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Correlation Study between Oxygen Permeability and Free Volume of Ethylene−Vinyl Alcohol Copolymer through Positronium Lifetime Measurement

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On developing progress of a functional semicrystalline polymer, one of the most practical subjects is to elucidate physical property of the amorphous region. Recent development of the functions such as permeability and ionic conductivity often demands the microscopic understanding especially for the states of the amorphous region. Thus, free volume property of the amorphous phase is believed to be crucial to such functions.

The free volume has been so far discussed through a theoretical treatment evaluated on the basis of relevant parameters such as a glass transition temperature and a thermal expansion coefficient of a specific volume.[1,2] The recent efforts using positronium, Ps, lifetime measurement, however, shed light on an experimental approach to quantifying the free volume.[3−10] This technique enable to estimate the hole size at a nanoscale and its fraction. It has been shown that the estimated hole size and fraction significantly relate to the free volume property of polymer materials.[3−10]

In this work, we report a research for obtaining the relationship between the oxygen permeability and the free volume of ethylene−vinyl alcohol copolymer, EVOH, which is a typical semicrystalline polymer, and also show a substantial evidence that the relationship follows the free volume theory.[11−16]

EVOHs having various ethylene contents, x_e (0, 8, 27, 32, 38, 44, 49, and 74 mol %), were used for the experiment, which are coded as EVOH-X (X denotes the ethylene content). EVOH-0 corresponds to poly(vinyl alcohol) (saponification value = 99 mol %). Low-density polyethylene, LDPE, was employed for the sample for x_e = 100 mol %. EVOH-0, -32, -38, and -44 were commercial products of NIPPON GOHSEI. EVOH-8, -27, and -49 were obtained by saponification of poly(ethylene−vinyl acetate), EVA, having the corresponding ethylene content with sodium hydroxide in methanol. EVOH-74 was prepared by saponification of EVA with 74 mol % ethylene content (Levapren 700-HV, BAYER) in *tert*-butanol/methanol = 6/4. EVOH-27, -32, -38, -44, and -49 were molded by injection, while EVOH-74 was molded by press. EVOH-0 and -8 were prepared by solution cast on a glass plate from the 8 wt % water solution of each polymer. Grass transition temperatures, T_g, for the samples were observed by differential scanning calorimetry, DSC. As a result, T_g monotonically decreased in the range from 70 down to −80 °C with an increase of ethylene content, x_e. T_g for EVOH-74 is around room temperature; therefore, it is concluded that the copolymer which has an ethylene content below ~74 mol % is in a glassy state at room temperature.

It should be pointed out that each series of the samples for the Ps lifetime and oxygen transmission rate, OTR, measurements was prepared via the different process. The difference of the physical property between them was tested in terms of the crystallinity, which was determined by DSC. The difference of the crystallinity was ranging from 0% to 5% being within a range of the error.

The OTR measurement was carried out at 20 °C and 0% RH. The cast films with ~7 μm thickness were used. The dependence of OTR on x_e was shown in Figure 1. OTR varied exponentially and increased remarkably above $x_e \sim 30$ mol %. In addition to this, the obtained value well agrees with previous reported data.[17,18]

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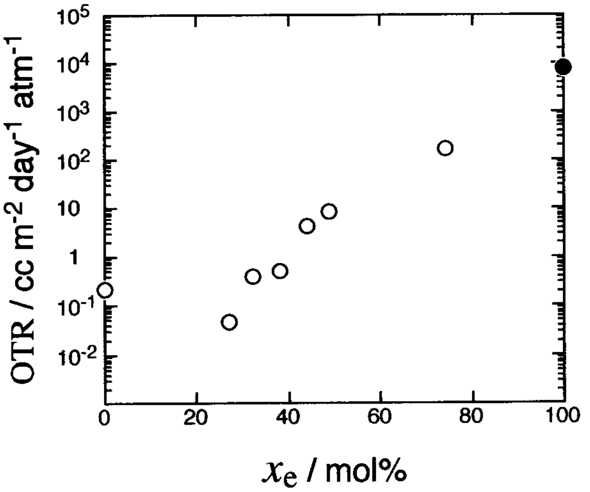

Figure 1. Variation of the oxygen permeability (OTR: oxygen transmission rate) for ethylene–vinyl alcohol copolymer, EVOH, as a function of ethylene unit content, x_e. OTR was determined in the conditions as the following: sample thickness, 7 μm; temperature, 20 °C. The open circle denotes the value measured using the apparatuses (OXTRAN 10/20 or 10/50, MOCON/Modern Control Inc.), while the closed circle represents that quoted from the literature.[21]

