Hydrophobic Graphene Oxide as a Promising Barrier of Water Vapor for Regenerated Cellulose Nanocomposite Films

Ling Xu,† Jian Teng,† Lei Li,† Hua-Dong Huang,† Jia-Zhuang Xu,† Yue Li,† Peng-Gang Ren,‡ Gan-Ji Zhong,§† and Zhong-Ming Li‡*†

†College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, People’s Republic of China
‡Institute of Printing, Packaging Engineering and Digital Media Technology, Xi’an University of Technology, Xi’an, Shaanxi 710048, China

Supporting Information

ABSTRACT: Regenerated cellulose (RC) films exhibit poor water barrier performance, which seriously restricts its applications. To address this issue, an impermeable and hydrophobic graphene oxide modified by chemically grafting octadecylamine (GO-ODA) was utilized to enhance the water vapor barrier performance of RC nanocomposite films. Compared to the neat RC film, more than 20% decrease in the coefficient of water vapor permeability ($P_{\text{H}_2\text{O}}$) was achieved by loading only 2.0 wt % GO-ODA. The promising hydrophobicity of GO-ODA effectively retarded the formation of hydrogen bonding at the relatively weakened interface between GO and RC, compensating for the diffusion of water vapor molecules at the interface; on the other hand, the fully exfoliated GO-ODA nanosheets were inclined to align with the surface of the as-prepared RC nanocomposite films during hot-pressure drying, creating a much more tortuous pathway for diffusion of water molecules. The new insights could be valuable for widening application of cellulose such as packaging.

INTRODUCTION

Among the most of environmentally friendly polymers, cellulose is considered as a promising packaging material substitute for petroleum-based polymers, which is the most abundant biomass material in nature from plants, tunicates, bacteria, and so forth.1,2 It has excellent properties such as mechanical robustness, hydrophilicity, biocompatibility, and biodegradability. More importantly, its severe problem of insufficient water resistance because of the abundant hydrophilic hydroxyl groups in cellulose molecular chains,11,12 restricting its packaging application for water-sensitive food and drug.

It has been well established that the incorporation of layered nanofillers with high aspect ratio into polymers is an effective strategy to fabricate high-barrier nanocomposite films.13–15 The layered nanofillers are expected to act as impermeable obstacle and force a tortuous pathway for gas molecule diffusion, which significantly enhances the barrier performance of nanocomposite films. Graphene oxide (GO) derived from graphene nanosheets is a quasi two-dimensional (2D) honeycomb lattice material with abundant oxygen-containing functional groups on its basal planes and edges, such as hydroxyl, epoxide, carbonyl, and carboxyl. These chemical functional groups make GO strongly hydrophilic, which promotes complete exfoliation and homogeneous dispersion of GO in the polar polymer matrix and improves the interfacial bonding significantly.16–19 Hence, GO is considered as a forward-looking candidate for preparing high-barrier polar polymer-based nanocomposite films. For instance, Huang et al. prepared RC/GO nanosheet composite films with a permeability coefficient of $1.0 \times 10^{-16}$ cm cm$^{-2}$ s$^{-1}$ Pa$^{-1}$, exhibiting 1000 times increased oxygen barrier performance.20 Wang et al. reported layer-by-layer assembly deposition of GO/poly(lactic acid)/polyethyleneimine, which effectively created a tortuous pathway to obstruct permeating molecules with a reduction in oxygen permeability by 99.0%. Although GO could increase the oxygen barrier performance of polymer composites by several hundred times, their water vapor barrier performance was hardly improved.21 Because of the high affinity of GO to H$_2$O, hydrogen bonding is easily formed between H$_2$O molecules and the hydrophilic oxygen-containing functional groups of GO. It results in easy diffusion of H$_2$O molecules between the GO and polymer matrix. The interfacial bonding between GO and polymer matrix is destroyed, disabling to resist water vapor permeation. Therefore, to effectively improve the water vapor barrier perform-

Received: October 18, 2018
Accepted: December 17, 2018
Published: January 8, 2019
ance of polymer/GO composites, restraining formation of hydrogen bonding between H$_2$O molecules and GO is the requisite, for example, through destroying the high affinity to H$_2$O of GO.

