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# Bio-inspired cross-linking with borate for enhancing gas-barrier properties of poly(vinyl alcohol)/graphene oxide composite films

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ABSTRACT

The demand for flexible and transparent barrier films in industries has been increasing. Learning from nature, borate ions were used to cross-link poly(vinyl alcohol) (PVA) and graphene oxide (GO) to produce flexible, transparent high-barrier composite films with a bio-inspired structure. PVA/GO films with only 0.1 wt% GO and 1 wt% cross-linker exhibited an $O_2$ transmission rate <0.005 cc $m^{-2}$ $day^{-1}$, an $O_2$ permeability <$5.0 \times 10^{-20}$ $cm^3$ cm $cm^{-2}$ $Pa^{-1}$ $s^{-1}$, and a transmittance at 550 nm >85%; thus, they can be used for flexible electronics. Fourier transform infrared spectrometry and X-ray photoelectron spectroscopy indicated that the outstanding barrier properties are attributed to the formation of chemical cross-linking involving borate ions, GO sheets, and PVA, similar to the borate cross-links in high-order plants. Comparing our experimental data with the Cussler model, we found that the effective aspect ratio was significantly increased after cross-linking, suggesting that cross-linking networks connected GO with each other to form ultra-large impermeable regions. A feasible green technique, with potential for commercial production of barrier films for flexible electronics was presented.



## 1. Introduction

Many fields need flexible gas barrier films. These films are used in food packaging, pharmaceutical, and electronics, because oxygen makes food spoil, degrades pharmaceutical products, and destroys electrical devices. For several decades, polymers have been fabricated as barrier films because of their excellent flexibility, light weight, transparency, cheap price, and easy processing. Although polymer films have many exceptional properties, their gas barrier performance

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fits the requirements of food packaging only, but it is not enough for electronics. The requirements of oxygen transmission rate (OTR) for food packaging and flexible electronics are $10^2$–$10^0$ cc $m^{-2}$ $day^{-1}$ and $10^{-2}$–$10^{-6}$ cc $m^{-2}$ $day^{-1}$, respectively [1,2]. For example, the barrier requirements of liquid crystal display (LCD) and organic light-emitting device (OLED) are $10^{-3}$ and $10^{-5}$ cc $m^{-2}$ $day^{-1}$, respectively.

