Structure dependence of water vapor permeation in polymer nanocomposite membranes investigated by positron annihilation lifetime spectroscopy

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ABSTRACT

Incorporation of nanoplatelets is known to be effectively in the reduction of gas permeation of polymer membranes, which has been typically attributed to the torturous path effect. However, the measured water vapor transmission rates (WVTR) from the poly(vinyl alcohol) (PVA)/graphene oxide (GO) nanocomposite membranes are found to be smaller than the theoretical values calculated by the Bharadwaj model based on the torturous path effect. This discrepancy is indicative of the existence of other structural factors responsible for the WVTR that are rarely discussed in literature. In this work, the positron annihilation lifetime spectroscopy (PALS), a widely recognized method for characterization of the atomic-scale microstructure of polymers, is employed herein to study the free volume of the PVA/GO composite membranes. The free volume size of the composite membrane decreases with increasing GO contents, and the fractional free volume (FFV) decreases with the increase of annealing temperature. Strong dependence of the WVTR of PVA/GO on the FFV and crystallinity has been revealed, indicating that, along with the nanoplatelets-induced torturous path effect, they are important factors affecting the water vapor permeation of polymer nanocomposite membranes.

1. Introduction

The free volume theory of polymers developed by Fox and Flory et. al. [1–4] is based on the idea that molecular chain motion in the bulk state depends on the existence of holes. The holes arising from the irregular packing of chains in amorphous regions is defined as free volume holes. A variety of physical properties of polymers are closely related to the free volume holes [5–9], e.g. the diffusion coefficient (D_c) [10–13]. The relations between free volume and D_c were developed by Cohen and Turnbull [14], as shown in Eq. (1):

$$D_c = A \exp(-B/f) \tag{1}$$

where f is the fractional free volume (FFV), and A, B are the constants. It is well known that the permeability coefficient (P) is the product of the solubility coefficient (S_c) and D_c, but the relations between FFV and S_c are not always obvious, resulting in complicated relationship between FFV and P in polymers. In polymer nanocomposites, P is affected by many factors, and the correlations between P and FFV becomes even more unclear. Moreover, the characterization of nanoscaled free volume holes using traditional experimental techniques is extremely

difficult. Therefore, most of the works on the permeability of polymer nanoplatelet composites [15–18] (PNCs) focus on the filler-induced torturous path effect [19], and unfortunately, exclude the free volume effect. Several empirical models [19] have been developed to describe the permeation in PNCs, e.g. the Nielsen model, [20] the Cussler model [21] and the Bharadwaj model [22]. While they have been successfully validated by many experimental results [23–28], all the models are based on the assumption that the incorporated nanoplatelets do not affect the physical characteristic of the polymer matrix. Obviously, this is not always the case. For instance, since the water permeability data [29] were found to be lower than the values predicted from the models, theoretical calculations [30] suggest that the effect of nanofiller on the chain mobility of polymer matrix shall be taken into consideration. The variation of D_c in PNCs has been found to depend on the FFV in addition to the tortuosity factor [31].

In this work, poly(vinyl alcohol) (PVA)/graphene oxide (GO) composites were prepared and characterzied to reveal the roles of the FFV and other structure factors on water vapor permeability of the composites. PVA has been widely used as packaging materials [32] for food, medicine and electronic devices due to its low cost, non-toxicity,

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excellent transparency, biodegradability and outstanding gas barrier properties [17,18,33–35]. Nevertheless, under high relative humidity conditions, PVA absorbs a large amount of water and is readily plasticized by water molecules, leading to dramatically reduced barrier properties [17,35,36]. GO, a two-dimensional nanosheet with lamellar structure, possesses a large amount of functional groups on the surface, which enables the formation of interfacial bonding between GO and polar PVA matrix. Although the introduction of GO nanosheets into PVA is known to yield the nanocomposites with much improved gas barrier properties [17], the underlying mechanism still remains elusive.

2. Experimental

2.1. Membrane preparation

The PVA/GO composite membranes were prepared by tape casting method from aqueous solution of PVA and GO. Commercial PVA powder was purchased from Aladdin Industrial Incorporation (Shanghai, China), with the degree of polymerization of 1700 and the saponification degree no less than 99%. The solid GO films were purchased from Nanjing XFNANO Materials Tech Co., Ltd (Nanjing, China), in order to obtain the few-layer GO nanosheets, the GO films were stripped and dispersed in distilled water by an ultrasonic cell crusher (VCX750, Sonics & Materials, Inc., USA). The PVA powder was then mixed with the GO solution to yield the aqueous casting solution under magnetic stirring and ultrasonic dispersion. The hybrid solution was cast on a fused silica plate and dried in a natural convection oven at 45 °C. The PVA/GO composite membranes were peeled off from the fused silica plate for the subsequent tests.

