Water and oxygen permeation through transparent ethylene vinyl alcohol/graphene oxide membranes

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Abstract
We prepared ethylene vinyl alcohol (EVOH)/graphene oxide (GO) membranes by solution casting method. X-ray diffraction analysis showed that GOs were fully exfoliated in the EVOH/GO membrane. The glass transition temperatures of EVOH were increased by adding GOs into EVOH. The melting temperatures of EVOH/GO composites were decreased by adding GOs into EVOH, indicating that GOs may inhibit the crystallization of EVOH during non-isothermal crystallization. However, the equilibrium melting temperatures of EVOH were not changed by adding GOs into EVOH. The oxygen permeability of the EVOH/GO (0.3 wt%) film was reduced to 63% of that of pure EVOH film, with 84% light transmittance at 550 nm. The EVOH/GO membranes exhibited 100 times better (water vapor)/(oxygen) selectivity performance than pure EVOH membrane.

Key words: graphene oxide, ethylene vinyl alcohol, permeability, selectivity, water vapor

1. Introduction
Ethylene vinyl alcohol (EVOH) is one of the best known oxygen barrier materials in use today, with excellent gas barrier properties, processability, and sensitivity to moisture [1-3]. The permeation of oxygen and water vapor can lead to damage in electronic devices and the decomposition of foods. Barrier films can enhance the lifetime of electronic devices, and are required for food packaging or volatile solvents packaging and moisture sensitive products. Graphene oxide (GO) is the intermediate for graphene, and can be obtained by chemical oxidation of natural graphite [8-10]. Kim and coworkers [10] were the first to demonstrate that the oxidative form of graphene (GO) is itself an excellent gas barrier to oxygen. Subsequently, Nair and coworkers [4] have reported that helium permeation is inhibited by GO but water permeation is not impeded by GO.

Yang and coworkers [11] have shown that a polyethyleneimine (PEI)/GO multilayer membrane exhibits good oxygen/hydrogen selectivity. For a transparent oxygen barrier, poly(vinyl alcohol) (PVA)/GO membranes are the best among the reported membranes consisting of GO and polymers [10]. The oxygen transmittance rate (OTR) in PVA/GO (0.3 wt%) composite coated film has been reported to be 86 times lower than that of pure polyethylene terephthalate (PET) film, at 60% relative humidity (RH), with 73% light transmittance [10]. Thirty layered PEI/GO membrane has been reported to have 18 and 45 times lower OTR than pure PET film at 100% RH and 0% RH, respectively [11]. Gas barrier properties of various polymer/GO membranes have also been reported for polymers such as PVA [10], polyurethane [12], polycarbonate [13], and poly(ethylene terephthalate) [14].

Gas permeability (P) is the product of diffusivity (D) and solubility (S) which can be obtained from the solution of Fick’s second law of diffusion as described elsewhere [10,15,16]. In our previous work, we showed that both the D and S of oxygen are decreased by dispers-
Water and oxygen permeation through graphene oxide membranes

2. Experimental

2.1. Preparation of GO

Flake graphite powder (19 μm nominal particle size) was supplied from Asbury Carbon. GO was synthesized from purified conventional flake graphite by modified Hummers method [8,9] as reported in our earlier work [10].

2.2. Preparation of EVOH/GO film

EVOH (32 mol % ethylene) was supplied from Kuraray. EVOH/GO nanocomposites were prepared by solution mixing method, of EVOH in a colloidal solution of GO. EVOH (3 g) was dissolved in distilled water and isopropyl alcohol (IPA) (water/IPA weight ratio = 1) at 353.15 K and the solution cooled to 313.15 K. A colloidal solution of GO was added to the EVOH solution and mixed for 24 h at 313.15 K. EVOH/GO hybrid solution was cast onto PET film at 363.15 K and then dried for 1 h. The films were dried again in a vacuum oven at 373.15 K for 4 h. A series of EVOH/GO nanocomposite films with different GO loadings were similarly prepared. EVOH/reduced GO (RGO) solutions were synthesized by chemical reduction using hydrazine monohydrate for the chemical reduction. Fig. 1a shows the morphology of graphite, with a nominal particle size of 19 μm. We prepared the GOs from graphite by modified Hummers method [8-10]. The FE-SEM image of GO sheets on lacey carbon film and dried at room temperature. Nominal melting temperatures of the samples were measured by differential scanning calorimeter (DSC-Q10) with a heating rate of 20 K/min. In order to measure the melting temperatures of isothermally crystallized samples, the samples were heated up to 483 K and held there for 5 min, and then cooled quickly (-80 K/min) to the designated crystallization temperature. When the isothermal crystallization procedure was finished, the samples were heated again with a heating rate of 20 K/min. The OTR of films (dimension 10 × 10 cm) was measured with Illinois Instrument Model 8001. The water vapor transmission rate of films (dimension 10 × 10 cm) was measured with Permatran-W 3/33 MA (US, Mocon) according to the standard test method ASTM F 1249.

