Bio-Based Artificial Nacre with Excellent Mechanical and Barrier Properties Realized by a Facile In Situ Reduction and Cross-Linking Reaction

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Supporting Information

ABSTRACT: Demands for high strength integrated materials have substantially increased across various kinds of industries. Inspired by the relationship of excellent integration of mechanical properties and hierarchical nano/microscale structure of the natural nacre, a simple and facile method to fabricate high strength integrated artificial nacre based on sodium carboxymethylcellulose (CMC) and borate cross-linked graphene oxide (GO) sheets has been developed. The tensile strength and toughness of cellulose-based hybrid material reached 480.5 ± 13.1 MPa and 11.8 ± 0.4 MJm⁻³ by a facile in situ reduction and cross-linking reaction between CMC and GO (0.7%), which are 3.55 and 6.55 times that of natural nacre. This hybrid film exhibits better thermal stability and flame retardancy. More interestingly, the hybrid material showed good water stability compared to that in the original water-soluble CMC. This type of hybrid has great potential applications in aerospace, artificial muscle, and tissue engineering.

KEYWORDS: bio-based, artificial nacre, in situ reduction and cross-linking, graphene oxide, high strength and toughness

Natural composites of seashell nacre and bones with hierarchical micro- and nanostructures have been studied for at least half a century due to their extraordinary mechanical properties, complemented by rare biological functionalities.¹⁻³ Consequently, several strategies (e.g., layer-by-layer (LBL) deposition, freezing–drying, and filtration) were proposed to mimic them,⁴⁻⁶ especially nacre that possessed ordered brick-and-mortar arrangement of inorganic nanotablets (95 vol %) and a small amount of biomacromolecules.⁵ Inspired by the intrinsic relationship between the structures and the mechanical properties lying in the natural nacre, different types of nacre-like layered nano-composites have been fabricated with two-dimensional (2D) inorganic additives, including glass flakes,⁷ alumina flakes,⁸ graphene oxide,⁹ layered double hydroxides,¹ nanoclay,¹ and flattened double-walled carbon nanotubes.¹⁰ Recently, 2D graphene has attracted much research interest owing to its outstanding electrical, thermal, and mechanical properties,¹¹ and many graphene-based devices have been fabricated¹² such as bulk composites,¹³ one-dimensional fibers,¹⁴ and supercapacitors.¹⁵ As the water-soluble derivative of graphene, graphene oxide (GO), with many functional groups on the surface, is one of the best candidates for fabricating artificial nacre because functional surface groups allow for chemical cross-linking to improve the interfacial strength of the adjacent GO layers. Until now, several methods have been developed to functionalize individual GO sheets and enhance the resultant mechanical properties, including divalent ion (Mg²⁺, Ca²⁺) modification,¹⁶ polyaallylamine¹⁷ or alkylamine functionalization,¹⁸ glutaraldehyde (GA) treatment,¹⁹ π–π interaction,¹⁹ and hydrogen bonding.²⁰ Although the obtained strength and stiffness are significantly enhanced, graphene introduction in their presence in very small quantities (~0.001–0) of polymer to obtain desirable results for strength requires more studies. In nature, self-supporting macroscopic organisms, especially the higher plants, rely on the combined microscopic stiffness and strength of plant cell walls. These cellular building blocks depend heavily on borate...
chemistry to form reinforced intercellular networks. For the healthy growth of many plants, borate is required, where 0.01 dry wt % significantly increases the mechanical properties of plant tissue. Borate ions have the ability to form covalent bonds with oxygen-containing functional groups in counterion environments and with different pH that makes it the cross-linker of choice in plants and a vital nutrient for nearly all plant species that require mechanically sound structures. In this paper, inspired by borate chemistry in natural plants and strength enhancement in GO sheets, we employed a simple in situ reduction and cross-linking reaction to fabricate a hybrid film composed of GO and sodium carboxymethylcellulose (CMC). This hybrid bio-based film can exhibit an artificial nacre structure, although the amount of GO is very small (0.7%). Importantly, this hybrid system shows great improvement in mechanical properties only by in situ reduction and cross-linking. The strength and toughness can reach 480.5 ± 13.1 MPa and 11.8 ± 0.4 MJm$^{-3}$, respectively, which is about 3.55 and 6.55 times that of natural nacre. At the same time, the barrier property can be dramatically improved by this method.

