

# EFFECT OF BORIC ACID ON THE OXYGEN GAS BARRIER PROPERTIES OF POLY(VINYL ALCOHOL-CO-ETHYLENE)/GRAPHENE OXIDE NANOCOMPOSITE FILMS

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## ABSTRACT

A facile technique that combines solution spray-coating and crosslinking method was used to prepare cross-linked composite-coated nylon films involving boric acid (BA), graphene oxide (GO) and poly(vinyl alcohol-co-ethylene) (EVOH). Accordingly, the cross-linked poly(vinyl alcohol-co-ethylene)/graphene oxide nanocomposites (EVOH/4GO/xBA) coated nylon films were prepared using BA cross-linking method to study the effect of BA towards oxygen (O<sub>2</sub>) barrier property. In this study, borate ions, originated from BA, used as cross-linkers. The EVOH/4GO/xBA composites were prepared with a fixed amount of GO (4 wt%) and different amounts (where x = 0, 4, 8, 10, and 12 wt%) of BA with respect to EVOH. Successively, the different composite solutions were coated on modified nylon sheets at 50 °C by spray-coating technique, after that; the coated films were dried at 70 °C for 1h to fabricate O<sub>2</sub> barrier films. The O<sub>2</sub> barrier properties of all the composite-coated films increased dramatically in comparison to pure nylon sheet, and EVOH/4GO/12BA exhibited almost 83% decline in oxygen gas transmission rate (O<sub>2</sub>GTR) compared to the pure nylon substrate. Wide angle X-ray diffraction patterns (WAXD) and fracture-sectional FESEM analyses specified that the higher oxygen barrier properties of the coated films are due to the formation of cross-linking between borate ions, GO, and EVOH. The cross-linked EVOH/4GO/xBA films could be used successfully in the field of flexible electronics (LCD and solar cells).

## 1. INTRODUCTION

The flexible oxygen (O<sub>2</sub>) gas barrier films have many applications in different fields, such as electronics, pharmaceutical, and food packaging. The excellent flexibility, light weight, low-cost, and ease of processing of polymer film make them as suitable material for the preparation of barrier films in comparison with traditional materials (e.g., glass, wood, metal and ceramics). But, oxygen barrier properties of commercially available polymer films are not sufficient for the application in food packaging as well as electronics. Graphene has engrossed tremendous attentions as a novel barrier material due to its large aspect ratio and unique planar structure [1, 2]. Graphene oxide (GO) which is a parent element of graphene contains abundant oxygenated functional groups on their basal planes and edges. These chemical functional groups help to improve interfacial adhesion between GO and polar polymer matrix. The uniform distribution, high alignment of GO and good interfacial interaction between GO and polymer matrix are essential to improve the barrier properties of GO based polymer matrix [3-5]. However, the presence of defects and holes in GO sheets may increase the permeability of gases through the GO based polymeric composite. Actually, many gaps would exist in the GO based polymeric composite and gas molecules can easily permeate through these gaps, resulting higher gas transmission rate. Crosslinking is a very useful method to reduce these gaps [6,7]. Borate ions can

successfully crosslink GO based polymer composites and improve barrier properties of the composites. Yan et al. [6] synthesized borate cross-linked graphene oxide-chitosan films with improved barrier and mechanical properties compared to pure chitosan film. Lai et al. [7] also prepared cross-linked poly (vinyl alcohol)/GO nanocomposite film with high mechanical and oxygen barrier properties using borate ions as cross-linker.

Poly(vinyl alcohol-co-ethylene) (EVOH) is a semi-crystalline copolymer of vinyl alcohol and ethylene monomer units, and has good gas barrier properties [8]. BA has been already used as cross-linking agent for polymeric material [9,10]. Herein we report the preparation of new borate-crosslinked EVOH/GO composite (EVOH/GO/BA) coated nylon films via spray-coating at 50 °C, followed by thermal treatment. These composite coated nylon films exhibited very low oxygen gas transmission rate ( $O_2$ GTR) values in comparison to bare nylon film.

