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Preparation of κ-Al_2O_3/resin composite coating on polyethylene terephthalate foil for gas-permeation barrier

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Abstract

Surface of κ-alumina (κ-Al_2O_3) nanoplatelets was grafted by 3-(trimethoxysilyl)propyl methacrylate (MPS) molecules over a broad MPS/κ-Al_2O_3 weight ratio from 0 to 0.9 in water/ethanol mixtures. The organic grafting resulted in a hydrophobic alumina surface with a contact angle greater than 90° from an initially hydrophilic surface with a contact angle of about 25°. The MPS-grafted nanoplatelets were dispersed in organic, ultraviolet (UV) curable resin with solids concentrations ranging from 0.01 to 0.15 weight fraction to form a coating layer of 50 μm on polyethylene terephthalate (PET) foil of 100 μm in thickness initially. The coated foil showed a maximum of 20% reduction on both water-vapor and oxygen-gas permeations when compared to that of the bare PET foil. The coated foil also showed a reduced transmission of visible light at wavelengths < 500 nm. This became particularly pronounced as the κ-Al_2O_3 fraction in resin was increased. A high transmission ($> 80\%$) yet remained for the visible light with wavelengths greater than ~ 550 nm over the κ-Al_2O_3 fraction examined (up to 15 wt%).

Keywords: B. Nanocomposite; κ-Al_2O_3; Coating; UV-curable resin; Gas barrier

1. Introduction

Layered organic/inorganic nanocomposites targeting for gas-barrier applications have received much attention over the last decades owing mainly to their increased resistance to permeation of water vapors and gas molecules [1–5]. The permeation resistance stems primarily from the increased tortuosity for gas molecules to diffuse through the composites due to presence of the aligned or aggregated impermeable fillers such as inorganic nanoplatelets or nanosheets with a high length-to-width (i.e., aspect) ratio dispersed in polymeric matrix by either intercalation or delamination/exfoliation of the fillers phase [5]. Relative permeability has been found to decrease markedly as the aspect ratio and the volume fraction of inorganic layers were increased [3,4]. When properly controlled, an improved mechanical strength together with retention of impact resilience is simultaneously attainable at low filler content without impairing optical transparency and overall weight increase of the composites [5]. On the one hand, many reports have addressed use of natural or synthetic layered crystals as the impermeable filler for the desirable barrier property against water vapors and various gases [1–15]. The layered crystals include graphite, graphite oxide, metal chalcogenides, metal phosphates, clays and layered silicates, layered double hydrides, etc. Among them, clays and layered silicates are widely used mainly because of their abundant availability and the ability to allow organic monomers/polymers to intercalate or exfoliate inside galleries of the layered hosts so that a uniform distribution of the fillers in polymeric matrix results with a desirable architecture. For those layered silicates with the 2:1 phyllosilicate structure, in particular, montmorillonite, hectorite and saponite are commonly used in the layered nanocomposites [4].

On the other hand, crystalline alumina or aluminum oxide (Al_2O_3) of various polymorphs, e.g., α-, γ-, δ-, θ-, η-, χ-, and κ-Al_2O_3, has been used in an astounding array of technological applications due to its good thermal, chemical, dielectric, and wear-resistant properties [16–19]. The orthorhombic structured κ-Al_2O_3 [20] presenting a lamellar morphology, in particular,

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has been reported by Chen et al. [21] who first used the κ-Al_2O_3 nanoplatelets in UV-curable resin to form an anti-wear, protective coating on poly(vinyl chloride) plastics. The composite coating resulted in an increased abrasion resistance as much as 16.6% when compared to that of the pure poly (vinyl chloride) plastics without the coating. Nonetheless, gas-permeation property of the coating consisting of the κ-Al_2O_3 nanoplatelets as the filler phase has yet to be examined to the authors' knowledge. In this study, κ-Al_2O_3 nanoplatelets were first grafted by 3-(trimethoxysilyl)propyl methacrylate (MPS) molecules so that the inorganic platelets can be dispersed in ultraviolet (UV) curable organic resin to form a composite coating on plastic foils by a facile doctor-blade process. Effect of the MPS modification on wettability, dispersion, and gas-permeation property (including water vapor and oxygen gas) of the κ-Al_2O_3 coating was examined.

2. Experimental procedure

The κ-Al_2O_3 particles were kindly provided by Prof. F.-S. Yen at the National Cheng Kung University (Taiwan). The particles have been reported to present a particle size of about 500 nm to 1 μm with a lamellar structure consisting of layered κ-Al_2O_3 nanoplatelets stacking one another with a typical layer thickness of about 20–50 nm separating by 10 nm apart between the layers [21]. As shown in Fig. 1, the as-received κ-Al_2O_3 particles are of irregular shape with a broad particle-size distribution by transmission electron microscopy (TEM, JEM-2100F, JEOL, Tokyo, Japan). The inset shows that the particles indeed consisted of aggregated crystallites assembled densely by one another with a primary size typically in a range of 5 to 20 nm. In Fig. 2, X-ray diffractometry (MAC MXP III, Japan) confirmed the orthorhombic κ-Al_2O_3 structure (JCPDS no. 52-803) of the particles with a calculated crystallite size of 6.8 nm determined from the Scherrer's equation. The calculated size is in good agreement with the TEM observation. In addition, the particles showed a Brunauer–Emmett–Teller (BET) surface area of 30.18 m^2/g determined by nitrogen adsorption–desorption (ASAP 2020, Micromeritics, U.S.A.) at the boiling point of liquid nitrogen (77.4 K).