RESULTS AND DISCUSSION

In a typical preparation, GO was synthesized by Hummers’ method. Well-dispersed CMC–GO borate-linked nanocom-
posites were fabricated by a simple solution-casting technique followed by cross-linking phenomena to obtain a desirable film with high strength, thermal stability, water stability, and good barrier properties. A possible mechanism for the hybrid is shown in Figure 1, in which graphene layers after cross-linking with borate strongly interact with CMC through hydrogen bonding. This dual binding effect of boron covalent bonding with hydroxyl moieties of GO and hydrogen bonding interactions between GO and CMC plays an important role in film properties.

Figure 2 shows the scanning electron microscopy (SEM) images for the cross sections of the hybrid film. Compared with the smooth surface of pure CMC in Figure S1 (Supporting Information), a clear layered structure appeared when the GO concentration reached 0.7%, which suggests that a self-assembly of GO in the film happens. The nanostructure of the hybrid films clearly indicates the graphene layers. These layers are compactly arranged in all hybrid films containing different concentration of graphene oxide with borate (0.09%) (Figure 2a) and film without borate (Figure 2b).

Furthermore, when the concentration of GO increases to 4.9%, the SEM (Figure 2c) shows that the layered structure disappears, which indicates that the GO could not be dispersed very well when the concentration of GO was increased. SEM-EDS (energy-dispersive spectroscopy) mapping and EDS spectra were also employed to confirm the presence and distribution of B element in the hybrid film, as shown in Figure 2d,e. It should be noticed that the intersheet spacing in cross-linked hybrid films seems to be less than that in the film without cross-linking. These closely packed layers may have played a role in enhancing film strength. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectra were also employed to characterize the structure of hybrid films and CMC.

Figure S2 (Supporting Information) shows XRD diffractions of graphite, GO, CMC, and hybrid films. The XRD peak of GO was at approximate 2θ = 10.66, proving successful oxidation of graphite. CMC showed a broad peak at 2θ = 22.39, indicating semicrystalline structure.26 It should be noticed that these hybrid films with low concentrations of GO (<2.9%), with the diffraction peak at 2θ = 10.66 attributed to GO, was absent, suggesting exfoliation of GO in modified films. When the concentration of GO was increased to 4.9%, the hybrid film showed the peak of GO indicating the accumulation of GO in the film, which was also confirmed by SEM (Figure 2c). FTIR analysis for the hybrid films prepared under different conditions is presented in Figure 3. Pure CMC displayed peaks at 1050, 1440, and 1600 cm⁻¹ corresponding to C=O stretching, asymmetrical modes, and symmetrical modes of carboxylate ions, respectively26 in Figure 3a,5. Characteristic peaks appearing at 1724, 1040, 1630, and 3370 cm⁻¹ for pure GO were attributed to C=O, C−O, C=C, and OH stretching, respectively27 (Figure 3b,3). Interestingly, it was found that when the reaction system was heated above 90 °C, the GO peak at 1724 cm⁻¹ attributed to C=O was not present in the hybrid films, indicating partial reduction as some oxygen-containing groups were removed from the hybrid film.28 Additionally, a slight color change took place in the hybrid film when the temperatures were greater than 90 °C (Figure S3, Supporting Information), which also indirectly gives proof for the reaction between the GO and CMC. When the sample was further cross-linked with borate, an additional peak was observed at 1110 cm⁻¹ that can be attributed...
Furthermore, stretching frequencies of CMC shifted to high energy in all hybrid films (e.g., 1440 cm$^{-1}$ shifted to 1450 cm$^{-1}$ and 1600 cm$^{-1}$ to 1610 and 1620 cm$^{-1}$), which was more prominent and showed strong H-bonding between GO and CMC (Figure 3a). Further color change can be observed (Figure S3). For the borate cross-linked film, the peak at 1110 cm$^{-1}$ attributed to tetrahedral borate became broad when the temperature was increased, which suggested that the cross-linking between the borate and GO can be accelerated at relatively high temperature (Figure 3c).

