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Physical aging of glassy perfluoropolymers in thin film composite membranes. Part II. Glass transition temperature and the free volume model

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ABSTRACT

Thin film composite (TFC) membranes for gas separation often comprise a thin selective layer of a glassy polymer, which, however, suffers from physical aging, i.e., gas permeance decreases with time. This study aims to provide a mechanistic understanding of the effect of physical aging on permeance reduction in TFC membranes. The Part I study reports gas permeances in two-layer TFC membranes comprising perfluoropolymers of Teflon® AF or Hyflon® AD with thicknesses of 50–400 nm. In this Part II study, apparent glass transition temperature (T_g) of thin selective layers was determined in situ over time using a nano-thermal analysis (nano-TA). Physical aging decreases gas permeances and increases apparent T_g, and the rate of changes is more significant for thinner selective layers. For example, N_2 permeance decreases from 1000 gpu to 550 gpu while apparent T_g increases from 160 °C to 172 °C after aging for 2000 h in a membrane with 100-nm-thick Teflon AF1600. The measured T_g values are used to derive polymer fractional free volume and physical aging rate. A simplified free volume model is used to successfully correlate the gas permeance reduction with T_g increase during physical aging. Polymers with good stability of permeability should have low physical aging rate and high fractional free volume.

1. Introduction and Background

Glassy polymers have been widely explored for membrane gas separation, due to their rigid structure and strong size sieving ability [1,2]. However, when these polymers are made into thin film composite (TFC) membranes, their gas permeability often decreases with time due to physical aging, which limits their potential for industrial applications [3–6]. For example, Part I of this study investigates TFC membranes with selective layers of glassy perfluoropolymers such as Teflon® AF1600 and Hyflon® AD and demonstrates that gas permeance decreases with time, and the decrease is more significant for membranes with thinner selective layers [7,8]. The reduction rate of gas permeability in polymers may be decreased by blending with nanoparticles [9–11]. However, there lacks a understanding of the relationship between polymer structure and gas permeability reduction, especially for thin films in TFC membranes.

Glassy polymers are at non-equilibrium state, and polymer chains relax toward lower energy states over time (i.e., aging), decreasing polymer specific volume (V) [12–14]. As shown in Fig. 1, the decrease in V decreases polymer fractional free volume (f), a key parameter determining gas diffusivity and thus permeability in polymers [4,15]. The f value is usually estimated as follows:

$$f = \frac{V - V_o}{V} \tag{1}$$

where V_o is the specific occupied volume at 0 K and it is estimated as 1.3 times the van der Waals volume [16]. The van der Waals volume is usually estimated using Bondi's group contribution method [16].

The permeability of gas component A (P_A in Barrer) in non-porous polymers can be related to the f by [17–20]:

$$P_A = A_A \exp\left(-\frac{B_A}{f}\right) \tag{2}$$

where A_A is a pre-exponential factor (Barrer) and B_A is a constant increasing with increasing penetrant molecule size.

The aged polymer has lower free volume or more compact structure than the unaged one. To reflect the difference, a concept of equivalent glass transition temperature (T_g^E) is defined in Fig. 1. A hypothetical polymer with a glass transition temperature of T_g^E is

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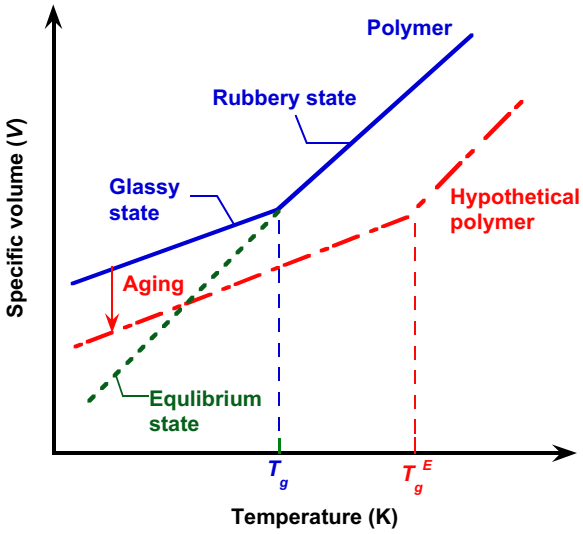

Fig. 1. Schematic of polymer specific volume (V) as a function of temperature. The polymer has a glass transition temperature of T_g. Physical aging decreases V, and the aged polymer has an equivalent glass transition temperature of T_g^E (or apparent T_g).

assumed to have the same thermal expansion coefficients as the unaged polymer, and the same specific volume as the aged polymer at the temperature of interest. Therefore, the aged polymer is considered to have a glass transition temperature of T_g^E (or apparent T_g), which is higher than the original T_g to differentiate the aged polymer from the unaged one. Consequently, the f value for the aged glassy polymer can be related with the apparent T_g using the following equation [19–22]:

$$f = f_0 + \alpha_g(T - T_g) \tag{3}$$

where f_0 is a constant indicating the free volume at T_g, and α_g is thermal expansion coefficient of the polymer at glassy state. The values of f_0 and α_g are regarded as constants during the aging process [23]. Eq. (3) can be used to estimate the f values for polymer thin films at various thicknesses and aging times, since both film thickness and aging time influence the T_g values.