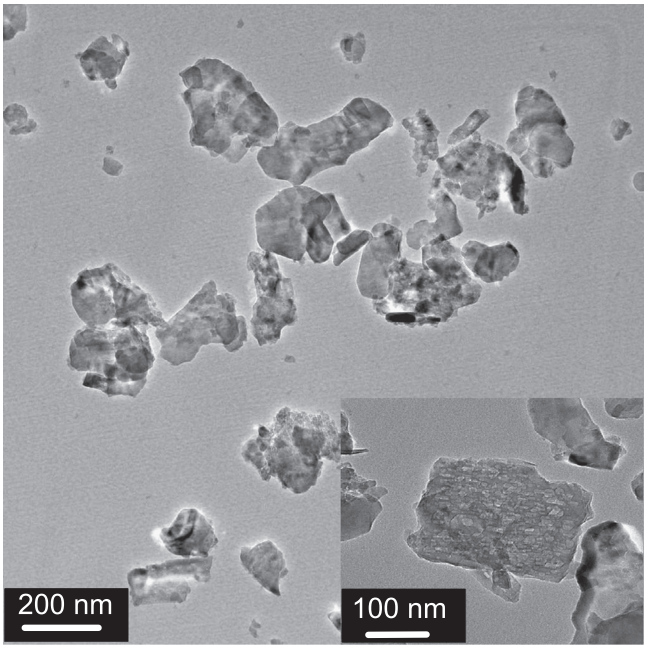

Fig. 1. Microstructure of κ-Al_2O_3 nanoplatelets by transmission electron microscopy. The inset shows stacked texture of crystallite aggregates.

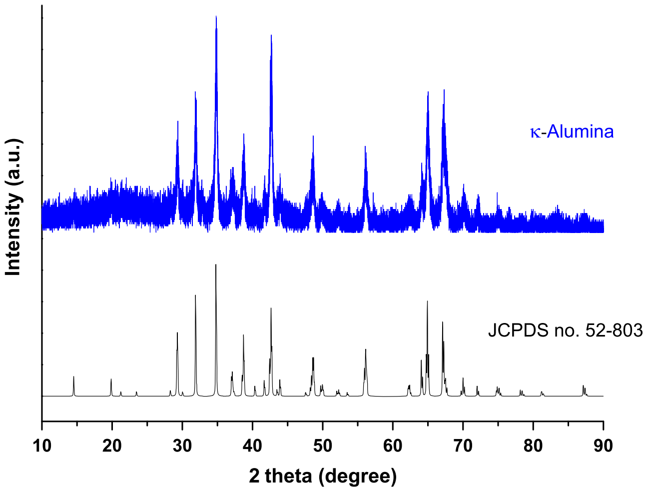

Fig. 2. X-ray diffraction pattern of κ-Al_2O_3 nanoplatelets.

Grafting of reagent-grade 3-(trimethoxysilyl)propyl methacrylate (MPS, 98%, $H_2C{=}C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$, molecular weight 248.35, Aldrich, U.S.A.) onto the as-received κ-Al_2O_3 particles was carried out by following a method reported by Bauer et al. [22]; to which, the particles were added in solvent mixtures consisting of the MPS molecules with a weight ratio of $MPS{:}H_2O{:}ethanol=1{:}1.5{:}3$ at pH of 4 and reaction temperature of 70 °C under reflux. The MPS/κ-alumina weight ratio varied from 0 to 0.9. De-ionized water was from Millipore Super-*Q* Plus system with an electrical resistivity of 18.2 MΩ cm at 25 °C, and the solution pH was adjusted with reagent-grade hydrochloric acid (Sigma-Aldrich, U.S.A.). The suspensions were stirred vigorously, and the polymer-grafted particles were then separated from the solution by centrifugation at 8500 rpm (Mikro 20, Hettich, Germany) and rinse in ethanol-water solvents for three times repeatedly, before being dried in oven at 70 °C for 24 h. Some of the as-received and the MPS-grafted κ-Al_2O_3 particles were mixed uniformly with potassium bromide in a weight ratio of 1:10 and were pressed into pellets for Fourier transform infrared spectroscopy (FTIR, Spectrum RXI, Perkin Elmer, U.S.A.) over wavenumbers from 600 to 4000 cm^{-1}. Elemental distribution of the surface-modified particles was also examined by field-emission X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe, ULVAC-PHI, Japan). In addition, contact angle of the MPS-grafted particles was determined by a sessile drop-shape analyzer (FTA 2000, First Ten Angstroms Inc., U.S.A.); to which, water drops were dispensed from a syringe pointed vertically down onto the surface-smooth powdered pellets prepared by uniaxial compaction. Water profiles on the samples were captured by an optical system at 25 °C [23,24].