The cross-linking was also investigated by X-ray photoelectron spectroscopy (XPS) measurements. Figure 3b shows the XPS survey spectra for unmodified and modified films with 0.7% GO + CMC and 0.7% GO + CMC + 0.09% borate. Peaks at 284.8, 286.5, and 286.8 eV can be attributed to C=C, C–OH, C–O–C, respectively. The C 1s XPS spectrum of modified film reveals a large decrease in C–OH hydroxyl signals that are clearly present in unmodified film, suggesting successful cross-linking of borate with a hydroxyl group of GO. Furthermore, peaks for C–O–C in modified film were reduced prominently, indicating that removal of oxygen-containing species could play a role in the partial reduction of GO. To further verify the reduction of GO, the Raman spectra were also employed (Figure 3c). The Raman spectra of GO in all hybrid films showed two peaks at 1340 cm$^{-1}$ (D band) and 1598 cm$^{-1}$ (G band) that can be assigned to first-order scattering of the $E_{2g}$ phonon of sp$^2$ carbon atoms and the size of in-plane sp$^2$ domains, respectively. It is found the D/G intensity ratio (1.7 for GO–CMC + borate at 90 °C, 1.3 and 1.4 for GO + CMC films at 90 and 120 °C, and 1.2 for GO) increased gradually when the reaction temperature was increased or the film was cross-linked with borate. This increase in D/G intensity ratio that is actually due to an increase in the number of sp$^2$ domains further confirms GO reduction in CMC with borate. So, based on the above analysis, the reaction temperature and borate addition played an important role in GO reduction in our process.

At last, UV−vis spectra were employed to characterize the sample of hybrid films prepared in different reaction temperatures (Figure S3, Supporting Information). It is found that the sample exhibited the same peak centered at 233 nm with GO ($\pi$ → $\pi^*$ transitions of the aromatic C=C bonds) when the sample was prepared under lower temperature (<60 °C). This peak shifted to 270 nm for hybrid films with a reaction temperature of 90 and 120 °C, indicating the reduction of graphene oxide. Additionally, it is found that borate introduction can also accelerate this process, as indicated by the color change (Figure S3, Supporting Information). These results were also in accordance with the above analysis. Typical stress−strain curves of the prepared samples are shown in Figure 4a. Tensile strength and toughness of pure CMC were 96.1 ± 4.6 MPa and 3.2 ± 0.8 MJm$^{-3}$, respectively. It was found that the tensile strength and toughness can be dramatically enhanced by introduction of GO. When the GO (0.7%) was introduced into the film at room temperature, the tensile strength and toughness of the hybrid films were 187.3 ± 15.6 MPa and 4.9 ± 0.8 MJm$^{-3}$, respectively.

