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Material properties

Surface modified graphene oxide/poly(vinyl alcohol) composite for enhanced hydrogen gas barrier film

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ABSTRACT

A series of novel polyethyleneimine (PEI) modified graphene oxide (PEI-mGO) filled poly(vinyl alcohol) (PVA) nanocomposite (PEI-mGO/PVA) films were prepared by solution-casing for hydrogen gas barrier applications. Hydrophilic PEI was used to simultaneously reduce and modify graphene oxide sheets, thereby facilitating a homogeneous dispersion of PEI-mGO in the PVA matrix. The effects of PEI-mGO on the morphology and properties of the nanocomposite films were examined by Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetric analysis and field emission scanning electron microscopy. Analogous GO/PVA composites were also prepared and characterized for comparative purposes. The PEI-mGO/PVA nanocomposites showed higher thermal and mechanical stability as well as remarkable improvement in hydrogen gas barrier properties compared to the PVA film; specifically, the PEI-mGO/PVA film having 3.0 wt% of PEI-mGO content exhibited almost 95% decrease in GTR and permeability values compared to PVA film.

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1. Introduction

The utilization of alternative energy sources, such as hydrogen to replace natural energy resources is a great challenge to the researcher for the minimization of air pollution and global warming problems [1,2]. The fabrication of hydrogen gas storage tanks is very important to utilize hydrogen energy for various engineering and industrial applications including hydrogen fuel cells, petroleum recovery and refining, production of biodiesel, food and chemical processing, aerospace, power generation, etc. [1–5]. Nowadays, polymeric materials are given special attention for a variety of packaging applications (food, pharmaceuticals, electronics and hydrogen storage tank) due to their lightweight, flexibility, low cost and ease of processing as compared with traditional materials such as glass, wood, metal and ceramics [1–3]. However, the application of commercially available polymers as gas barrier materials (packaging materials) is often limited due to their higher gas permeability for different gases (e.g., hydrogen, oxygen, carbon dioxide and nitrogen) and higher transparency [1]. The fabrication of a hydrogen gas barrier polymeric material is extremely challenging due to the very small size and low density of hydrogen molecules. It is reported that the barrier properties of polymers are expected to be significantly enhanced due to the creation of “tortuous paths” for diffusing molecules by the addition of impermeable nanofillers (nanoclays, exfoliated graphite, and graphene and metal nanoparticles) to a polymer matrix [3]. However, the difficulties in exfoliating clay aggregates during melt-state processing limit the use of clay materials for the preparation of barrier materials. The appropriate polymeric materials for the fabrication of hydrogen storage tank should have good mechanical and film-forming properties, with good thermal stability as well as high gas barrier properties. Graphene, a two-dimensional atomically thin honeycomb lattice having very high aspect ratio, has generated intense amount of interest for nearly a decade due to its outstanding

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chemical, mechanical, thermal, gas barrier, electron transport and thermoelectric properties [1–8]. Therefore, incorporation of graphene to a polymer matrix has achieved a number of improved properties with promising applications in many areas, such as fuel cell, solar cell, aerospace, antifouling coatings, gas barrier (packaging), electronics, medicine [1–13]. Molecular simulations and experimental studies have revealed that graphene (defect free) is impermeable to all gas molecules [1,7]. Therefore, graphene based polymer nanocomposites have gained wide acceptance as high barrier polymeric materials, although homogeneous dispersion of graphene within the polymer matrix and effective interfacial interaction with the polymer matrix are the key factors to utilize of the appealing properties of graphene in the polymer/graphene nanocomposites. Graphene oxide (GO) has the widest potential to achieve the high-performance nanocomposite because GO can be prepared on a large scale to meet the demand for nanofillers for composite preparation, and chemically tailored to maximize its interaction with the polymer matrix [4,5,8]. GO contains many oxygen containing functional groups, which promote the complete exfoliation in different solvents and uniform dispersion of graphene oxide with the polymer matrix [3,4,6]. However, the inherent defects and holes in GO sheets diminish the gas barrier properties of the composites, and GO is also unstable in water where it slowly converts to small humic acid structures [9]. Therefore, other stratagems are needed to prepare graphene-based polymeric composites. One feasible solution is to use reduced GO (rGO) because it has less defects [1]. However, it is very difficult to prepare rGO-based polymeric films because rGO is incompatible with both hydrophilic and hydrophobic polymers, and rGO sheets tend to form agglomerate by π–π stacking and van der Waals attractive interactions. The surface modification of GO sheets before or during reduction is expected to play a very important role in tailoring its structure and properties and it enables excellent dispersion of reduced graphene with the polymer matrix in different solvents. Therefore, proper surface functionalization of GO is needed to produce well exfoliated and high-quality graphene sheets which can form high-performance nanocomposites for diverse applications [5,8]. It is highly desirable to prepare high-performance graphene/polymer nanocomposite in an ecologically-friendly solvent such as water. In this regard, polyethyleneimine (PEI) is unique because it can simultaneously modify and reduce GO and form water dispersible and high quality graphene sheets (PEI-mGO) [8,10]. Poly(vinyl alcohol) (PVA), a highly polar, semi-crystalline and water-soluble biodegradable polymer, has several applications in the areas of packaging, fuel cells and coatings, etc. [1,4,11–14]. The hydrophilic and water-dispersible nature of PEI-mGO and PVA can make excellent compatibility between them in water, and hydroxyl groups of PVA can form intermolecular hydrogen bonds with the amine moieties and remaining oxygenated groups of PEI-mGO. Therefore, the special properties of PVA as polymer matrix and PEI-mGO as nanofiller motivated us to choose them for the fabrication PEI-mGO/PVA nanocomposite films as super hydrogen barrier films (PEI-mGO/PVA).

