Preparation of Ethylene Vinyl Acetate Copolymer/Graphene Oxide Nanocomposite Films via Solution Casting Method and Determination of the Mechanical Properties

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Published online: 07 Jan 2015.

To cite this article: Mohsen Bahmanyar, Sajjad Sedaghat, Ahmad Ramazani S.A. & Hossein Baniasadi (2015) Preparation of Ethylene Vinyl Acetate Copolymer/Graphene Oxide Nanocomposite Films via Solution Casting Method and Determination of the Mechanical Properties, Polymer-Plastics Technology and Engineering, 54:2, 218-222, DOI: 10.1080/03602559.2014.958772

To link to this article: http://dx.doi.org/10.1080/03602559.2014.958772

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Preparation of Ethylene Vinyl Acetate Copolymer/Graphene Oxide Nanocomposite Films via Solution Casting Method and Determination of the Mechanical Properties

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GRAPHICAL ABSTRACT

Ethylene vinyl acetate/graphene oxide (EVA/GO) nanocomposite films were prepared via solution casting method. The morphological studies investigated using SEM and XRD methods and the results confirmed the formation of likely exfoliation structures and good interaction between matrix and fillers. The results of permeability measurements showed that films have good resistance against oxygen. Mechanical measurements revealed that Young’s modulus and tensile strength of EVA have improved with introducing GO because of proper dispersion of GO into matrix and good interaction between them; however, elongation at break decreased due to formation of strong and rigid polymer/filler network preventing to elongate polymer chains.

Keywords
Ethylene vinyl acetate copolymer; Graphene oxide; Mechanical properties; Permeability

INTRODUCTION

Graphene, a single layer of carbon atoms in a hexagonal lattice, has recently attracted much attention due to its novel electronic and mechanical properties [1]. Graphene is usually prepared by the reduction of its precursor graphene oxide (GO) [2], a typical pseudo-two-dimensional oxygen-containing solid in bulk form, possesses functional groups including hydroxyls, epoxides, and carboxyls [3–6]. The chemical groups of GO have been found to be a feasible and effective means of improving the dispersion of graphene. Additionally, functional side groups bound to the surface of GO sheets may improve the interfacial interaction between graphene oxide and the matrix [7].

Ethylene-vinyl acetate copolymer (EVA) is a random copolymer synthesized from ethylene monomer and vinyl acetate (VAc) co-monomer [8]. It shows great commercial potential in the packaging industry due to its well-known good...
mechanical properties, specifically good processability and increased stiffness in molded parts, high resistance to tearing and toughness and significant moisture barrier properties. However, their gas barrier property is not significant to keep the quality of food therefore, it is necessary to modify EVA in order to use in food packaging industry.

On the other hand, in recent year polymer/graphene nanocomposites have attracted much attention in science and also industries. These nanocomposites have improved properties in comparison of pure polymers and even microcomposites.

The improvement usually occurs in tensile modulus, mechanical strength, permeability and flame retardant. Depending on the level of diffusion of polymeric chains between graphene oxide layers, it is possible to have intercalated or exfoliated nanocomposites. In an intercalated state the polymeric chains enter to free space between graphene layers and increased the layer distance, while in an exfoliated state the graphene layers completely separated and disperse into polymeric matrix.

In this study, we synthesized graphene oxide via modified Hummer’s method and used it to prepare EVA/GO nanocomposite films. The films were prepared via solution casting method and various properties of them were characterized. The results showed that impermeable nanocomposite films with good morphological structure and improved mechanical properties were obtained. Accordingly, these films had enough potential to use in packaging industries.

EXPERIMENTAL

Materials

Ethylene vinyl acetate with 18% and 28% vinyl acetate was purchased from Hyundai Petrochemical of Korea. Toluene was obtained from Merck and used as solvent. Sulfuric acid, sodium permanganate, potassium nitrate, hydrogen peroxide, hydrochloric acid and ethanol were prepared from Merck and used as obtained without any purification. Natural false graphite was purchased from Dae-Jung Chemical-Co, South Korea.