Figure 4. Stress−strain curves. (a) From 1 to 6 for CMC, CMC + borate, 0.7% GO–CMC at room temperature, 0.7% GO–CMC at 60 °C, 0.7% GO–CMC at 90 °C, 0.7% GO–CMC + borate at 90 °C. (b) Tensile strength and toughness comparison of hybrid film with other reported nanocomposites. (c) Proposed synergistic mechanism for modified film. (d) SEM image for fracture morphology; inset shows modified film with microcrack extension where GO sheets are pulled out.
film can reach 320.5 ± 6.5 MPa and 8.3 ± 0.5 MJ m⁻³. The strong hydrogen bonding between the GO and CMC chain increases the interfacial strength of the resultant nanocomposites. These results are also similar to previous reports.³⁴,³⁵ Interestingly, when the solution containing the GO and CMC was heated above 90 °C, the color of the obtained film changed into a slightly deep color due to the in situ reduction reaction, and the tensile strength and toughness of the hybrid film was increased to 411.0 ± 10.2 MPa and 10.8 ± 0.5 MJ m⁻³ respectively. Compared with pure CMC film, the tensile strength and toughness of the hybrid film were increased 4.28- and 3.38-fold, respectively (Figure 4a). It is believed that such great improvement is mainly attributed to the following reasons, except the hydrogen bonding. (I) Strong interaction caused by in situ reduction. Compared to GO, reduced GO can improve the tensile strength dramatically in polymer-like CMC.³⁶,³⁷ This is because GO does not efficiently combine with CMC due to the repulsive interaction of oxygen-containing functional groups on the surface of GO nanosheets and CMC. Reduced GO, other than hydrogen bonds, also has strong van der Waals forces for the improved interaction with CMC. The decrease in interlayer distance between graphene nanosheets after removal of some oxygen-containing groups and π-interactions between GO and CMC can play important roles in improved film strength.³⁸,³⁹ In our experiment, it was proven by FTIR, Raman, XPS, and UV–vis spectra that the in situ reduction of GO took place when the temperature was above 90 °C (see Figure 3 and Figure S2, Supporting Information). The film prepared with high temperature will increase film strength from 320.5 ± 6.5 MPa (room temperature about 20 °C) to 411.0 ± 10.2 MPa. At the same time, the obtained film is stable enough in water for more than 1 h, as shown in Figure S4 (Supporting Information) due to the hydrophobic character of reduced GO, while the CMC film will be destroyed within 30 min. This can be attributed to GO reduction in the polymer under different reaction temperatures.⁴⁰–⁴² Based on the above analysis and results, it is safe to say the in situ reduction plays an important role in increasing the mechanical performance of the GO–CMC hybrid film. (II) Good dispersion of GO in CMC with relative high molecular weight. CMC with low molecular weight can reduce the mechanical performance of the obtained film (Figure S4, Supporting Information). Three types of CMC with different molecular weight (700, 250, and 90 kg/mol) in our hybrid film for tensile strength enhancement were investigated, keeping other experimental conditions constant, as shown in Figure S4 (Supporting Information). The tensile strength was increased from 265.5 ± 11.5 to 411.0 ± 10.2 MPa when the molecular weight of CMC was increased from 90 to 700 kg/mol, indicating that the mechanical performance of the bio-hybrid film can be improved with high molecular weight CMC. This is because high molecular weight CMC can have more intralink GO nanosheets compared to low molecular weight CMC. That requires more energy to induce interlayer slippage with increasing stress. However, for high molecular weight CMC, the dispersion of GO is a great challenge. Our relatively low-temperature heating method improved graphene oxide dispersion in the CMC. It is found the viscosity of CMC can be reduced and flow ability was improved when the temperature was increased (Figure S4, Supporting Information). Such a technique was also recently reported to enhance the dispersion of graphene oxide in polymers to obtain a remarkable increment in film mechanical properties.⁴³ Additionally, in our experiments, when the concentration of GO in the solution was increased from 0.3 to 4.9%, the strength of the obtained film was also reduced to 260.0 ± 4.8 MPa and 6.4 ± 0.8 MJ m⁻³ due to the accumulation of GO.
in the film (Figure S5, Supporting Information), which was observed by SEM (Figure 2c). These results are similar to previous reports; when GO concentration exceeds 3%, it started to agglomerate in the polymer.14–16 Furthermore, less concentration of GO in our media does not affect the final thickness of the films and was controlled (30–40 μm) by taking an equal volume of solution (Figure S6, Supporting Information). Thus, by controlling GO dispersion in CMC with high molecular weight using a smart technique may be an important building block for high strength GO–CMC artificial nacre hybrid films.

In nature, small quantities of borate can significantly increase the mechanical properties of plant tissue. In our system, when a trace amount of borate was introduced, the strength and toughness was further improved (Figure 5c). Like plants, borate ions can make covalent bonds with oxygen-containing functional groups in our film. Only a small amount of borate can increase film strength due to strong hydrogen bonding between GO sheets and borate ions through ester bond formation.24 When 0.09% borate was introduced, the tensile stress and toughness for 0.7% GO + CMC was 480.5 ± 13.1 MPa and 11.8 ± 0.4 MJm−3, respectively, which is comparable with steel.9 When boron concentration was increased further, the strength reduced gradually due to aggregation of borate ions. To check the role of borate in the hybrid film, we also fabricated and evaluated CMC films cross-linked only with borate.

