that of the concurrent diffusion process. Namely, the behavior indicates that the molecular motions of polymer chains in the amorphous regions are restricted. However, absorption curve of sigmoid shape is not seen in Figs. 4 and 5, and all absorption and desorption curves are of the pseudo-Fickian type. This suggests
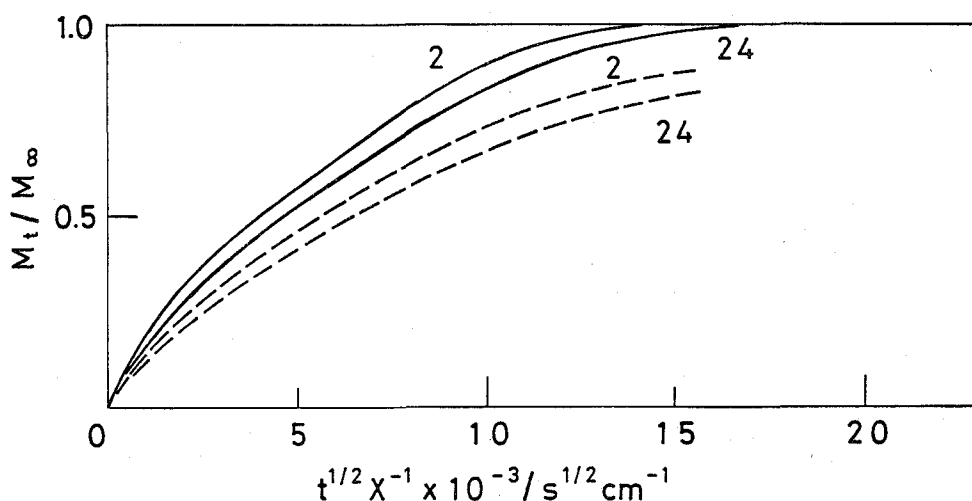

Fig. 4. Fickian plots at concentration of 2.60×10^{-2} g/g for water vapor in nylon 6,6 films at 30°C. ——: absorption, — —: desorption.
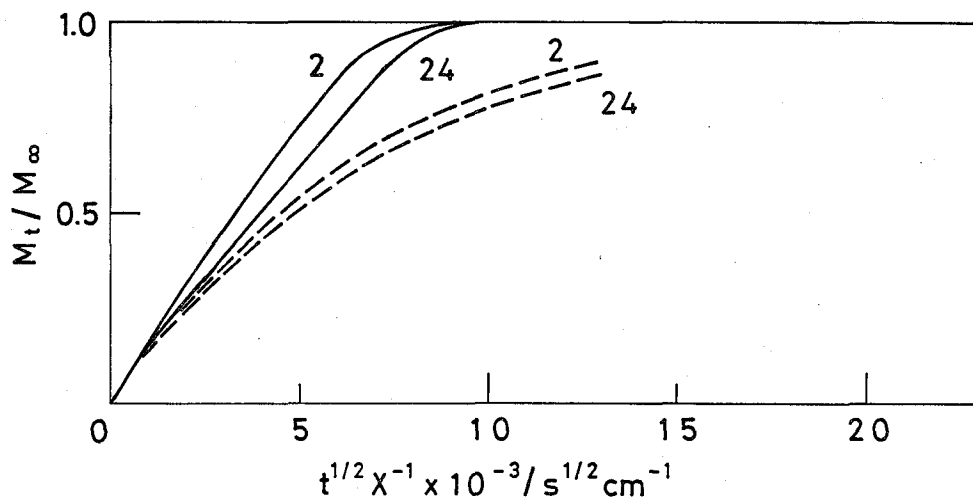
Fig. 5· Fickian plots at concentration of 6.69×10^{-2} g/g for water vapor in nylon 6,6 films at 30°C. ——: absorption, — —: desorption.

in the present system that deviations from the behavior controlled by purely Fickian mechanism are not so pronounced. The result may be ascribed in part to moderate rate of crystallization of the polymer. If the crystallization rate is moderate, restrictions imposed on the molecular motions of polymer chains in the amorphous regions, due to the growth of crystallites, may be considered to be not so strong. Also, it is seen in the figures that the non-Fickian behavior for absorption and desorption curves is suppressed at the higher concentration. This implies that with increasing final uptake of water vapor, the penetrant-polymer system concerned approaches to the glass transition region and that the restrictions imposed on the polymer chains would be weakened rather easily by the penetration of water molecules.