In the past two decades, inorganic clay platelets had been blended into polymers to improve their barrier properties. The improvement was ascribed to tortuosity effects resulting from dispersing clay that had a high aspect ratio [3–7]. The literature [8–11] has demonstrated that the oxygen permeabilities of polymer films have been reduced; however, their barrier performance still does not fit the requirements of flexible electronics. For instance, Yeun et al. [9] cast a PVA/saponite film on a polypropylene substrate to form a composite film; it showed a permeability of $1.4 \times 10^{-17}$ $cm^3$ cm $cm^{-2}$ $Pa^{-1}$ $s^{-1}$ and an OTR of 0.55 cc $m^{-2}$ $day^{-1}$. This OTR is very insufficient for LCD and OLED. Recently, graphene, which has an ultra-large aspect ratio, is developed as a novel barrier material. It has been made as free-standing graphene films [12,13] or has been blended into a polymer matrix to form composite films [14–17]. In 2008, Bunch et al. [17] proved that a monolayer graphene exhibits perfect gas barrier properties, as even the smallest helium did not pass through it. In 2010, Compton et al. [18] incorporated only 0.02 vol% functionalized graphene into a polystyrene membrane matrix and reduced its oxygen permeability by 25%. In 2012, Nair et al. [13] prepared a free-standing graphene oxide (GO) film and found that the film showed excellent ability to block gases. However, this GO film is not transparent and has insufficient mechanical strength for practical applications. Huang et al. [16] fabricated a poly (vinyl alcohol) (PVA)/GO composite barrier film with 0.72 vol% GO and indicated that its oxygen permeability was reduced by 98%, but the transparency was also significantly reduced because of the aggregation of GO. Although previous studies added GO sheets into a polymer matrix to enhance barrier properties, they still could not obtain a film that fits the light transmittance and OTR requirements of flexible electronics. Possible reasons for the insufficient barrier performance are the aggregation of GO at high content (low aspect ratio) and the poor adhesion between the polymer and GO sheets (interfacial spaces). Therefore, the GO loading should be low to ensure that it disperses well in the polymer matrix and prevents a decrease in transparency. However, it can be expected that many spaces (within loose polymer coils in amorphous regions) would exist between the GO sheets because of a low GO loading. These spaces would let oxygen molecules to pass through, resulting in a low barrier performance (Fig. 11). Crosslinking is a normal method to reduce the spaces between polymer chains. Park and coworkers have point out that significant enhancement in mechanical stiffness and fracture strength of graphene oxide paper can be achieved upon crosslinking with a small amount of $Mg^{+2}$ and $Ca^{+2}$ [19]. They also generate chemically cross-linked graphene oxide sheets by addition of polyallylamine to an aqueous suspension of graphene oxide sheets [20]. The cross-linked graphene oxide sheets showed increased stiffness and strength relative to unmodified graphene oxide paper. Kong et al. reported chemical cross-linked polyimide/graphene oxide nanocomposite films. The nanocomposites showed enhanced tensile properties due to the presence of exfoliated GO in the polyimide matrix as well as crosslinking between poly(amic acid), which is a precursor of polyimide, and GO by Mg ions [21]. Satti et al. demonstrated a way of making graphene oxide/polymer composite by covalent chemical bonding [22]. Graphene oxide sheets crosslinked with poly(allylamine) hydrochloride by carbodiimide coupling. The crosslinking of GO with the polymer enhances the mechanical properties of the composites. Bioinspired layered GO/poly(vinyl alcohol) nanocomposite films are prepared by Liu and coworkers recently [23]. After the crosslinking of the interfacial region by using borate as an agent, the tensile strength of the GO/PVA nanocomposite films increased to twofold higher than that of nacre at the expense of ductility. Despite the great progress in the mechanical properties of crosslinked GO/polymer nanocomposites, the effect of crosslinking on the gas barrier performance of nanocomposite films has not been systematically investigated. To improve the barrier performance without sacrificing the transparency, we learn from nature to apply borate ions for cross-linking to fabricate PVA/GO films. Higher-order plants utilize borate for cross-linking structural polysaccharide rhamnogalacturonan II (RG II) to strengthen their intercellular structure [24]. An et al. [25] indicated that GO films cross-linked with borate have an ordered structure similar to that of the plant cell wall. Zhao et al. [26] prepared a polyelectrolyte/GO composite film with a brick-and-mortar structure, which shows high mechanical and barrier properties. We expect that PVA/GO films formed from cross-linking with borate would also have an ordered and dense impermeable structure similar to that of the plant cell wall or the brick-and-mortar structure. Fig. 11 depicts the formation of PVA/GO composites from cross-linking with borate. It indicates that oxygen permeability can be reduced as a result of the cross-linking between GO and PVA, which blocks the spaces in the PVA/GO film; thus, when $O_2$ was passed through the composite film, it wiggled and followed a much longer gas diffusion pathway, leading to an ultra-low permeability. To the best of our knowledge, no publications have been devoted to the effects of chemical cross-linking on the barrier properties of PVA/GO composites. This study used borate ions to cross-link PVA and GO, which enhanced the interfacial adhesion. Bio-inspired cross-linking networks were produced, and they improved the barrier properties of PVA/GO composites. A simple technique that combines solution blending and cross-linking methods was used to prepare PVA/GO composite films consisting of borate cross-linkers.

## 2. Experimental

### 2.1. *Synthesis of GO*

We used modified Hummers' method [27,28] to synthesize GO. First, 2.0 g $NaNO_3$ and 280 mL concentrated $H_2SO_4$ were mixed in a flask, with continuous stirring for 2 h, to obtain a clear solution. Next, 4.0 g graphite powder (SFG44 from TIMCAL) was added into the flask, which was then placed in an ice bath, before adding 16 g $KMnO_4$ slowly into the mixture. (Caution! $KMnO_4$ is highly reactive and should be handled