Tensile strength for CMC + borate improved from 96.1 ± 4.6 to 128.5 ± 5.6 MPa (Figure 4a,2), indicating that the borate can improve the strength of CMC by cross-linking but not as much as the reduced GO. It is well-known that the hydrophilic film, such as CMC, was sensitive to humidity. Tensile stress for pure CMC is reduced from 96.1 ± 10.5 to 65.5 ± 5.8 MPa when the humidity was reduced from 20 to 50% (Figure S4, Supporting Information). The GO introduction still cannot reduce the sensitivity of humidity due to its hydrophilic character. For the film of 0.7% GO + CMC, the tensile stress was reduced from 407 ± 5.5 to 358 ± 10.1 MPa under a humidity change from 20 to 50% (Figure SSc, Supporting Information). When the hybrid film was reacted and cross-linked with a small amount of borate, the mechanical property remained almost unchanged, indicating that the borate cross-linking played an important role in maintaining its mechanical property at high humidity when compared to unmodified film (Figure SSc, Supporting Information). A possible mechanism for the hybrid film is illustrated in Figure 1. Like GO, CMC also has hydroxyl and carboxylate groups that can interact with GO by hydrogen bonding.47 The borate can cross-link with hydroxyl moieties present on GO and produce H-bonding interactions with CMC. In our bio-based hybrid film, only a slight amount of GO (0.7%) and borate (0.09%) can give excellent improvement in mechanical properties. Dual binding effect of CMC with GO sheets by hydrogen bonding and close-packed GO sheets by reduction of space due to borate cross-linking gives the film excellent performance. Compared to other nacre-inspired nanocomposites, the tensile strength of this bio-based hybrid film increased 3.55 times that of natural nacre (80–155 MPa),48 1.22 times that of montmorillonite (MTM) cross-linked with PVA (400 MPa),21 1.52 times that of Al2O3–chitosan composites (315 MPa),22 2.99 times that of GO–PVA composites (162 MPa),49 2.33 times that of GO–chitosan (206 MPa),50 and 3 times that of a GO–borate cross-linked composite (160 MPa).24 The synergistic toughening of borate cross-linked GO and CMC offered the advantage of high strength and toughness compared with those of other nanocomposites (such as GO–PMMA,51–53 GO–PVP,54 rGO–GA,52 GO-MgCl2,55 rGO–PAPB,54 rGO–GA,52 rGO–PCDO,56 rGO–PDA,55 MTM–PVA,57 rGO–DWNT–PCDO), as shown in Figure 4b. The typical proposed fracture morphology of our nacre-like nanocomposites is shown in Figure 4c. In the early stretching process, the hydrogen bonding among the CMC molecules is destroyed, accompanied by the slippage between adjacent CMC molecules, and the GO nanosheets resist the sliding, resulting in the stress uniformly being dispersed in the GO nanosheets and CMC. Meanwhile, much more energy is dissipated in the process of stretching CMC molecules. The CMC molecules are stretched from the surface of GO after a further stretching process. Further loading results in the breaking of covalent cross-linking between borate and GO nanosheets and curved edges of GO nanosheets (Figure 4d). It is clearly shown that the GO nanosheets were curved in the bio-based nanocomposites. Additionally, it was found that the tensile strength can be controlled by the preparation temperature (reaction temperature or drying temperature) (Figure 5b). The film prepared with a relatively higher temperature (>90 °C) can improve the mechanical performance, and drying under mild temperature (40–60 °C) can also obtain a relatively better mechanical performance. These results also give indirect proof that the reduction and cross-linking take place among the GO, borate, and CMC, which agrees well with FTIR, XPS, Raman spectra, and UV analysis. Most interestingly, the borate cross-linked hybrid film was so stable in water that it can keep its shape for more than 1 week, while the sample without borate will dissolve after 2 h, as shown in Figure 5c. That is to say, water-resistant bio-based film can be synthesized from water-soluble CMC. Graphene is believed to be impermeable to all gases and liquids, which makes it tempting to exploit this material as a barrier film.57 The gas barrier properties of the modified films are also characterized Figure S7ab (Supporting Information), demonstrating the effect of GO loadings on barrier properties of fabricated film. The GO introduction results in ultralow gas permeability. The oxygen permeability for hybrid film at 45% RH containing only 0.7% GO and 0.09% borate decreased from 0.0216 to 0.009 mL μm·m−2·day−1·kPa−1. While films with 4.9% GO had even lower value of 0.0009 mL μm·m−2·day−1·kPa−1. The oxygen permeability was markedly lower (less than 1 order of magnitude lower) than that of commercial ethylene–vinyl alcohol copolymer films (0.001 to 0.01 mL μm·m−2·day−1).
kPa⁻¹), which are commonly used as oxygen barrier films.⁵⁷ Like oxygen permeation, these closely packed layered structures of GO and borate in CMC also helped to reduce the penetration of water molecules, as water vapor permeability improved with increased concentration of GO, as shown in Figure S7b (Supporting Information). It decreased from 0.363 to 0.201 gm·mm⁻²·day⁻¹·kPa⁻¹ for films containing 0.7% GO and 0.09% borate. The maximum concentration of GO (i.e., 4.9%) could reduce water vapor permeability at 0.179 gm·mm²·day⁻¹·kPa⁻¹. These improved barrier properties in formulated film can be due to tortuous pathways present in layers of GO and CMC for both gas and water diffusion.⁵⁸ It is known that GO platelets show good fire retardancy properties due to its rigid carbon net. The thermal stability of the bio-based hybrid nanocomposites is also good. Figure 6a–c illustrates the fire retardancy characteristics for the hybrid film and pure CMC. When exposed to fire, the surface of the CMC film quickly burned after a few seconds, and the shape of the sample was completely destroyed. For the hybrid film, the flame was extinguished after a few seconds and the shape remained even after 1 min exposure to the flame (Figure 6b). Limited oxygen index (LOI) values for pure CMC, 0.7% GO + CMC, and 0.7% GO + CMC + 0.09% borate are 23.83, 27.34, and 28.30%, indicating that the GO and a trace amount of borate can indeed improve the retardant property of the hybrid film.

