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Accounting for the degree of swelling in polyimides with a free volume distribution theory

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Abstract

In this paper, an ideal swelling curve is demonstrated based on Kirchheim's free volume distribution theory. When a series of solvents with different molar volumes are used to measure the swelling degrees of a polymer, the ideal swelling curve can give a good explanation for the polymeric swelling if the range of molar volumes is broad enough. The precondition is that the polymeric free volume distribution becomes the deciding factor in swelling. This requires the solvents to have strong affinities for the polymer and for the swelling degrees to be small. The ideal swelling curve has been tested with a series of swelling experiments that involved two polyimides (HQDPA-DMMDA and ODPA-DMMDA) and four polar solvents (water, MeOH, EtOH, and i-PrOH). The ideal curve approach is able to interpret the abnormal phenomenon discovered by Jonquières et al. when they observed the swelling degrees of some cross-linked unsaturated polyesthers in polar alcohols.

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1. Introduction

The permeation coefficient is one of the most important parameters for polymer membrane materials [1]. Permeation is composed of solution and diffusion processes according to the solution-diffusion theory. Generally, the diffusion process is taken as the dominant step for the permeation of gas molecules in polymer membranes. Consequently, the dynamic diameters of gas molecules and free volume parameters of polymer materials have been introduced into the theory to describe the diffusion phenomenon [2]. For the permeation of a liquid solvent in a polymer membrane, the solubility is considered to be dominant. Therefore, thermodynamics parameters are often used to calculate the interaction intensity between solvent molecules and polymer segments. For example, the Flory–Huggins interaction parameter χ [3] and the Hildebrand solubility parameter δ [4] are the well-known single thermodynamics interaction parameters. In recent years, some new polarity parameters have been introduced into the polymer membrane field to explain the polymeric swelling degrees [5–8]. Although multi-parameter methods, such as UNIFAC [9], are precise in calculation of solubilities, some single parameter theories are still widely used. Dimroth and Reichardt's $E_T(30)$, which is measured by solvatochromism [10], is an effective polarity parameter as shown by Jonquières et al. [6–8]. Nakaie and co-workers explained the swelling degrees of peptide resins with a composite polarity parameter (AN + DN). They found that (AN + DN) was more precise than $E_T(30)$ [5]. Although there are other polarity parameters, such as Kamlet–Taft's π^*, α, β, only $E_T(30)$ and (AN + DN) have been frequently used for polymeric swelling degrees until now.

Generally, the interaction parameter χ and solubility parameter δ are used to fit non-polar solvents systems, and $E_T(30)$ is used for polar systems. However, these parame-

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ters have some inadequacies. For example, when Jonquières et al. evaluated the influence of cross-linking degrees of some unsaturated polyesthers on their swelling degrees in polar alcohol solvents, they found an $E_T(30)$ polarity threshold for a highly cross-linked unsaturated polyester [6]. This means that the change of swelling degree is not continuous. When $E_T(30)$ is lower than the threshold value, the swelling degree will remain almost constant, and the swelling degree will show a sharp increase when $E_T(30)$ is higher than the threshold value.

In this paper, the solvent molar volumes and polymeric free volume distribution are used to explain the $E_T(30)$ threshold in the typical swelling degree curve. The curves were tested by swelling experiments that were carried out with two polyimide membrane materials and four polar solvents.

2. Theory

One of the characteristics of polymer materials is the free volume, which is the available space for the permeation of solvent molecules. The fraction of free volume (FFV) is generally used for the characterization of free volume and it can be calculated by Bondi or Paul's method [11]. Helium gas is often taken as a probe to detect the maximum FFV. Free volume is composed of many microcavities with different sizes. According to Kirchheim's theory, the distribution function of free volume is a Gaussian function as follows [12]:

$$f(V_\mathrm{h}) = \frac{1}{\sigma_\mathrm{v}\sqrt{\pi}} \exp\left[-\frac{(V_\mathrm{h} - V_\mathrm{h}^0)^2}{\sigma_\mathrm{v}^2}\right] \tag{1}$$

where V_h^0 is the average cavity volume, V_h is the cavity volume, and σ_v is the width of distribution. Fig. 1 is a typical curve of the distribution function in Eq. (1). Recently a new technique named PALS (positron annihilation lifetime spectroscopy) has been widely used to detect the free volume of polymer materials [13–15]. The distribution graphs measured with PALS are similar to the curve in Fig. 1.