Concentration Dependence of Diffusion Coefficient

As is discussed in the previous section, the absorption and desorption processes of the present system are non-Fickian. Therefore, the true value of the mutual diffusion coefficient of the system can not be determined directly from the observed absorption and desorption curves. However, deviations from the Fickian behavior are not so pronounced that, as far as the nature of the dependence of diffusivity on concentration is concerned, it may be allowed to estimate an apparent diffusion coefficient D_{app} by analyzing the absorption and desorption curves. The value of D_{app} thus estimated is expected to be not far from that of the mutual diffusion coefficient. As is seen in Figs. 4 and 5, features of desorption curves are close to Fickian behavior compared with those of absorption curves. Therefore, we estimated the values of apparent diffusion coefficient by analyzing the results of desorption runs.

Two procedures to determine the initial diffusion coefficient from absorption and desorption curves have been quoted.[12] One calculates from the slope of the initial linear part of the curves, another from the half-time, which is the abscissa

value where $M_t/M_\infty = 0.5$ in the Fickian plot. When the diffusion process is govern-ed only by the Fickian mechanism, both procedures give the same value for the initial diffusion coefficient. In the present study, since the initial liner part of desorption curves was limited to short times, the latter procedure was employed in order to make errors as small as possible.

If we define the half-time $(t/X^2)_{1/2}$ as square of the abscissa value where $M_t/M_\infty = 0.5$ and R_d as reciprocal value of $(t/X^2)_{1/2}$, then the initial diffusion coefficient for desorption D_d is given by

$$D_d = \frac{\pi}{64} R_d \qquad (1) .$$

The relationship between D_d and the mutual diffusion coefficient D was derived by Crank[13] as follows:

$$D_d = \frac{1.85}{C_0^{1.85}} \int_0^{C_0} (C_0 - C)^{0.85} D \ dC \qquad (2)$$

where C_0 is the initial concentration for desorption measurements, that is, in the present experiments concentration of water at absorption equilibrium. It is diffi-cult to solve Eq. (2) analytically and an approximate procedure was proposed by Kishimoto and Enda.[14] It is assumed in this procedure that D may be expressed as a function of concentration by a polynomial,

$$D(C) = D_0 + k_1 C + k_2 C^2 + k_3 C^3 + \cdots \cdots \qquad (3)$$

where D_0 is the value of D at zero concentration and k_1, k_2, k_3, etc. are unknown coefficients. Substituting Eq. (3) in Eq. (2) and integrating yields the same order polynomial for D_d as for D,

$$D_d = D_0 + k_1' C + k_2' C^2 + k_3' C^3 + \cdots \cdots \qquad (4)$$

where

$$k_1 = 2.85 \ k_1', \quad k_2 = \frac{3.85 \times 2.85}{2!} k_2' = 5.486 \ k_2'$$

$$k_3 = \frac{4.85 \times 3.85 \times 2.85}{3!} k_3' = 8.871 \ k_3' \cdots \cdots \qquad (5) .$$

Hence, if we can fit the data of D_d to Eq. (4) successfully, then D is estimated from Eqs. (3) and (5). Kishimoto and Enda suggested that third order equation is sufficient even in the case that D varies over several hundred times with con-centration. We employed the method described above to calculate the apparent diffusion coefficient D_{app} from D_d.