3. Results and Discussion

3.1. Morphological characterization

Fig. 1a shows the morphology of graphite, with a nominal particle size of 19 μm. We prepared the GOs from graphite by the modified Hummers method [8-10]. The FE-SEM image of the edge of dried GOs is shown in Fig. 1b. The layered structure of the dried GOs can be seen. We prepared a RGO solution by using hydrazine monohydrate for the chemical reduction. Fig. 1e shows the electron transparency of RGO sheets on lacey carbon grid, showing the typical image of graphene. Fig. 1d shows the XRD patterns of graphite, dried GO, EVOH and EVOH/GO composite (GO 0.3 wt%). A sharp reflection is seen at 2θ = 26.4° for graphite powder, which corresponds to the interlayer spacing (d) of 0.34 nm. The broad peak of dried GO particle is present.
GO composites. However, the slopes in the Hoffman-Weeks plots are increased by the addition of GO and RGO into EVOH, as seen in Fig. 2b. The increase of slopes may be due to the fact that the surface energy of crystalline EVOH may be decreased by the hydrogen bonding interaction between the crystal surface and GO [27]. Another possible reason for the increase of slopes is that the critical nucleus size of EVOH may be increased by the GO or RGO [27].

3.3. Permeation of oxygen and water vapor

To study the oxygen and water vapor barrier properties, 12 μm EVOH/GO and EVOH/RGO composite films were coated on a 23 μm PET substrate using the bar-coating method. As can be seen from an optical picture in Fig. 3a, the film (GO 0.15 wt%) is very transparent. The light transmittance of the film was measured by UV-vis at 550 nm. In Fig. 3b, light transmittance is 95.8% for the EVOH/GO composite film containing 0.1 wt% GO and 84.8% for the film containing 0.3 wt%. With increasing

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<th>Table 1. Thermal properties of EVOH/GO and EVOH/RGO composites</th>
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<td>GO/RGO (wt%)</td>
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EVOH: ethylene vinyl alcohol, GO: graphene oxide, RGO: reduced GO. *Non-isothermal glass transition temperatures \(T_g\) and melting temperatures \(T_m\) were measured during second heating. Non-isothermal crystallization temperatures \(T_c\) were measured during cooling at a rate of 20 K/min. \(^1\)Equilibrium melting temperatures.

3.2. Thermal properties of EVOH/GO and EVOH/RGO composites

We investigated the thermal properties of EVOH/GO and RGO composites by differential scanning calorimeter. The glass transition temperature of pure EVOH is about 334.6 K, as shown in Table 1. The glass transition temperature of EVOH/GO and RGO composites was increased about 1.6 K by adding GO or RGO 0.3 wt% into EVOH. The increase of glass transition temperature may be due to the hydrogen bonding interaction between GO or RGO and EVOH [10].

The nominal melting temperature of EVOH/GO composites was decreased by adding GOs into EVOH, as shown in Fig. 2a. These results are in contrast to the results of PVA/GO [10]. The decrease of melting temperature of EVOH/GO composites may indicate that GO inhibits the crystallization of EVOH. However, the nominal melting temperature of EVOH/RGO is almost constant over the composition range from zero to 0.3 wt%. This result may be due to the reduced hydrogen bonding interaction between the EVOH and RGO compared to those in EVOH/GO composites. X-ray photoelectron spectroscopy analysis showed that the carbon to oxygen ratio of GO and RGO is 1.81 and 6.39, respectively. So, we can surmise that the hydrogen bonding interaction in EVOH/RGO composite is weaker than that in the EVOH/GO composite, which results in the different melting behavior in Fig. 2a.

In order to obtain the equilibrium melting temperatures of EVOH/GO and EVOH/RGO composites, we performed Hoffman-Weeks plots [26] as seen in Fig. 2b. The equilibrium melting temperatures of EVOH were not changed by the addition of GOs or RGOs. These results are consistent with those of PVA/GO composites. However, the slopes in the Hoffman-Weeks plots are increased by the addition of GO and RGO into EVOH, as seen in Fig. 2b. The increase of slopes may be due to the fact that the surface energy of crystalline EVOH may be decreased by the hydrogen bonding interaction between the crystal surface and GO [27]. Another possible reason for the increase of slopes is that the critical nucleus size of EVOH may be increased by the GO or RGO [27].

