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Hybrid nanocomposite film with enhanced moisture barrier properties

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ABSTRACT

In this study, hybrid nanocomposite films were prepared by a sol-gel method. Al_2O_3 particles of 100 nm diameter were mixed with small SiO_2 nanoparticles of 10 nm in a coating solution. After coating onto a plastic sheet, the water vapor transmittance rate (WVTR) was reduced from 12.2 to 0.15 g m^{-2} day^{-1}. However, due to the particle aggregation in the Al_2O_3/SiO_2 system, pore size of the barrier coating remained constant despite the Al_2O_3/SiO_2 ratio. To avoid particle aggregation and to reduce the WVTR, vanadium oxide was added in the coating solution to suppress the aggregation of nanofillers via dehydroxylation. From BET analysis, the addition of vanadium oxide resulted in a smaller pore size to further inhibit water vapor penetration. The WVTR was lowered to 0.095 g m^{-2} day^{-1} at a relative humidity of 100%, corresponding to an improvement of 99.2% compared to that of the pristine PET.

1. Introduction

In the past decades, the use of polymer films for food packaging, medicines, and electronics has considerably increased due to their low cost, low density and outstanding mechanical properties (strength, stiffness, and toughness). However, due to the low crystallinity and free volume [1,2], water vapor can easily penetrate through polymer films, and thus restricts the reliability of utilizing polymers on packaging applications. In order to overcome these issues, various approaches have been used to reduce water vapor penetration through polymeric films [3–12]. Among these methods, formation of organic-inorganic hybrid nanocomposite at a molecular level is a convenient and effective sol-gel approach [4,7,8]. In this method, inorganic oxide nanoparticles with polymeric binders are coated over polymeric substrates to create a barrier thin film with small pore volume and pore size [13] to reduce the overall water penetration rate through the coated films. The presence of nanoparticles results in tortuous paths for water molecules diffusion, and reduces water vapor penetration. Inorganic particulate nanomaterials, such as aluminum oxide (Al_2O_3), silicon oxide (SiO_2), and titanium dioxide (TiO_2), have been widely applied in these barrier coatings because of their excellent barrier properties [14–16]. However, in the coating or drying stages, the aggregation of oxide nanoparticles regularly occurs due to their surface hydroxyl groups and results in non-uniform thin films with large pores [17]. Besides enlarged pore sizes, particle agglomeration can further generate voids or defects within polymer binder matrix which results in a high water vapor permeability [18]. To avoid particle aggregation in the coating fluids, the nanoparticle surfaces can be capped by compatible polymeric binders to segregate particles for better suspension stability. For example, nanoparticles with epoxy oligosiloxane resin have been shown to effectively create uniform transparent thin films for moisture barrier [7]. However, the pore size is still too large so that the well-dispersed nanocomposite still exhibit low moisture barrier characteristics.

To further reduce the water vapor transmission rate (WVTR) using sol-gel coatings, further reduction in pore size is necessary. Theoretically, when mixing spherical particles with different sizes together, [19] one can obtain much smaller pore sizes than the smallest particle diameter. As the pore size reduces to be around 1 nm, a low WVTR in the range of 10^{-2} to 10^{-3} g m^{-2} day^{-1} [20] can be achieved. To prove this concept, in this study, large Al_2O_3 particles of 100 nm diameter are mixed with small SiO_2 nanoparticles of ~10 nm in the sol-gel coatings. To avoid particle aggregation, vanadium oxide is also added in the coating solution to suppress the aggregation of nanofillers via dehydroxylation. The coating solutions are then coated on plastic PET sheet, and the WVTR of the resulted hybrid nanocomposites are measured to find the optimum SiO_2 /Al_2O_3 volume ratio. The microstructure of the hybrid nanocomposite coatings, such as coating morphology, surface area, and pore sizes, are also characterized to elucidate the permeability reduction mechanisms.

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2. Experimental and methods

2.1. Materials

Sodium silicate (~ 30% silica, and specific weight 9.5–10.5) was supplied by RongXiang Industry Co., Ltd., Taiwan. Vanadium (V) oxytriethoxide (≥ 95%, $VO(OC_2H_5)_3$), Acetic acid (≥ 99%, CH_3COOH), Isopropyl alcohol (≥ 99%, C_3H_8O), Polyethylene glycol (M_w~380–420, $H(OCH_2CH_2)_nOH$), and sulfuric acid (95–98%, H_2SO_4) were purchased from Sigma-Aldrich. Nanoparticles α-alumina oxide, with an average particle size of 100 nm (~ 99.999%, α-Al_2O_3) was obtained from Advanced Ceramics Nanotech Co., Ltd., Taiwan. Sodium hydroxide (≥ 97%, NaOH) and isoamyl acetate (≥ 95%, IAA) were used for pH adjustment and as a dispersant, respectively. The PET sheets (100 µm in thickness, Universal film, Japan) were used as the substrate.

2.2. Preparation of Al_2O_3 nanocomposite suspension

The hybrid nanocomposite suspension was synthesized via the sol-gel method. The weight ratio of α-Al_2O_3/sodium silicate mixture was fixed at 23:77 and then the mixed solution was adjusted at pH 9 using NaOH solution. 95% IAA was introduced to the above mixture and continually stirred to form a well-dispersed solution at room temperature.