Figure 6 shows concentration dependence of D_d and D_{app}. Unifilled and filled circles represent D_d of the sample films 2 and 24, respectively. Solid lines refer to D_{app} for each sample. Both diffusion coefficients exhibit the concentra-tion dependance, especially in the low concentration region. Furthermore, if a comparison is made at a certain concentration, the values of D_d and D_{app} for the sample film 2, which was sliced off at a depth close to the surface of the sheet, are slightly greater than the respective values for the sample film 24, which was sliced off near the central layer. This result may be attributed to the difference of the degree of crystallinity, that is, as the existence of crystalline regions restricts the molecular motions of polymer chains in the amorphous
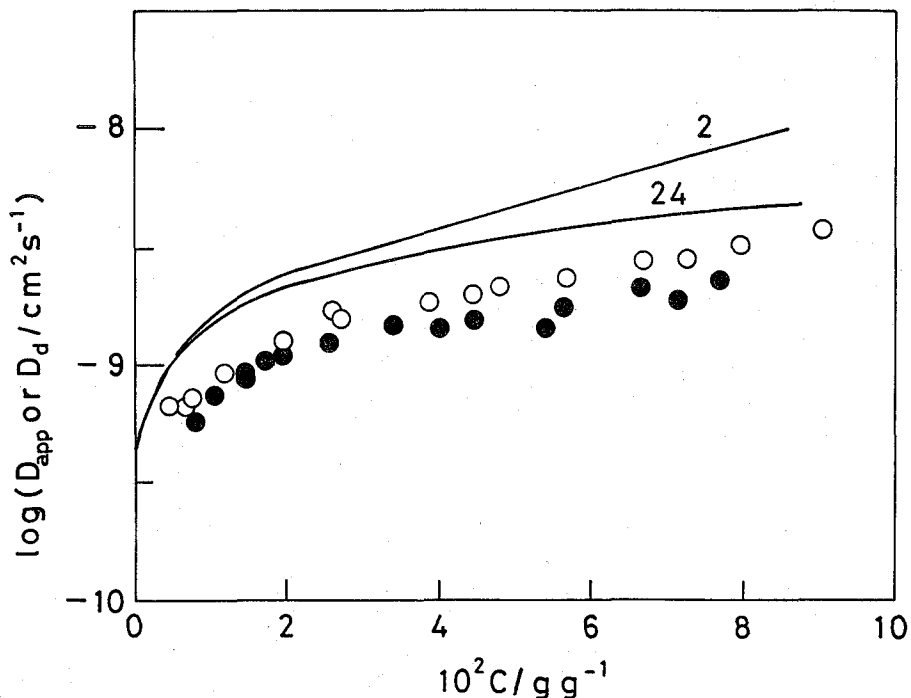
Fig. 6. Concentration dependence of diffusion coefficients. ○: D_d for No. 2,
●: D_d for No. 24, ———: D_{app}.

regions, the imposed restrictions of the sample film 24, whose degree of crystallinity is suggested to be higher as mentioned above, may be slightly stronger than those of the sample film 2.

CONCLUSIONS

Among the sample films which were prepared by slicing off parallel to the surface of an injection-molded nylon 6, 6 sheet, two sample films sliced off respectively at depths near the surface and the central layar of the sheet were mostly used to observe the absorption and desorption behavior of water vapor. Integral absorption from, and desorption to, zero concentration were investigated at 30°C by the weighing method.

The amount of water at absorption equilibrium decreased gradually with increasing the depth from the surface of the sheet and then leveled off. This result was interpreted by assuming that water molecules are absorbed exclusively in the amorphous regions, and a measure of the degree of crystallinity of the sample films was estimated from the equilibrium concentration of sorbed water at given relative humidities. The depth profile of the degree of crystallinity thus estimated agreed well with that determined from density measurements.

The absorption and desorption curves were of the pseudo-Fickian type. The non-Fickian behavior became less apparent with increasing the final concentration

(9)

for absorption. This implies that the restrictions imposed on the molecular motions of polymer chains in the amorphous regions become weaker with increasing water concentration in the film. The apparent diffusion coefficient which was calculated by analyzing desorption curves was greater for the sample film sliced off at a depth close to the surface of the sheet than for the film sliced off near the central layer. The result is ascribed to the fact that molecular motions of polymer chains in the amorphous regions of the latter film, whose degree of crystallinity is higher, are more restricted due to the presence of the crystallites.

ACKNOWLEDGEMENTS

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