Two groups of the PVA/GO nanocomposites were prepared. The first group is the PVA/GO membranes containing different GO volume contents, which is used to investigate the effect of tortuosity on the water vapor transmission rate (WVTR). The second group is the PVA/GO membranes with a fixed GO content, but annealed at different temperatures for 2 h. It is thought that tortuosity induced by GO remains constant in the second group of the samples, while the variation of annealing temperature changes the structure (e.g. FFV and crystallinity) of the composites. The labels and details of the two sample groups are listed in Table 1. The optical image of the PVA/GO membranes is shown in Fig. 1. Apparently, with the increase of the GO contents, the composites become darker in color and show reduced transparency. The morphology of them characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM) are shown in Fig. S1, Supporting information.

2.2. Positron Annihilation Lifetime Spectroscopy (PALS)

The PALS, a unique method for the free volume measurement, is employed herein to determine the FFV of the PVA/GO composites. Positron, the first discovered anti-particle, can pick up an electron to

Table 1
Details of PVA/GO composite membranes.

Sample label	Weight ratio of GO and PVA	GO volume content in PVA/GO membrane [vol%]	Annealing temperature [°C]
PVA/02GO	0.02: 10	0.15	Null
PVA/04GO	0.04: 10	0.29	Null
PVA/06GO	0.06: 10	0.43	Null
PVA/08GO	0.08: 10	0.57	Null
PVA/10GO	0.10: 10	0.72	Null
PVA/04GO100	0.04: 10	0.29	100
PVA/04GO120	0.04: 10	0.29	120
PVA/04GO140	0.04: 10	0.29	140
PVA/04GO160	0.04: 10	0.29	160
PVA/04GO180	0.04: 10	0.29	180
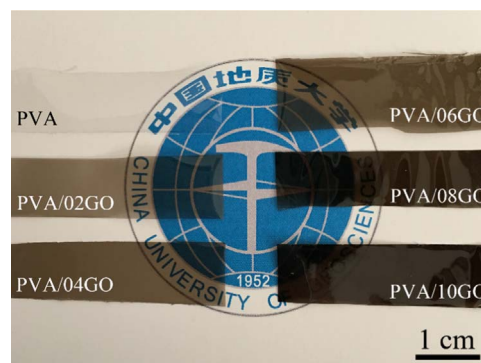
Fig. 1. Photo of PVA and PVA/GO composite membranes in natural light. The thickness of samples are around 50 μm.

form a neutral atom called Positronium (Ps). There are two states of Ps: the para-Ps (p-Ps) and the ortho-Ps (o-Ps). During the collisions with the walls of free volume holes, the positron of an o-Ps atom picks up an electron to annihilate into two photon, which is called o-Ps pick off annihilation. In polymers, the lifetime of o-Ps pick off annihilation is usually in the range from 1 to 10 ns, which is determined by the size of the free volume holes, and its intensity is proportional to the fraction of the free volume holes.

Positron lifetime measurements were performed using a conventional fast-fast coincidence lifetime spectrometer with a time resolution of 250 ps in full width at half maximum (FWHM). A 10 μCi ^{22}Na source is sandwiched between two pieces of identical samples. For each sample, two lifetime spectra are collected with a total count of 10^6 for each spectrum. To satisfy the sample requirements of PALS, the multilayer membranes were stacked together to ensure that the total thickness of them are more than 1 mm on each side of the positron source. The testing temperature and relative humidity (RH) were at 23 °C and 55 RH%, respectively. Analysis of positron lifetime spectra is performed using the finite-term lifetime analysis PATFIT [37] program. All the measured spectra are resolved into three components (τ_1, τ_2 and τ_3) using PATFIT for discrete analysis. The long-lived component τ_3 is attributed to the o-Ps pick-off annihilation in free volume holes in amorphous regions. The radius (R) and average size (V) of free volume holes are evaluated from τ_3 from Eqs. (2) and (3), respectively [38]:

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \tag{2}$$

$$V = \frac{4}{3}\pi R^3 \tag{3}$$

where R is the radius of free volume hole and $\Delta R = 0.1656$ nm [39,40] is derived from fitting the observed o-Ps lifetimes in molecular solids with known hole sizes. The formation probability of o-Ps, I_3, is correlated with the intensity of the free volume. The FFV is evaluated using Eq. (4), where A can be approximatively regarded as a constant, with the value of 0.0018 Å^{-3} [41–44].

$$f = AVI_3 \tag{4}$$

2.3. X-ray diffraction (XRD)

XRD analysis was carried out on Bruke D8-Focus, Germany with Cu Kα radiation (λ = 1.54 Å), the voltage of 40 kV and the current of 40 mA. The data was recorded over the range of 5° to 45°, with the scanning rate of 0.05 s/step and the step of 0.01°. The crystallinity (X_c) of PVA obtained from XRD is calculated according to Eq. (5), where A_t is the area of total XRD pattern, and A_a is the area of amorphous region.

$$X_c = \frac{A_t - A_a}{A_t} \tag{5}$$