2.3. Formulation of hybrid nanocomposite film

The hybrid nanocomposite films were produced by mixing. The preparation of silica nanoparticles and vanadium solution were presented in previous works [21,22]. The nanofiller of Al_2O_3 nanoparticles, silica nanoparticles and vanadium solution with different volume ratios were prepared correspondingly into 2-mL hybrid nanocomposite suspension. All the nanoparticle mixtures were sonicated for 5 min in a sonication bath. The solution was coated on a PET sheet for three cycles. Each cycle consists of two steps: the first step was coating a thin film layer using Meyer rod (#5, Taiwan Honor Precision Corp.), which is 6.35 mm in diameter and 400 mm in length, and the second step was drying the coated film at room temperature. Finally, the hybrid nanocomposite films were dried at room temperature for a day.

2.4. Characterization and measurement

The crystal patterns of hybrid nanocomposite films were recorded on X-ray diffractometer (XRD) (Ultima IV, Rigaku) with Cu Kα radiation, operating at 40 kV and 40 mA. The data were collected in range of 10°–60° at a scanning rate of 1.0° min^{-1}. The surface morphology and cross-section of the hybrid nanocomposite films were observed using field-emission scanning electron microscope (FE-SEM) (Nova Nano SEM230, FEI). The thickness of films was recorded using built-in scale with vertical mount holder. The chemical bonds of hybrid nanocomposite were analyzed by Fourier transform Infrared spectroscopy (FTIR) (spectrum GX, PerkinElmer). To measure the specific surface area, hybrid nanocomposite powder was scraped off from the dried film on the substrate. Then, the specific surface area of the collected powder was determined by nitrogen adsorption/desorption using the Brunauer–Emmett–Teller (BET) method (ASAP 2020, Micromeritics). The barrier properties of the hybrid nanocomposite were evaluated by MOCON instrument (Aquatran model 2, MOCON) to obtain WVTR. All samples were masked with aluminum foil using a 5 cm^2 water vapor exposure area at temperatures 23 °C and 100% relative humidity (RH).

Table 1
The composition of SiO_2/Al_2O_3 films and permeability.

Sample	Compositions of volume ratio		WVTR (g m^{-2} day^{-1})
	Al_2O_3	SiO_2	
PET	–	–	12.188
Al_2O_3	1	–	4.313
SiO_2:Al_2O_3 = 5:1	1	5	0.151
SiO_2:Al_2O_3 = 10:1	1	10	0.134
SiO_2:Al_2O_3 = 15:1	1	15	0.121

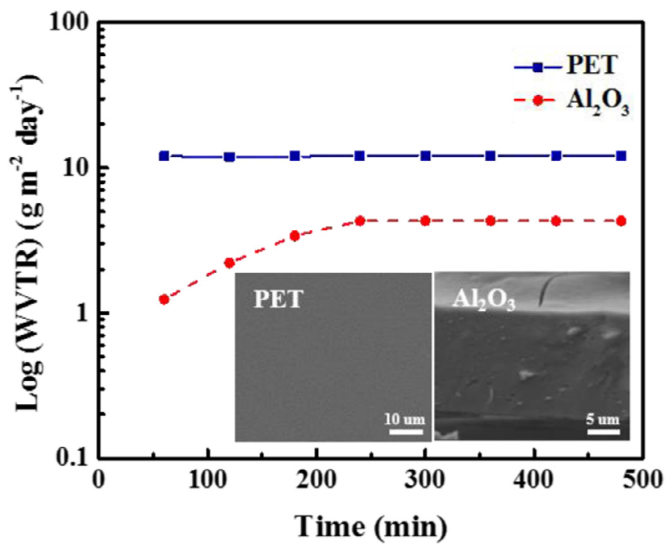

Fig. 1. WVTR values with and without Al_2O_3 coated film on PET.

Table 2
Structural characteristics for barrier films.

Sample	Surface area (m^2/g)	Pore size (nm)
Al_2O_3	86	19.5
SiO_2:Al_2O_3 = 10:1	124	15.5
VO_2:SiO_2:Al_2O_3 = 5:10:1	133	12.8
VO_2:SiO_2:Al_2O_3 = 10:10:1	156	12.2
VO_2:SiO_2:Al_2O_3 = 15:10:1	205	7.4

3. Results and discussions

3.1. Water barrier characteristics of SiO_2/Al_2O_3 films

The nanocomposite sol-gel coatings with two different particle sizes can effectively inhibit water penetration (Table 1). Fig. 1 shows the WVTR measurements of PETs with and without barrier coatings. The WVTR of the pristine PET films is approximately 12.2 g m^{-2} day^{-1}. After coated with an Al_2O_3 thin film, which has a thickness of ~ 12 µm, the WVTR reduces to 4.3 g m^{-2} day^{-1}, but still in the same order as the pristine PET, indicating the pores are still too large to reduce water vapor penetration, even with 100 nm Al_2O_3 nanoparticle coatings. To further the pore size of the coatings, 10 nm SiO_2 nanoparticles are added to fill the space between the 100 nm Al_2O_3 particles. The addition of SiO_2 nanoparticles leads to narrower pore sizes (Table 2). Thus, as indicated in Fig. 2, WVTR reduces drastically to ~ 0.15 g m^{-2} day^{-1} after coating with the SiO_2/Al_2O_3 films. Initially, the increase of the ratio of SiO_2/Al_2O_3 can help reduce WVTR. As the ratio increases, WVTR reaches a plateau at around SiO_2/Al_2O_3 ≈ 10, possibly due to the aggregation of nanoparticles during the drying stages.