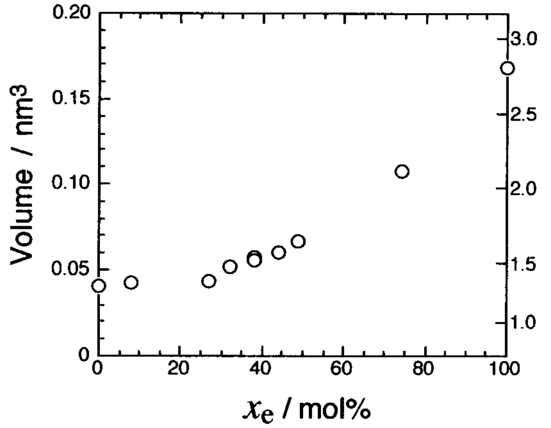

Figure 2. Variation of the free volume size V_f of EVOH as a function of x_e. V_f was estimated by using eq 1 and $V_f = {}^4/_3\pi R^3$. The corresponding o-Ps lifetimes are indicated on the right-hand axis.

The orthopositronium, o-Ps, lifetime was measured using a conventional fast–fast coincident system, which has a time resolution of ~300 ps. The positron source was 7.5×10^5 Bq ^{22}Na sealed up with Kapton foils. The measurements were performed at 20 °C. The obtained decay curves with total counts of ~1 million were fitted by a nonlinear least-squares method and were resolved into three components by using the PATFIT-88 computer program. The Ps cavity radius R [nm] was estimated by using the following equation[19] introduced from the model for a spherical hole:

$$\tau = 0.5\left[1 - \frac{R}{R + 0.166} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + 0.166}\right)\right]^{-1} \tag{1}$$

where τ [ns] represents the annihilation lifetime of o-Ps. The free volume size V_f is estimated with the equation $V_f = {}^4/_3\pi R^3$. The procedure for obtaining the free volume size through the positronium lifetime measurement has been well established.[10]

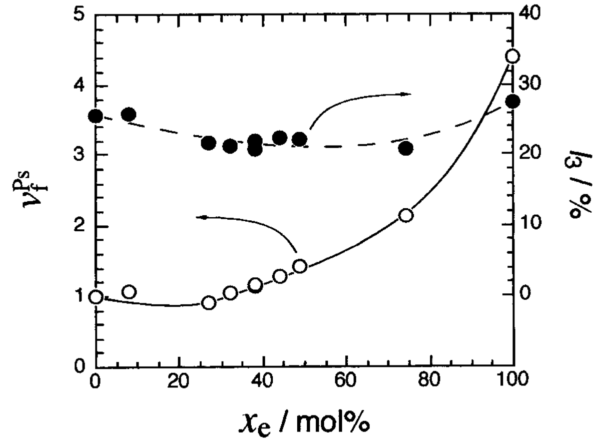

Figure 3. Variation of the relative fractional free volume v_f^{Ps} of EVOH as a function of x_e. v_f is a relative value estimated with eq 2 using the datum of poly(vinyl alcohol) as a criterion. The o-Ps intensity, I_3, was plotted on the right-hand axis, which scarcely influences the variation of v_f^{Ps}. The solid and broken lines are to guide the eye.

The variation of V_f is shown in Figure 2 as a function of x_e. The free volume sizes obtained are comparable with that of oxygen molecule (~0.013 nm^3). V_f increased with the increase of x_e, significantly above 30 mol %. The increase of V_f may be interpreted on the basis of the reduction of the interaction between the hydroxy monomer units due to the hydrogen bonding.

The absolute value of the fractional free volume v_f cannot be obtained from only the positron lifetime measurement. A relative fractional free volume v_f^{Ps} is defined using the following equation:

$$v_f^{Ps} \equiv \frac{I_3(x_e)\ V_f(x_e)}{I_3(0)\ V_f(0)} \tag{2}$$

where I_3 [%] is the intensity of o-Ps. It is understandable from the following points that the absolute value of the fractional free volume is not essential. Although it should be generally considered that the o-Ps yield is controlled not only by the structure but also by the electronegativity of the constituents,[20] the variation of I_3 scarcely contributed to the estimation of v_f^{Ps} in this case. As shown Figure 3, the range of I_3 was 24 ± 3%, whereas the deduced volume size was ranging from 0.04 to 0.18 nm^3, suggesting that the fractional free volume concerns mainly the free volume size.