## 2. EXPERIMENTAL

### 2.1. Materials

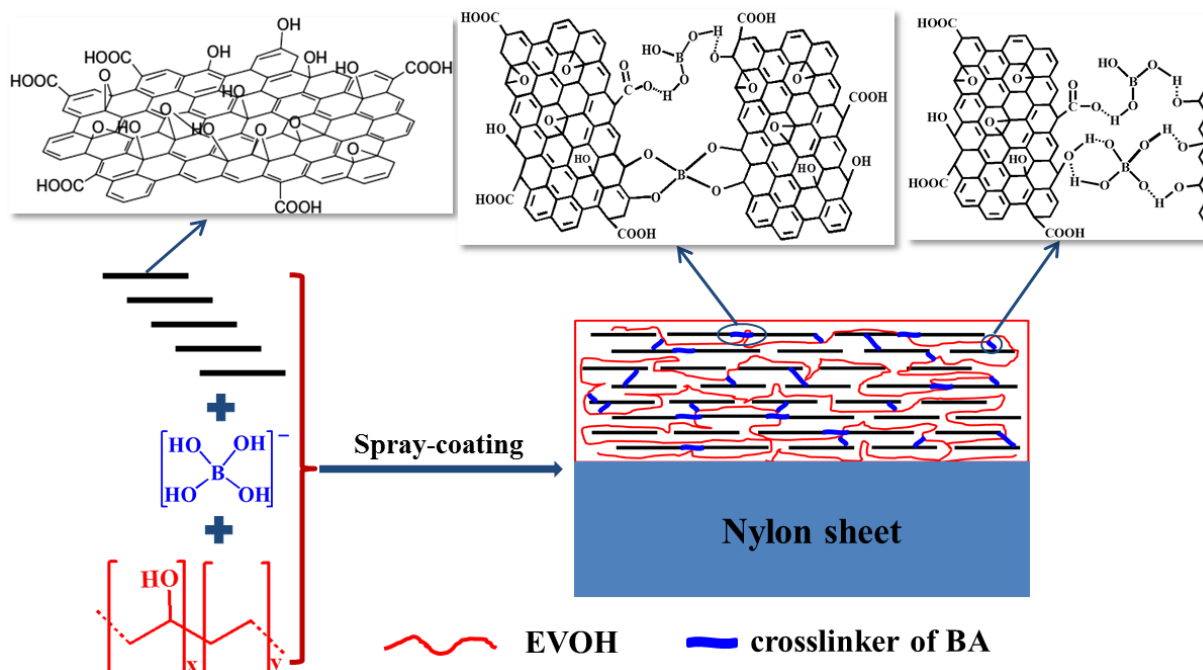
Graphite was purchased from Sigma Aldrich, Germany. EVOH was purchased from Sigma Aldrich, USA. Kolon Kopa<sup>®</sup> KN173HI Nylon 6 Resin film, acetone, ethanol, hydrogen peroxide, sulfuric acid, hydrochloric acid, potassium permanganate, boric acid, trichloroacetic acid and N,N-dimethyl formamide (DMF) were purchased from Samchun Pure Chemical Co. Ltd., South Korea. The chemicals used in this research were of analytical grade and were used without further purification.

### 2.2. Characterization

The morphology of prepared GO was observed by Atomic Force Microscope (AFM) (Veeco; model AP 0100) in non-contact mode. AFM experiment was prepared by casting a drop of GO (0.01%, w/v) deionized (DI) water solution on polished silicon wafer. X-ray diffraction (XRD) analyses were directly performed on the composites with Cu irradiation at the scanning rate of 2°/min in the range of 5–50°. The fracture-sectional field emission scanning electron microscopy (FESEM) measurements of EVOH/4GO/xBA-coated nylon films were carried out by sputtering osmium prior to examination using a FESEM (JSM-6701 Jeol, Japan). The oxygen gas transmission rates ( $O_2$ GTRs) of all films were measured using a GDP-C (Brugger Feinmechanik GmbH) gas permeability machine at 100 kPa pressure and at 25 °C. Graphite oxide was prepared according to the procedure reported in literature [1,2].