Characterization

Scanning electron microscopy (SEM) images were taken from fracture surface of samples by using Hitachi S-4160 (Japan). The X-ray diffraction (XRD) test was done by XRD STOE, Germany with 40 kV. To determine oxygen permeability, an apparatus based on a modified version of ASTM 1434D method was utilized. Pure oxygen was fed to a stainless steel cell via steel tubing with regulated control valves. The internal diameter of the cell was 90 mm. Prepared films were placed between the cell plates and fastened with pairs of nuts and bolts. For a one-dimensional flux through an isotropic media \( J \) is described by Fick’s first law of diffusion:

\[
J = D \Delta C / l
\]

where \( C \) is the concentration of permanent, \( D \) and \( l \) are diffusion coefficient and thickness of homogeneous film, respectively. For gases the concentration is expressed in terms of partial pressure. Analogous to Eq. (2) we obtain:

\[
J = P \Delta P / l
\]

Permeability of gases calculated from the rearrangement of Eq. (2):

\[
P = l J / \Delta P
\]

where \( J \) is the gas volumetric flow rate per unit area \( (\text{cm}^3 \text{ (STP) cm/ (s cm^2 cmHg)}) \), \( l \) the thickness of film \( (\text{cm}) \), \( \Delta P \) pressure difference across the film \( (\text{cmHg}) \) and \( P \) is the permeability \( (\text{cm}^3 \text{ (STP) cm/ (s cm^2 cmHg)}) \). Permeability is usually expressed in barrer so 1 barrer is equal to \( 7.5005 \times 10^{-15} \text{ m}^2 \text{ /s Pa} \) or \( 10^{−10} \text{ cm}^3 \text{ (STP) cm/ (s cm^2 cmHg)}) \).

Synthesize of Graphene Oxide

Graphene oxide was synthesized according to modified Hummers method. Briefly, 2 g of graphite powder and 1 g of NaNO₃ were mixed with 46 ml of concentrated H₂SO₄ at 0°C in ice bath and it was stirred for 30 min. Then 6 g of KMnO₄ was slowly added into the mixture and stirring was continued for 2 h. Initially, temperature should be lower than 20°C. Subsequently, it was increased to 35°C and 65°C while stirring continued for 30 and 40 min, respectively. After that, 90 ml deionized water was added to the mixture and the temperature was increased up to 100°C. The concentration of the solution was reduced by adding 280 ml distilled water and hydrogen peroxide (30 wt.%). Finally, graphene oxide was isolated from the mixture by centrifugation and washed with diluted hydrochloric acid (HCl 5 wt.%) to eliminate metal ions, then was washed with deionized water to remove the extra amount of HCl. The mixture was filtered and obtained solid was dried at 60°C for 2 days.

Preparation of Nanocomposite Films

To prepare nanocomposite films, various amount of GO was introduced into EVA (18 and/or 28) solution (5 wt.%). Then the mixture was stirred for 3 h at 80°C under reflux. The obtained homogeneous solution was casted on the glassy plate and dried at ambient temperature for 24 h. Then the plate was immersed into 1 wt.% sodium hydroxide solution for neutralization. After that, the film was removed from the plate and dried at room temperature.

RESULTS

Permeability Measurements

The permeability (P) as a function of GO loading for EVA18 and 28 are illustrated in Fig. 1. As can be seen, in both EVA18 and 28 introducing small amount of GO into
polymeric matrix dramatically reduced permeability of films probably due to the longer diffusive path that the penetrants must travel in the presence of the filler. A sheet-like morphology of GO is also particularly efficient in maximizing the pathway length due to possessing the large length-to-width ratio.

Comparing Figs. 1a and 1b, we see that the amount of vinyl acetate monomer in EVA can also influence the permeability of nanocomposites. In other words, increasing vinyl acetate caused the increase in permeability due to reducing in crystalline of polymeric matrix.

**Morphological Characterization**

**X-ray Diffraction**

XRD patterns of graphite, graphene oxide, and chemically reduced graphene are illustrated in Fig. 2. As can be seen, there is a strong and sharp peak at $2\theta = 8.6^\circ$ corresponding to the interlayer spacing of 0.83 nm in the XRD pattern of GO which is in the range of values that have previously been reported\(^{[20]}\).