This work reports the synthesis, characterization and gas barrier properties of a series of novel nanocomposite films (PEI-mGO/PVA) fabricated from different feeding amounts (wt%) of PEI-mGO with a fixed amount of PVA. Analogous GO/PVA nanocomposite films were also prepared for comparison with the PEI-mGO/PVA films. Structure and morphology of the nanocomposites have been determined by different characterization techniques. It was attempted to understand the effects of the GO and PEI-mGO fillers on the properties of the respective composites, i.e., GO/PVA and PEI-mGO/PVA. Also, the gas barrier properties of these PEI-mGO/PVA films were systematically investigated and compared with GO/PVA nanocomposites to study the effect of addition of PEI-mGO toward the hydrogen gas barrier properties.

2. Experimental

2.1. Materials

Expanded graphite was obtained from TIMCAL, Ltd. (Switzerland). Concentrated sulfuric acid (H_2SO_4, 95%), hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) were purchased from Samchung Pure Chemical Co. Ltd. (Korea). Potassium permanganate ($KMnO_4$) was obtained from Junsei Chemical Co. Ltd. (Japan). Sodium nitrate ($NaNO_3$), PVA (~88% hydrolyzed, Mw ~ 74,800) and polyethyleneimine (PEI, Mn ~10,000) were purchased from Sigma–Aldrich (USA). The materials were used without further purification. The polyethyleneimine modified GO (PEI-mGO) was prepared according to the method reported in literature [10].

2.2. Characterization

Fourier transform infrared spectroscopy (FTIR) was carried out using a Nicolet 6700 spectrometer (Nicolet Instrument Company, USA) at room temperature over a frequency range of 4000–400 cm^{-1}. X-ray diffraction (XRD) analysis was performed on a D/Max 2500V/PC diffractometer (Rigaku Corporation, Japan) with Cu-Kα targets (λ = 0.154 nm) at a scanning rate of $2^{\circ}\cdot min^{-1}$ under a voltage of 40 kV and a current of 100 mA. Tensile tests were carried out on a universal testing machine (Instron model 5567A, USA) equipped with a 100-N load cell with an extension rate of 5 mm min^{-1} and gauge length of 25 mm. Field emission scanning electron microscopy (FE-SEM) measurements were carried out in a JSM-6701F (JEOL, Japan) to determine the morphology of the fracture surface. After mechanical testing, samples were coated with a thin layer of gold prior to FE-SEM characterization. Hydrogen gas barrier properties of the pure PVA, GO/PVA and PEI-mGO/PVA films at 25 °C were determined using a GDP-C gas permeability tester (Brugger Feinmechanik GmbH, Germany). A hydrogen flow at 100 kPa and 80 cm^3 min^{-1} was fed to one side of a 2.5 cm diameter film sample.

2.3. Fabrication of PEI-mGO/PVA and GO/PVA composites

A controlled amount of the PEI-mGO dispersion was added to the PVA solution, and the mixture was sonicated for 2 h. The homogeneous PEI-mGO/PVA dispersion was then cast into a Petri dish for film formation at 50 °C until its weight equilibrated. The obtained composite films were kept at 50 °C under vacuum for three days to remove entrapped water from the films. The composite films with different wt% of PEI-mGO were prepared by the same procedures. The composite films with PEI-mGO contents of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 wt% were denoted as PEI-mGO0.5/PVA, PEI-mGO1.0/PVA, PEI-mGO1.5/PVA, PEI-mGO2.0/PVA, PEI-mGO2.5/PVA and PEI-mGO3.0/PVA, respectively. The films with neat PVA and GO/PVA nanocomposites (GO0.5/PVA, GO1.0/PVA, GO1.5/PVA, GO2.0/PVA, GO2.5/PVA and GO3.0/PVA) were prepared by a similar procedure. The probable structure of PEI-mGO/PVA composite with hydrogen bonding interaction site between PEI-mGO and PVA is shown in Scheme 1.

3. Results and discussion

3.1. FTIR analysis

FT-IR analysis was performed to confirm the structure of PEI-mGO as well as to monitor the interaction between the PVA and the PEI-mGO in the PEI-mGO/PVA composites, as shown in Fig. 1. The PEI-mGO showed new peaks at 1463 (C–N stretching) and

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