Using the free volume concept,[11] Doolittle[12] proposed the empirical relationship concerning the dependence of a glass transition on viscosity for hydrocarbons. Subsequently, the theoretical basis for the exponential nature of the relationship was established by Cohen and Turnbull.[13] Diffusivity of a gas molecule was discussed using the Einstein–Stokes relationship (inversely proportional to viscosity). Fujita[14,15] and Vrentas and Duda[16] refined the theory and applied to practical polymer–solvent systems. According to their issues, a relationship between v_f and the diffusion coefficient of the molecules D can be expressed as

$$\ln D = A - \frac{\gamma v_f^*}{v_f} \tag{3}$$

where v_f*, A, and γ represent the critical free volume, a constant, and a numerical factor, respectively. Here, γ lies between 0.5 and 1 based on the definition of Cohen and Turnbull. This equation has been extensively

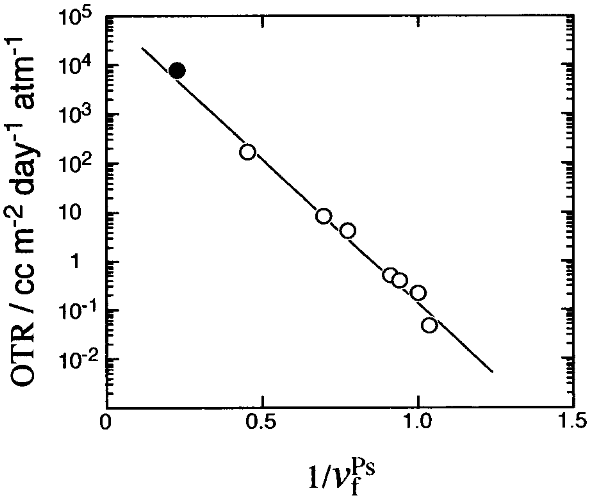

Figure 4. Relationship between OTR and the reciprocal v_f^{Ps} for EVOH. The OTR data of the open circle were obtained with OXTRAN 10/20 or 10/50, while that for LDPE represented by the closed circle was taken from the literature.[21] The semilog plots were well fitted by eq 4 with the correlation coefficient of 0.9999.

adopted to various systems.[1-9] Permeability P is generally expressed as $P \propto \ln D + \ln S$, where S is the affinity between a diffusing molecule and a matrix. The present binary systems give a narrow range of S for oxygen gas so that the variation of S could be negligible. Assuming $\ln S \sim$ constant, we obtain the equation

$$\ln P = B - \frac{\gamma v_f^*}{v_f} \tag{4}$$

with B being a constant for the present system. The relationship between the reciprocal fractional free volume and the oxygen gas permeability is plotted on a semilog scale as shown in Figure 4. The good linearity obtained indicates that the correlation significantly follows the theory. The value of the slope for the fitted line (~14) is somewhat reasonable compared with that suggested by Cohen and Turnbull, which corresponds to the critical free volume, v_f^*, being 10 times larger than v_f.[13]

The amorphous region is in a glassy state below $x_e \sim$ 74 mol % (at room temperature), whereas it is in a rubbery state above that according to the results from DSC as mentioned above. The free volume theory for a diffusion of molecules is based on the assumption that a segmental motion of a polymer chain acts as a thermal jumping unit. Nevertheless, the relationship is well fitted by eq 4 in the entire range of x_e. This suggests that the local motion of the segments, which is relevant to the free volume observed, is enough active to regulate the permeation process even below $x_e \sim$ 74 mol %. It is expected that the ethylene units allow the polymer chains to be flexible, according to the fact that a glass transition of the pure polyethylene occurs at a temperature below −20 °C. Thermal dependence of the free volume parameters is necessary for further detailed discussion.

In conclusion, we examined the relationship between the oxygen permeability and the free volume for the ethylene−vinyl alcohol copolymer as the ethylene content varies, which significantly followed the free volume theory. The evidence suggested that the molecular mechanism of the gas permeation can be considered on the basis of the local motion of the polymer segments and the free volume size. The results may assist further developments for the engineering application of the functional polymers to gas barrier materials. To distinguish between the effects of the crystallinity and the free volume on the permeability more in detail, the systematic investigation by combination of the dynamic mechanical analysis, the small-angle X-ray scattering, and the positronium lifetime measurement is now being prepared and will be presented soon.

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