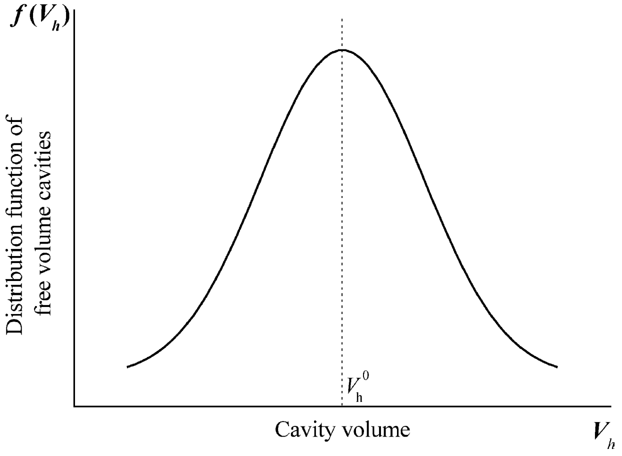

Fig. 1. Distribution function of free volume cavities.

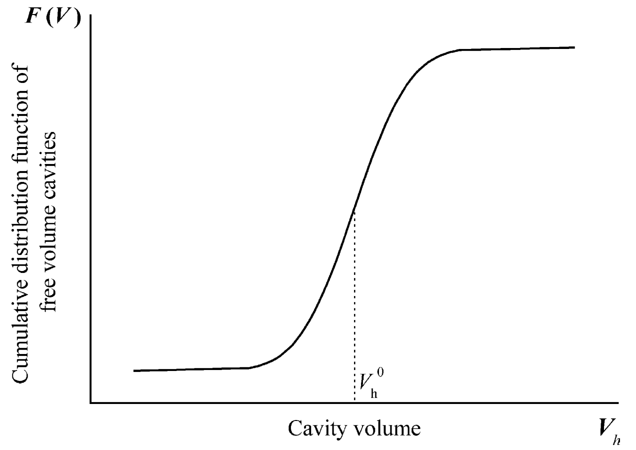

Fig. 2. The cumulative distribution function of unoccupied free volume cavities.

In an equilibrium swelling experiment, the solvent molecules will occupy the maximum number of free volume cavities at an equilibrium swelling state. When the swelling degree is small, the absorbed solvent molecules only occupy the cavities with larger volume than the solvent molecular and the cavities with slightly smaller volume than the solvent molecular. When a function $F(V)$ is introduced to describe the fraction of unoccupied cavities, the remaining fraction $1 - F(V)$ means the fraction of cavities occupied by the solvent molecules. The function $F(V)$ is the cumulative distribution of unoccupied free volume cavities. It is defined by the following equation:

$$F(V) = \frac{\int_0^\mathrm{V} f(V_\mathrm{h})\,\mathrm{d}V_\mathrm{h}}{\int_0^\infty f(V_\mathrm{h})\,\mathrm{d}V_\mathrm{h}} \tag{2}$$

where V is the solvent molecular volume. The curve of the cumulative distribution function $F(V)$ is shown in Fig. 2.

When a series of solvents with different molecular volumes are used to measure the swelling degree of a polymer, the cavity numbers of free volume will become the determinant factor in the swelling degree if the affinity between each solvent and the polymer is strong and the swelling degree is small. In other words, the number of cavities occupied by each solvent depends on the molecular volume of each solvent and the free volume distribution of the polymer. Assuming the number of occupied cavities is in proportion to the swelling degree ($\mathrm{mol_{solvent}}/g_\mathrm{polymer}$), a new swelling curve (Fig. 3) can be obtained from Fig. 2. The abscissa of Fig. 3 is the solvent molar volume instead of the cavity volume. If the polymer-solvent system is suitable, the experimental swelling curve will be similar to the typical curve shown in Fig. 3.

There are three linear regions in the ideal curve as shown in Fig. 3. If the solvents molar volumes distribute in one region, such as Region II, a linear relationship between swelling degrees and solvent molar volumes will be obtained. If the molar volumes cover two regions, such as Regions II and III, a threshold of swelling degree on molar volumes must exist.

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