Recently, grafting the long alkyl chains has been demonstrated to lipophilically modify the surface of GO, which can facilitate its uniform dispersion in the polymer matrix and impair high affinity to water. As reported, alkyamines such as octadecylamine (ODA) and dodecylamine (DA) showed ability to turn hydrophilic into hydrophobic of GO, promoting the application of GO in the non-polar polymers.$^{22-25}$ Lee et al. decorated GO with DA and observed improved mechanical, electrical, and barrier properties of linear low-density polyethylene nanocomposites by the addition of the functionalized graphene.$^{26,27}$

In this work, the RC/GO-ODA nanocomposite film was prepared via a green sodium hydroxide (NaOH)/urea solvent to initially dissolve cellulose, and then pressure was employed to orient the GO-ODA nanosheets during hot drying process. Effect of ODA content and morphology on water vapor resistance was investigated. To reveal the mechanism of water vapor diffusion in nanocomposite films, time-resolved attenuated total reflection Fourier transform infrared spectroscopy (ATR−FTIR) and 2D correlation analysis were preformed, which improved the spectral resolution and identified the sequence of spectral intensity changes in dynamic analysis.$^{28-31}$

### RESULTS AND DISCUSSION

**Synthesis of ODA-Grafted GO.** FTIR measurement is powerful to identify the chemical grafting of ODA chains onto GO, as illustrated in Figure 1. FTIR absorption peaks appear at 1070 (C−O−C absorption vibration), 1628 (C≡C in aromatic ring), 1730 (C=O stretching vibration), and 3430 cm$^{-1}$ (−OH absorption vibration), indicating the existence of oxygen-containing functional groups on the GO surface.$^{32-34}$ A new peak centered at 1470 cm$^{-1}$ (C−N stretching of amide) is observed after grafting, whereas the peaks of 1070 and 1730 cm$^{-1}$ disappear, owing to the nucleophile substitution and the amidation reaction between the −NH$_2$ group of ODA and C=O−C/−COOH groups of GO. Besides, the grafting of ODA is confirmed by the significant enhanced peaks at 2918 and 2830 cm$^{-1}$ (C−H stretching) as well as the new CH$_2$ absorption peak (720 cm$^{-1}$). The above results indicate the successful grafting of ODA chains to the surface of GO.$^{24,35,36}$

Figure 1B presents the X-ray diffraction (XRD) spectra of GO and GO-ODA. Apparently, the diffraction peak of GO is observed at 2θ = 9.6°, and the d-spacing is 0.92 nm. For GO-ODA, the d-spacing shifts to 1.8 nm with 2θ = 4.9°, in consistence with the chemical attaching of long ODA chains onto GO sheets. It is worth noting that another dispersing diffraction peak of GO-ODA appears at 2θ = 20.2°. It is related to the graphite structure, indicating the disappearance of partially oxygen-containing functional groups and the rearrangement of graphitic domains during the reaction of GO and ODA. This is also confirmed by the huge difference in hydrophilic−hydrophobic property between GO and GO-ODA (Figure 1C,D). GO exhibits a low water contact angle (WCA) of 38.2° because of the abundant oxygen-containing functional groups, whereas the WCA of GO-ODA reaches 125.8°. Therefore, the grafting process transforms the nanofillers from hydrophilic to hydrophobic, which is more desirable for water vapor barrier application.

Thermal gravimetric analysis (TGA) analysis was performed to calculate the grafting ratio of ODA on the surface of GO. As depicted in Figure 1E, a small weight loss (about 15.3%) of GO powder with the absorption of bound water occurs before 120 °C. A major weight loss of GO occurs above 120 °C,

---

**Figure 1.** FTIR spectra (A), XRD curves (B), WCA (C,D), and TGA curves (E) of GO and GO-ODA nanosheets.
attributing to the thermal decomposition of labile (120–270 °C) and stable oxygen-containing functional groups (above 270 °C). The hydrophobic ODA chains and the removal of hydrophilic groups minimize the absorption of bond water. Thus, GO-ODA exhibits high thermal stability and antipyrolysis (the weight loss is nearly zero) below 120 °C. In the range of 150–250 °C, GO-ODA shows a weight loss of about 11.0%, which is related to the physically absorbed ODA chains by electrostatic force and partially unstable and partially oxygen-containing functional groups of GO-ODA nanosheets. At high temperature above 250 °C, a significant weight loss of up to 65% originates from the pyrolysis of grafted ODA chains and oxygen-containing functional groups of GO-ODA nanosheets. 