Furthermore, the XRD patterns of pure EVA18 and EVA18/GO nanocomposites with 3 wt.% GO are presented in Fig. 3. As can be seen, both pure EVA and its nanocomposite showed similar XRD patterns. Also the GO diffraction peak disappeared in nanocomposites suggesting the polymer chains diffuse successfully between graphene nanosheets and probably exfoliated structure in nanocomposite film was achieved. In other words, the XRD results confirmed that the GO layers separated and the polymer chains diffuse between them and finally caused to eliminate GO peak.

**Scanning Electron Microscopy (SEM)**

Fig. 4 illustrated SEM images from fracture surface of EVA18/GO and EVA28/GO with 3% wt. GO. As can be seen, there is no phase diffraction between polymer matrix and nanofiller. On the other hand, there is good interaction between two phases.
Mechanical Properties

The effect of filler amount on the mechanical properties of prepared nanocomposites such as tensile strength, tensile modulus and elongation at break was investigated and the results are provided in Figures 5 to 7. The tensile modulus is one of the most important mechanical properties in polymeric nanocomposites. As illustrated in Fig. 5 for both EVA18 and EVA28 tensile modulus was increased as GO loading increased. So it decreased at least 70% by adding 5 wt.% GO. This behavior is due to good interaction between matrix and filler and also proper dispersion of filler into matrix. As can be seen, after adding 5 wt.% GO, tensile modulus decreased, probably due to agglomeration of filler into polymer matrix and formation of local stress concentration. Furthermore, the effect of GO addition on improvement of modulus is more evident in the EVA28/GO nanocomposites, probably due to better interaction of matrix and the GO and greater separation of layers.

The tensile strength of nanocomposites as presented in Fig. 6 showed the same behavior, so it increased as GO loading increased up to 5 wt.% and decreased after that. The elongation at break as function of GO loading is shown in Fig. 7. As we expected, incorporation of filler into polymer matrix has reduced elongation of polymer. This is because of reduction of deformation ability of polymer due to presence of filler, which makes the matrix more brittle.

Investigation of mechanical properties of prepared nanocomposite show that with increasing GO content up to 5 wt.%, the modulus and tensile increase while with increasing GO loading to 7 wt.%, they reduced due to filler agglomeration formation. Furthermore, elongation at break reduces by introducing GO into polymer matrix.

![SEM image of a) EVA18/GO and b) EVA28/GO nanocomposite film with 3 wt.% GO (3000 magnification).](image1)

**FIG. 4.** SEM image of a) EVA18/GO and b) EVA28/GO nanocomposite film with 3 wt.% GO (3000 magnification).

![Young’s modulus of a) EVA18/GO and b) EVA28/GO nanocomposite films as a function of GO content.](image2)

**FIG. 5.** Young’s modulus of a) EVA18/GO and b) EVA28/GO nanocomposite films as a function of GO content.

![Tensile strength of prepared) EVA18/GO and b) EVA28/GO nanocomposites as a function of GO content.](image3)

**FIG. 6.** Tensile strength of prepared) EVA18/GO and b) EVA28/GO nanocomposites as a function of GO content.
CONCLUSION

Graphene oxide (GO) was synthesized via modified Hummer’s method and the results were confirmed this synthesis. The prepared GO was used to prepare impermeable EVA/GO nanocomposite for packaging. The properties of prepared film were investigated. The permeability test revealed that the GO nanocomposite for packaging. The properties of prepared size. The prepared GO was used to prepare impermeable EVA/GO into the matrix. However, elongation at break reduced as well as Young’s modulus, were improved by incorporating GO into polymeric matrix dramatically reduced its permeability. Furthermore, the mechanical strength of prepared films that were prepared from pure EVA is not enough for packaging therefore, it is necessary to improve EVA mechanical properties. The results confirmed that mechanical strength, as well as Young’s modulus, were improved by incorporating GO into the matrix. However, elongation at break reduced probably due to the restriction effect of GO.

REFERENCES