



# Bio-inspired layered nanolignocellulose/graphene-oxide composite with high mechanical strength due to borate cross-linking



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## ABSTRACT

Inspired by the borate cross-linking used by higher plants to strengthen their intercellular structure, high mechanical strength-layered composites based on borate cross-linked nanolignocellulose/graphene-oxide platelets were developed. Borate treatment and graphene deposition on nanolignocellulose surface were carried out by a mechanochemical method. The borate content is used in very low in these composites. The orderly layered structures produced by the flow-directed assembly of individual nanolignocellulose/graphene oxide platelets resulted in a synergistic toughening effect. The bending strength and elasticity modulus of the produced composites were ~1.5 times higher than those of pure nanolignocellulose; they were also superior to those of lignin-based materials and comparable to those of medium density fiberboard (MDF) with resin. Such high-strength layered composites have potential as load-bearing materials in structural applications.

## 1. Introduction

In nature, higher plants depend on microcosmic strong cell walls to develop into self-supporting macroscopical organisms. It has been demonstrated that borate linkages are necessary for forming reinforced intercellular networks (Fig. 1); borate ions are an essential micro-nutrients for many vascular plants (And and Lukaszewski, 1998; Bolaños et al., 2004), and their deficiency causes many changes in the mechanical and physiological properties of plant tissues (Hu and Brown, 1994; O'Neill et al., 2001). Borates form covalent bonds with oxygen-containing functional groups, and lead to cross-link in plants tissues; they are also critical nutrients for almost all plant species that require mechanical integrity (O'Neill et al., 1996).

Lignocellulose is obtained from agricultural and forestry products, including agro-industrial residues, forest-industrial residues, energy crops, municipal solid waste, and other, has attracted increasing interest as a substitute for synthetic materials because of its rich and sustainable substances (Stolarski et al., 2015; Theng et al., 2015). Over the past few decades, it has attracted much interest as a substitute for synthetic materials, in particular, as a filler and reinforcing material in composites (Diop et al., 2017). At low concentrations, borate can enhance the structure of the cell-to-cell movement in higher plants by cross-linking the structural polysaccharide rhamnogalacturonan II (RG II) (O'Neill et al., 2001); this phenomenon increases the height of the

cell wall and supports the entire plant (Taiz and Zeiger., 2010). During mechano-chemical processing, lignocellulose undergoes splitting, breaking, deformation, volumetric changes, and other physical changes. With a gradual reduction in its size, the specific surface area continues to increase, resulting in nanolignocellulose (NLC), whose energy conversion properties, internal structure, physical and chemical properties are different from those of the parent lignocellulose (Xie et al., 2013).

The surfaces and edges of two-dimensional graphene oxide (GO) contain a large number of oxygen-containing functional groups (Cheng et al., 2015; Cheng et al., 2013; Gong et al., 2015), which are similar to those of two-dimensional simulations of carbohydrate polymers; therefore, GO is the best candidates for synthesizing high-performance layered composites (Li et al., 2012; Gong et al., 2016; Song et al., 2017; Yan et al., 2016). The two-dimensional (2D) and 1D building blocks act in a synergistic fashion for extraordinary strength and toughness produced by the sliding of platelets and fiber, crack deflection, and crack bridging (Wan et al., 2016; Wan et al., 2015). Although great progress has been achieved in enhancing the tensile mechanical properties of layered composites (Wan et al., 2017; Zhang et al., 2016a, 2016b), there are very few reports on layered composites with excellent bending strength. It has been reported that borate ions can be employed to cross-link NLC and graphene oxide to form a layered composite with strong interfacial interactions between NLC and GO (Yao et al., 2017), akin to

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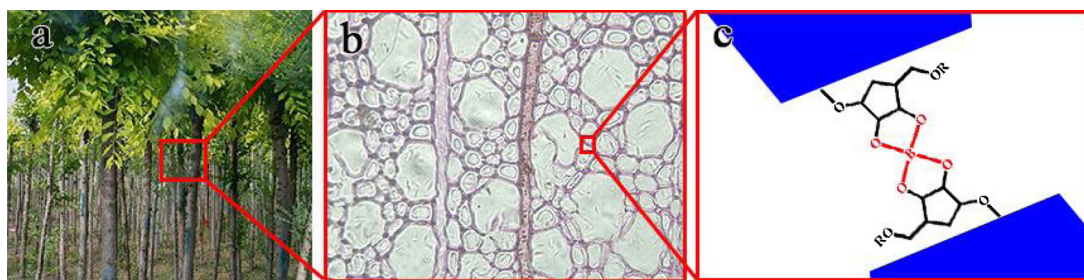


Fig. 1. (a) Digital picture of *populus tomentosa*. (b) Electron microscopy image of a section of *populus tomentosa*. (c) Schematic of borate crosslinking contiguous cell walls in *populus tomentosa*.

the monolayer polysaccharide chain on plant cell walls (And and Lukaszewski, 1998). The long borate cross-links provide enough space for the movement of NLC/GO platelets during loading and absorb high amounts of energy.

In this investigation, we tried to develop a multivariate chemistry by linking graphene nanosheets and NLC in a layered form through covalent bonds. It is noted that by mechano-chemical treatment with a minute amount of borate (0.1 M), in combination with flow-directed assembly, increased the strength of borate-modified NLC/GO (B-NLC/GO) layered composites by 76.5% compared to untreated NLC composites. Such excellent augmentation in mechanical properties by the incorporation of trace quantities of borate sets apart our B-NLC/GO composites from other polymeric-cross-linked materials (Chen et al., 2017).