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where $c^*$ is the saturated oxygen concentration in the film, $D$ is the oxygen diffusivity in the film, $S$ is the oxygen solubility in the film, and $P$ is the oxygen permeability [10].

The oxygen flux through the films is plotted with respect to time in Fig. 4. Model calculations by Eq. (1) fit the experimental data well. The oxygen diffusivity can be calculated from the slope of the straight line by Eq. (1). The oxygen solubility also can be calculated by Eq. (4). The oxygen molar flux of EVOH/GO (0.3 wt%) coated film is compared to the previous results for the PET and PVA/GO 0.3 wt% coated film by Kim et al. [10]. The oxygen molar flux of EVOH/GO (0.3 wt%) coated film is 123 times and 2 times lower than that of PET and PVA/GO (0.3 wt%) coated film [10].

We calculated the oxygen permeability of EVOH/GO and EVOH/RGO film without PET film by Eq. (5).

$$D = D_0 \left( \frac{1 - \phi_c}{1 + \frac{\alpha^2}{2} \phi_c} \right)$$

$$P = SD$$

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$$\frac{J}{P} = \frac{x_{GO}}{P_{GO}} + \frac{1 - x_{GO}}{P_{PET}}$$

where $x_{GO}$ is the ratio of the thickness of EVOH/GO to EVOH/GO/PET film. The oxygen permeability of EVOH/GO (0.3 wt%) film is $3.63 \times 10^{-15}$ mol s$^{-1}$ m$^{-1}$ Pa$^{-1}$, which is 63% of that of the pure EVOH film. The oxygen permeability of EVOH/RGO (0.3 wt%) film is $4.48 \times 10^{-15}$ mol s$^{-1}$ m$^{-1}$ Pa$^{-1}$, which is 78% of that of the pure EVOH film. The oxygen diffusivity of EVOH/GO (0.3 wt%) film is 1.4 times lower than that of the pure EVOH film.

The Nielsen approximation describes the increase in the tortuosity of the gas diffusion path by relating it to the volume fraction and aspect ratio of the crystal, as in the following equation [10,16]:

$$D = D_0 \left( \frac{1 - \phi_c}{1 + \frac{\alpha^2}{2} \phi_c} \right)$$

where $D_0$ is the diffusivity of polymer, $\phi_c$ is the volume fraction of graphene, and $\alpha$ is the aspect ratio of graphene [10]. The aspect ratio is a function of the smallest dimension of the graphene
increased by adding a very small amount of GO into EVOH. This may be due to the modification of the structure of PV A crystal line by the addition of GO. The oxygen solubility is decreased by the further addition of GO into EVOH as seen in Fig. 5b. In Fig. 6a, we plotted the relative value of water vapor permeability to EVOH. The water vapor permeability of RGO is lower than that of the GO. This may be due to the decrease of the interlayer spacing after reduction. Water molecules diffuse through the interlayer spacing [4], so the decrease of interlayer spacing may result in the reduced water vapor diffusivity. The decrease of water vapor permeability in the RGO/EVOH film compared to that of the GO/EVOH film may also be due to the decrease of oxygen to carbon ratio by the reduction. In Fig. 6b, EVOH/GO membranes exhibited 100 times improved (water vapor)/(oxygen) selectivity compared to EVOH pure membrane. These results point to the new possible applications of EVOH/GO films as an oxygen/water selective membrane.
4. Conclusions
We prepared EVOH/GO membranes by solution casting method. XRD analysis showed GOs were fully exfoliated in the EVOH/GO membrane. The thermal properties of EVOH were modified by the hydrogen bonding interaction between EVOH and GOs. The glass transition temperatures of EVOH/GO composites were increased by adding GOs into EVOH. Nominal melting temperatures of EVOH/GO composites were decreased by adding GOs into EVOH, indicating that GOs inhibit the crystallization of EVOH during non-isothermal crystallization. However, the equilibrium melting temperatures of EVOH were not changed by adding GOs into EVOH. The oxygen permeability of the EVOH/GO (0.3 wt%) film was reduced to 63% of that of pure EVOH film, with 84% light transmittance at 550 nm. The EVOH/GO membranes exhibited 100 times better (water vapor)/(oxygen) selectivity performance than pure EVOH membrane.

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References