Combining Eqs. (2) and (3) gives the following expression:

$$P_A = A_A \exp\left[-\frac{B_A}{f_0 + \alpha_g(T - T_g)}\right] \tag{4}$$

Eq. (4) gives a correlation between gas permeability at a given T and apparent T_g. As shown in Fig. 1, physical aging increases the apparent T_g, and thus decreases f and gas permeability.

To examine the relationship between f and gas permeability for TFC membranes during physical aging, reliable measurements of the T_g of the selective layer in situ are required. Though several techniques are available to measure T_g of thin polymer films, such as differential scanning nano-calorimetry [24] and ellipsometry [25,26], they cannot be used to monitor the T_g of the selective layer in the TFC membranes in situ due to the interference of the microporous support beneath the selective layer. Moreover, both experimental and simulation work have shown that the T_g of thin film glassy polymers depends on the processing history and substrates. For example, T_g of the thin films could be higher or lower than that of bulk polymers, depending on the interactions between the polymer and substrate [26–30], which again calls for techniques that can probe the T_g of the membrane selective layer in situ.

Recently, a new AFM-based technique, nano-thermal analysis (nano-TA), has been used to measure the softening temperature of thin films in situ [31,32]. Briefly, a resistive heater embedded in the cantilever controllably heats the AFM probe with a tip radius less than 30 nm. When the film surface in contact with the tip is heated, the local thermal expansion of the polymer will induce the upward deflections of the cantilever. Once the temperature rises above the "softening temperature" of the polymer surface, the tip would sink into the film, causing downward deflection. This onset of change in tip deflection direction provides a good estimate of the "softening temperature" (or apparent T_g or T_g^E) for the thin film at the nanoscale. This non-intrusive technique is ideal to monitor thin film properties in composite structures in situ as a function of aging time.

In this Part II of the study, the apparent T_g of the thin selective layers with various thicknesses and aging time in the TFC membranes was determined, and the results are correlated with the polymer f and thus gas permeance using a simplified free volume model. This work, for the first time, directly determined the T_g of the selective layer in TFC membranes during physical aging, and provides a quantitative interpretation of the relationship between physical aging and gas permeability reduction.

2. Experimental

2.1. Materials and preparation of TFC membranes

The materials and the preparation of TFC membranes were described in detail in the Part I of this study [7]. Briefly, TFC membranes were prepared by coating of perfluoropolymer solutions on top of polyethersulfone (PES) porous supports (PES-2 from Ultura™ High Recovery Membrane Technology, Long Beach, CA) using an automatic draw machine (DP-8301, The Paul N. Gardner Company, Pompano Beach, FL). Pure-gas permeance in the TFC membranes was determined using a constant pressure/variable volume apparatus at 35 °C [33].

2.2. Preparation of freestanding perfluoropolymer films

To prepare freestanding films, homogeneous solutions containing 15 wt% perfluoropolymers in Novec 7200 were first casted on a glass plate using a casting knife (The Paul N. Gardner Co., Pompano Beach, FL). Subsequently, the films were dried in the air for 18 h and then immersed in distilled water to detach from the glass plate. Finally, the films were dried in a vacuum oven at 80 °C for 24 h to remove the water and residual solvent. The films typically have a thickness of 10–20 μm. Pure-gas permeability of the obtained films was determined using a constant volume/variable pressure apparatus at 35 °C [33].

2.3. Determination of T_g in bulk polymers using differential scanning calorimetry (DSC)

The T_g of bulk perfluoropolymers was determined using differential scanning calorimetry (DSC) (DSC 204 F1, Netzsch-Geratebau GmbH, Selb, Germany). The samples were heated from 25 °C to 200 °C at a ramping rate of 10 °C/min under nitrogen purge. The T_g value is defined as the midpoint of the glass transition region during the first heating cycle.

2.4. Determination of apparent T_g of the selective layer in TFC membranes using nano-TA

Nano-TA (Anasys Instrument Inc., Santa Barbara, CA) measurements were performed using a custom-made thermal lever probe (AN2–300) with a heating rate of 2 °C/s and temperature