## 2. Materials and methods

### 2.1. Materials

Lignocellulose sourced from *Populus tomentosa* plants, was ultrasonically rinsed in deionized water (DI) for 25 min and dried at 80 °C for 24 h. GO sheets were supplied by XianFeng Nano Co., Ltd. Sodium tetraborate decahydrate was used as received from Shang Hai Aladdin Industrial Co., Ltd.

### 2.2. Fabrication of layered B-NLC/GO composites

Lignocellulose mixed with 0–2 wt.% graphene oxide was gradually added to a fresh sodium borate solution in water (0.001–0.4 M; total amount of borate combined with B-NLC/GO composite is shown in Table S1). The prepared suspension (1 L, 30 g/L) was refined in a colloid grinder with the rotor speed set at approximately 2880 rpm for 6 h. Later, the homogeneous B-NLC/GO mixture was vacuum filtered to prepare the stacked B-NLC/GO sheets. In the initial stages of filtration, NLC/GO sheets were forced rapidly onto the surface of the filter paper by water flow and randomly assembled (folded, crumpled, and wrinkled). As such, layers of NLC/GO platelets assembled at this stage were not particularly well-packed or arranged. After a short time, the filter was clogged by the deposition of NLC/GO sheets, and the water flow slowed considerably. Finally, layered B-NLC/GO composites were prepared by hot-pressing at a pressure of 120 °C under 2.5 MPa for 30 min.

### 2.3. Characterization

Boron concentration in the composites was measured at the IMSERC facility at Northwestern University (NU, USA) using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Varian Vista-MPX instrument, Varian, Inc., Palo Alto, CA, USA) equipped with a plastic sample introduction stage. The morphology of the B-NLC/GO composites was studied using scanning electron microscopy (SEM; Quanta FEG 250, USA) and transmission electron microscopy (TEM; Tecnai G2 F20, USA). Fourier Transform infrared spectroscopy (FTIR,

Nicolet 5700, USA) were collected in were recorded in the range of 400–4000  $\text{cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Fisher K-Alpha to characterize the valence states of the elements and compositional depth profiles of the composites. Solid-state  $^{11}\text{B}$  magic angle spinning-nuclear magnetic resonance (MAS NMR) spectra were collected at the IMSERC facility at NU on a 400-MHz solid-state NMR spectrometer. Raman spectroscopy was conducted on a multi-wavelength micro-Raman spectroscopy (Renishaw RM2000) using 532-nm incident radiation and a  $500\times$  aperture. The mechanical properties of the composites were evaluated on a dynamic mechanical analyzer (DMA; DMTA, TA Q800, USA), operating in a three-point bending mode. Isochronal scans were recorded from 30–260 °C at a heating rate of 2 °C  $\text{min}^{-1}$ , frequency of 1 Hz of frequency and amplitude of 15  $\mu\text{m}$ . The sample dimensions were 60 mm  $\times$  10 mm  $\times$  3 mm. A reducing force mode was engaged to adjust the static force during the test, minimizing creep. Dry nitrogen was continuously circulated in the DMA oven to limit water sorption during experiments. The three-point bending tests were performed using an Instron 3382 machine. The dimensions of the specimens for the bending test were 60 mm (length)  $\times$  10 mm (width)  $\times$  5 mm (thickness), and the loading rate was 0.05 mm  $\text{s}^{-1}$  up to failure. Ultraviolet spectrum was conducted on an ultraviolet and visible spectrophotometer (TU-1901, China).

## 3. Results and discussion

The fabrication process of layered B-NLC/GO composites is illustrated in Fig. 2. Lignocellulose and GO sheets were first dispersed in a sodium borate solution (0.1 M), after which the formed suspension was added to a colloid grinder. At this stage, lignocellulose undergoes splitting, breaking, and refinement to nanoscale; the GO sheets were adhered on the NLC surface by hydrogen bonding at the same time. When the final suspension was vacuum-filtered through a membrane, some of the borate initially passed through. However, the deposition of NLC/GO platelets quickly impeded the passage of borate through the membrane. The newly formed B-NLC/GO composite reduces the loss of borate and led to its homogeneous deposition within the laminated composite. When the thickness of the composite increased, the B-NLC/GO platelets were deposited on top of the composite (Putz et al., 2010). The incorporation of borate ions induced the formation of covalent borate orthoester bonds with NLC and the GO sheets via the hydroxyl groups on the surface of the composite. Finally, layered B-NLC/GO composites were prepared by a hot-pressing process, which formed additional cross-linking covalent bonds by dehydrating the sample.

Fig. 3a shows a SEM image of the NLC/GO composite. It can be observed that the GO sheets were embedded in the interconnected networks of NLC. After borate treatment (Fig. 3b), the number of GO sheets loaded on NLC significantly increased, which resulted in a decrease in the porosity of B-NLC/GO composites. The TEM images (Fig. 3c) of B-NLC/GO composites further confirmed that GO sheets were inserted into the NLC network to form ultrathin sheets. The diameter of individual NLC domains was about 330 nm. More importantly, the composition of the NLC/GO composite and B-NLC/GO composite

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