The integrity of the hybrid after burning can be attributed to the film’s thermal stability and a trace amount of boron,⁵⁸ which was confirmed by the thermogravimetric analysis shown in Figure 6d. These cross-linked compact GO layers providing hindrance for flame penetration and gas may help to enhance film performance.

CONCLUSION

In conclusion, inspired from natural nacre, we successfully fabricated a bio-based hybrid film with the structure of artificial nacre by a facile in situ reduction and cross-linking reaction between carboxymethylcellulose and graphene oxide. The artificial nacre showed excellent mechanical and barrier properties. The tensile strength and toughness of bio-based hybrid material reached 480.5 ± 13.1 MPa and 11.8 ± 0.4 MJm⁻³ only by introduction of a small amount of graphene oxide (0.7%) and borate (0.09%), which is 3.55 and 6.55 times that of natural nacre. Additionally, the barrier property of bio-based film can be improved dramatically due to its exclusive structure. The oxygen permeability for the hybrid film can reach 0.0009 mL·μm·m⁻²·day⁻¹·kPa⁻¹, which is 1 order of magnitude lower than those of commercial ethylene–vinyl alcohol copolymer films. At the same time, the barrier property and stability for water was also improved greatly due to its compact and tortuous structure, although the bio-based (CMC) film has hydrophilic characteristics. Our strategy would definitely provide a good method to design and fabricate some stronger and more ductile materials used in fields of electronics, aerospace, packaging, and medicine with green and renewable raw materials.

METHODS

Materials. Graphite powder (<20 μm) was from Sigma–Aldrich, and sulfuric acid (98%), hydrogen peroxide (30%), potassium permanganate (99.5%), and disodium tetraborate decahydrate (99.5%) were received from Sinopharm Chemicals Reagents Co. Ltd. NaCMC with different molecular weights (700, 250, and 90 kg/mol) were obtained from Aladdin Reagents (Shanghai) Co. Ltd. Deionized water with resistivity of 18 MΩ·cm produced by Milli-Q was used for all solution preparation.
Preparation of Graphene Oxide. GO was prepared from natural graphite powder by a modified Hummers’ method.21 The obtained GO was not dried and used directly in the form of solution. The concentration of GO in this solution was calculated by drying it at 120 °C overnight to remove any water content. GO concentration was maintained from 0.3 to 4.9% in hybrid films.