### 2.3. Preparation of EVOH/4GO/xBA composites

Firstly, the 50 mg EVOH was dissolved in 4 ml DMF solution at 60 °C by stirring. Then the EVOH/4GO solution was prepared by mixing 4 wt% of GO into EVOH solution, followed by ultrasonication for 1 h and stirring for 0.5 h at room temperature. A desired amount of BA was dissolved in DI water, and mixed the BA suspension into the EVOH/4GO solution. Next, the composite solution (EVOH/4GO/xBA) was sonicated for 2 h in an ice bath to obtain the homogeneous solution. Coating over modified nylon substrate was performed at 50 °C by spray-coating of the composite solution onto the modified nylon surface. The resulting composites coated films were designated as EVOH/4GO, EVOH/4GO/4BA, EVOH/4GO/8BA, EVOH/4GO/10BA, and EVOH/4GO/12BA. These nanocomposites contained 0, 4, 8, 10, and 12 wt% of BA with respect to EVOH. The synthesis procedure of EVOH/4GO/xBA nanocomposite-coated nylon sheets and the reciprocal interactions among EVOH, borate ions and GO are illustrated in Figure 1. EVOH coated nylon film also prepared by similar method in the absence of GO and BA.



**Figure 1:** Schematic diagram for the interactions among EVOH, borate ions and GO.

### 3. RESULTS AND DISCUSSION

#### 3.1. XRD analysis

Figure 2 shows the WAXD patterns for GO, BA, composite coated nylon film and pure EVOH. Pristine EVOH exhibited one distinct peak at  $2\theta = 20^\circ$  along less intense peaks at  $2\theta$  of  $10^\circ$  and  $40^\circ$ . The peaks at  $2\theta = 10^\circ$  and  $40^\circ$  almost disappeared in the borate treated EVOH/4GO/xBA composite films in comparison to the pure EVOH. However, in addition to the distinct peak at  $20^\circ$  ( $2\theta$ ), the EVOH/4GO/4BA and EVOH/4GO/12BA composite films showed new peaks ( $2\theta$ ) at  $8.3^\circ$  and  $7.5^\circ$ , respectively. Besides, the strong peak at  $2\theta = 28.1^\circ$  for BA was not found in EVOH/4GO/4BA and EVOH/4GO/12BA, suggesting BA play the role to produce cross-linker borate ions. The pure GO exhibited a strong peak at  $2\theta = 11.9^\circ$ , corresponding to the interlayer spacing ( $d_{sp}$ ) of  $7.4 \text{ \AA}$ . The intercalated EVOH macromolecules between the interlayer of GO sheets can increase the  $d_{sp}$  value from  $7.4 \text{ \AA}$  for the pure GO to  $11.8$  and  $12.6 \text{ \AA}$  for EVOH/4GO/4BA and EVOH/4GO/12BA composite films, respectively [6,9]. The typical diffraction peak corresponding to GO was not found in EVOH/4GO/xBA, signifying the formation of exfoliated GO nanosheets in the composite. EVOH/4GO showed a weak peak at  $2\theta = 9.0^\circ$ , signifying the intercalated stacks of GO sheets in the composite. The  $d_{sp}$  value is increased in the BA treated composite film in comparison to EVOH/4GO composite film, suggesting EVOH molecules are covalently crosslinked to the GO sheets. The interfacial adhesion between GO and EVOH in EVOH/4GO/xBA composite is expected to be much stronger due to the presence of abundant hydrogen bonds and covalent grafting. EVOH/4GO/12BA composite exhibited the more intense peak at  $2\theta$  of  $7.5^\circ$  and larger  $d_{sp}$  in comparison to the EVOH/4GO/4BA composite. It suggests that the higher amount of BA in EVOH/4GO/12BA composite can preferably help to form more cross-linked EVOH based GO network and larger GO-sheet regions.

#### 3.2. Morphology

Figure 3a and b are the fractured surface FESEM images of EVOH/4GO/12BA composite at different magnification. EVOH/4GO/12BA composite exhibited rough surface suggesting the formation of cross-linked structure. Some white threads were also found on the fracture surface of EVOH/4GO/12BA composite in comparison to neat smooth EVOH fracture surface (Figure 3c). The threads indicate the intensity of interactions between the GO sheets and EVOH polymer during the

crosslinking by borate ions [6,7]. The yellow color marked areas show the bigger GO regions by cross-linking of GO sheets, which is great advantage for blocking O<sub>2</sub> gas molecules (Figure 3b). Figure 3d depicts the picture of EVOH/4GO/12BA coated nylon film.