Preparation of CMC/GO Hybrid Films Cross-Linked with Borate. These hybrid films were synthesized in two steps. First, a clear 2% solution of CMC was prepared at room temperature with constant mixing. Second, GO with different concentrations ranging from 0.3 to 4.9% was added slowly, and after a homogeneous mixture was obtained, it was reacted and cross-linked with a 0.09% borate heating solution at 90 °C for about 8 h. Prominent color change of GO was observed at this stage. Equal volumes of this solution containing different concentrations of GO with borate and blank without GO and borate were poured into plastic Petri dishes and dried in the oven at 40 °C overnight.

Characterization. Film surface morphology was studied by SEM with a Hitachi S-4800 (Japan) with EDS mode. The films were frozen under liquid nitrogen, and after being vacuum-dried, cross sections of films were coated with gold and then observed. XRD experiments were carried out with a Bruker D8 Advance diffractometer (Germany). The recorded region of 2θ was from 5° to 30° with a scanning speed of 2°/min. FTIR spectroscopy was used to obtain spectra (Thermo Scientific Nicolet IN10 USA). XPS measurements were performed on an ESCALAB 250Xi photoelectron spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with Al Kα X-ray radiation as the X-ray source for excitation. Tensile tests of film samples were performed using a universal testing machine equipped with a 500 N load cell at room temperature and an average humidity of 20%. Film thickness (Figure S6, 35–40 μm) was first measured with SEM, which was found to be consistent with the surface profilometer (Veeco Dektak 150). The Vernier calliper was used to make sure that the thickness of the sample prepared with the same volume solution was in the range of 30–40 μm. Rectangular strips with a size of 2 × 30 mm were cut and analyzed with a span length of 10 mm at a rate of 1.0 mm/min; almost five samples were tested to check the reproducibility. Thermogravimetric analyses were performed on a Rubotherm Dynatherm HP (Germany) using the temperature range from 20 to 700 °C with a heating rate 10 °C/min. UV–visible spectra of the samples were measured on a UV–vis spectrophotometer (Hitachi U-4100). The water vapor permeability (WVP) was determined according to the ASTM E 96/E 96 M-05 standard. Approximately 3.0 g of CaCl₂ was used in a cylindrical bowl and then covered with the studied film attached with tape. Water vapor permeation (g·mm-1·kPa-1) was recorded for 7 days and calculated by the equation, WVP = mL/At × ΔP, where m is the weight of water permeated through the film, L is the thickness of film, A is permeation area, t is the time, and ΔP is the water vapor pressure difference between both sides of the film. Oxygen permeability measurements were determined at 45% humidity using a PERME-OX2/230 analyzer. LOI values were calculated on a JF-3 flame meter (Jiangning in Nanjing City) according to the method of GBT 24062–2009: at least five samples for each formulation were tested. The dimensions for each sample were 70–100 mm × 6.5 mm × 3 mm.

ASSOCIATED CONTENT

Supporting Information
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SEM and SEM-EDS mapping for blank, XRD patterns of graphite, GO, 0.3% GO + CMC, 0.7% GO + CMC, 0.7% GO + CMC + 0.09% borate, 1.1% GO + CMC + 0.09% borate, 2.9% GO + CMC + borate, 4.9% GO + CMC + borate and blank, UV–vis spectra for GO, CMC, GO–CMC and 0.7% GO + CMC + 0.09% borate at different reaction temperatures; stress–strain curves for CMC and 0.7% GO–CMC with different molecular weights, CMC–GO homogeneous mixture after heating at 90 °C and water stability comparison of CMC and 0.7% GO–CMC with different concentration of GO (1), for 0.7% GO–CMC (2), 1.1% GO–CMC (3), 2.9% GO–CMC (4), 0.3% GO–CMC (5), 4.9% GO–CMC without borate cross-linking, and (6) blank; (b) for 0.7% GO + CMC with different concentration of borate for cross-linking (0.09, 0.3, and 0.5%), respectively, from 1 to 3 and 4 for blank, tensile strength for 0.7% GO + CMC + 0.09% borate, 0.7% GO + CMC and blank at 20 and 50% RH; gas diffusion pathway for hybrid film, oxygen permeability and water vapor permeability for hybrid film with different concentrations of GO (PDF).

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