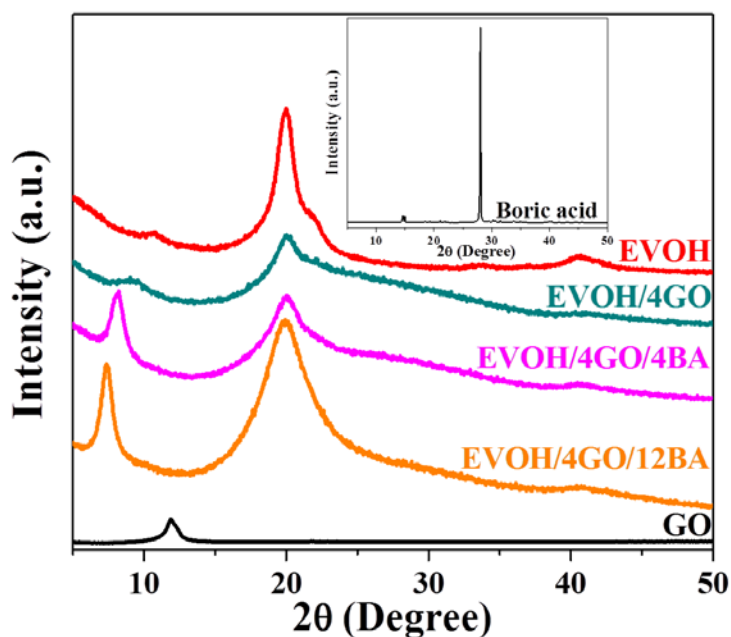


Figure 2: XRD patterns of EVOH, GO, BA (inset) and corresponding different kind of composites.

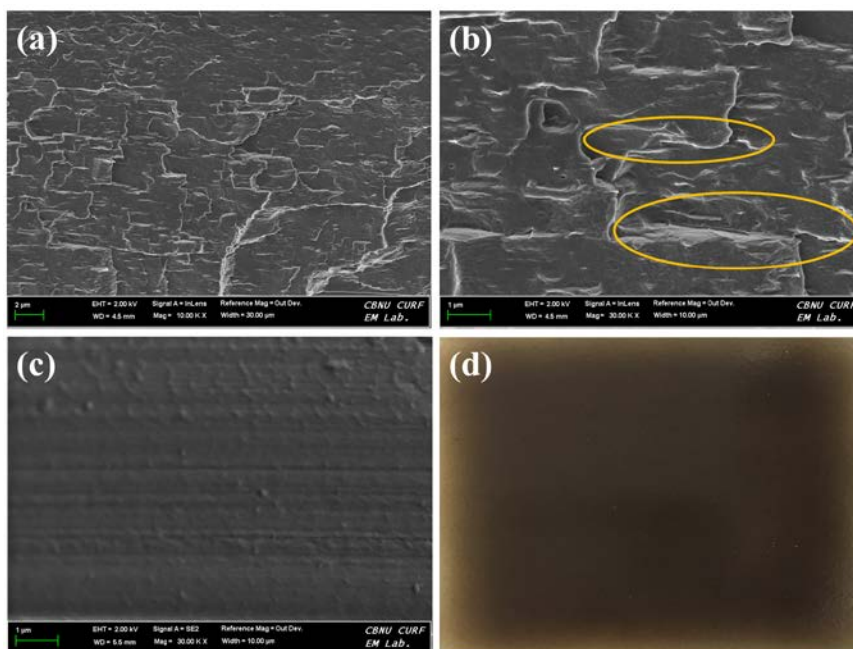


Figure 3: FESEM images of the fracture surface for (a) and (b) EVOH/4GO/12BA composites, (c) pure EVOH, (d) the picture of EVOH/4GO/12BA composite.

### 3.3. O<sub>2</sub> Gas barrier property

O<sub>2</sub>GTR was measured at 25 °C and 100 kPa, and Figure 4 shows the O<sub>2</sub>GTR values of pure nylon, EVOH/4GO, EVOH/4GO/4BA, EVOH/4GO/8BA, EVOH/4GO/10BA, and EVOH/4GO/12BA composite-coated nylon films. O<sub>2</sub>GTR values decreased dramatically in the EVOH/4GO/xBA composite-coated nylon films, compared to the pure nylon and EVOH/GO films. The

EVOH/4GO/12BA film exhibited almost 83% decline in O<sub>2</sub>GTR value compared to the pure nylon sheet. The excellent barrier properties of EVOH/4GO/xBA composite films were attributed to the hybrid cross-linked structure formation, as illustrated in Figure 1. Borate ions react with both EVOH and GO; after that, EVOH, GO, and borate ions link with each other through a crosslinking network formation. Therefore, largely impermeable regions formed which consisted of GO and the cross-linked PVA. The cross-linked composite with very high aspect ratio, inhibit the permeation of oxygen molecules by lengthening the diffusion pathway for oxygen molecules, resulting lower O<sub>2</sub>GTR values of the composites [6,7]. Besides, borate ions help to interconnect the GO sheets, so, the available area for diffusion of gas molecules through the composite decreases due to the formation of larger GO-sheet regions. Therefore, the gas molecules bound to move through longer and more tortuous pathway to pass through the composite films. EVOH/4GO/12BA exhibited lowest O<sub>2</sub>GTR value is due to the formation of more cross-linked EVOH based GO network and larger GO-sheet regions compared to other composites. The EVOH/4GO showed higher O<sub>2</sub>GTR value compared to the EVOH/4GO/xBA films. Actually, many gaps and holes would exist in the EVOH/4GO composite and oxygen molecules can easily permeate through these gaps. But, the crosslinking reduce these gaps and holes, resulting lower O<sub>2</sub>GTR value of the cross-linked composite films.

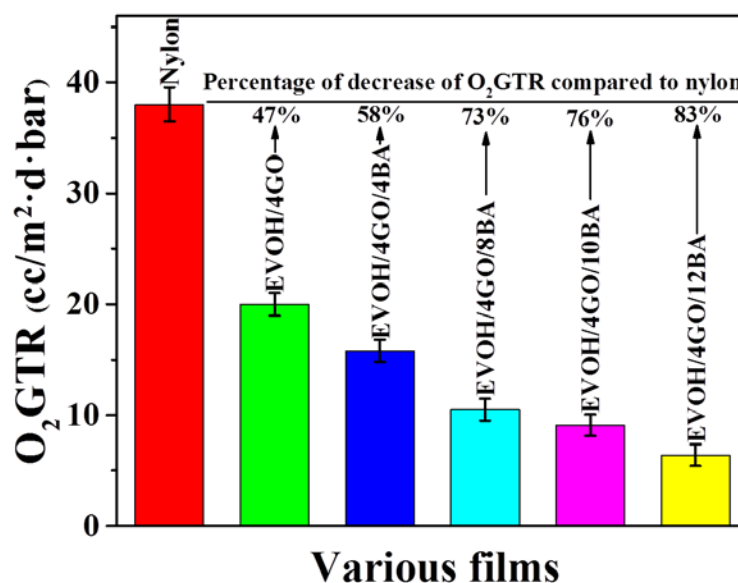


Figure 4: O<sub>2</sub>TR values of composite-coated and pure nylon films.

#### 4. CONCLUSIONS

The cross-linked EVOH/4GO/xBA composites-coated nylon films have been successfully prepared by spray-coating method, followed by thermal treatment. Borate ions were covalently grafted with both EVOH and GO sheets, and borate ions served as a bridge that combines EVOH with GO, resulting highly dense and cross-linked structure of the composite. The hydrolysis of BA yields the tetrahydroxyborate ions B(OH)<sup>4-</sup>. These borate ions react with the hydroxyl groups of EVOH and GO nanosheets, and produce orthoborate chemical bonds. The XRD analyses confirmed the strong interfacial interaction between the GO sheets with the EVOH matrix due to the cross-link effect of BA in EVOH/4GO/xBA composites. FESEM analyses confirmed the formation of tightly cross-linked network structure in EVOH/4GO/12BA composite. The cross-linked composite film (EVOH/4GO/12BA) with 4 wt% of GO and 12 wt% of BA exhibited an 83% decrease in O<sub>2</sub>GTR in comparison to the pure nylon film. The improvement of barrier properties of the cross-linked composite films is attributed to the synergistic effect of borate ions and GO sheets which form a dense and compact morphology of interconnected network between EVOH and GO sheets. The improved oxygen barrier properties of these cross-linked composite films could lead to their potential applications in food packaging and lightweight mobile gas storage containers in the near future.

## ACKNOWLEDGEMENTS

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