Taking the theoretical residue value at 250 °C into account, the grafting ratio of GO-ODA is about 21.4 wt %. **Structure of RC/GO-ODA Nanocomposite Films.** Individually exfoliated and uniformly dispersed nanofillers have been acknowledged as highly effective reinforced units for the polymeric matrix, while the aggregate nanofillers are harmful to the reinforced effects because of defects. In term of morphology, RC shows a dense texture but a rough surface with micropore defects (Figure 2a′), probably owing to sharp shrink of capillary force restrained under the extra pressure during the rapid desiccation at high temperatures. After introduction of GO-ODA, the fractured surface displays a homogeneous and denser texture and no micropore defects are observed when the GO-ODA content is below 5 wt % (Figure 2b–d). This characteristic surface indirectly suggests the efficient individual dispersion of GO-ODA and the barrier effect of sharp shrink of filler. Moreover, as indicated by the red arrow, GO-ODA is inclined parallel with the RC film surface, which is labeled by the white arrow. Such an orientation architecture of GO-ODA is profitable to enhance the barrier performance of the RC/GO-ODA film. Although the GO-ODA content reaches 5 wt %, there are some bulges of defect structure observed in the fracture surface of film (Figure 2e′), which is the aggregation of GO-ODA nanosheets (marked by white arrow) because of poor dispersion of high content filler.

Wide angle X-ray diffraction (WAXD) was performed to investigate the effect of GO-ODA on the crystalline structure of RC. 2D-WAXD patterns of RC and RC/GO-ODA films demonstrate similar homogeneous diffraction rings (Figure S2). It gives a hint that the formation of cellulose crystals is isotropic and the cooperation of GO-ODA has almost no effect on crystal modifications. It can be seen from Figure 3a that two strong diffraction peaks appear at 2θ = 16.4° and 17.6° in all RC/GO-ODA films, representing lattice planes (110)/(200) of cellulose II. These results confirm that nature cellulose is well dissolved in NaOH/urea solvent and successfully converted from cellulose I (nature cellulose) to cellulose II.30,39,40 Although the crystalline form is not altered by GO-ODA, the crystallinity (Xc) of RC films is largely affected. As shown in Figure 3b, the Xc decreases from 42.5 to 34.6% with the loading of GO-ODA. During the crystallization process of cellulose, the GO-ODA nanosheets act as a kind of nucleation inhibitor, which could reduce nuclei and confine the cellulose II crystal for perfection. At higher loading, the perfect cellulose crystal is further inhibited by the space restriction due to the dense structure of GO-ODA (probably a network) with oriented lamellar arrangement in the RC matrix.41,42

The interfacial interaction between RC and GO-ODA was detected by FTIR, as shown in Figure 4. Noteworthy, the well-known –OH stretching band at 3600–3000 cm⁻¹ is sensitive to hydrogen bonding, which shifts to higher wavenumber from 3318 to 3339 cm⁻¹ with the loading of GO-ODA. The red shift of the –OH stretching absorption peak clearly illustrates the weakened hydrogen bonding between the RC matrix and GO-ODA nanosheets.36,43 Such weakened interactions are attributed to the absent –COOH and –OH of GO and the insulation of grafting ODA restricts the formation of hydrogen bonds between RC and GO-ODA. Moreover, a particular peak of all samples at 895 cm⁻¹ represents the glycosidic C–H deformation with ring vibration contribution and –OH bending, proving the β-glycosidic linkages between glucose in cellulose. As reported, this small peak only appears in RC.44–46 This result also indicates that the nature cellulose is transformed from cellulose I to cellulose II after dealing with NaOH/urea aqueous solution.

**Water Vapor Transport Properties of RC/GO-ODA Nanocomposite Films.** With the oriented dispersion of GO-ODA nanosheets throughout the cellulose matrix, the water barrier properties of the nanocomposite films are expected to be improved. As shown in Figure 5, compared with the RC film, Pw/H₂O of RC/GO-ODA nanocomposite films is decreased within the certain filler content range. For instance, a more than 20% decrease in Pw/H₂O from 1.71 × 10⁻¹² to 1.35 × 10⁻¹² g cm⁻² s⁻¹ Pa⁻¹ is achieved for RC2. The addition of hydrophobic GO-ODA is an effective mean to enhance water barrier properties. Although GO-ODA weakens the interfacial

Figure 2. SEM images of cross-section of RC and RC/GO-ODA nanocomposite films: (a–e) are RC, RC0.5, RC1, RC2, and RCS, respectively; (a′–e′) are magnification of (a–e).
interactions with the cellulose matrix, which could be favorable for water permeability through the interface, the higher hydrophobicity of GO-ODA can compensate for this issue effectively. Note that the $P_{H_2O}$ of RCS is increased. It is attributed to the poor dispersion of GO-ODA (Figure 2c′) and poor interfacial interactions (Figure 2e′), resulting in damaged barrier walls.

To investigate the penetrative path of water vapor molecules in composite films, we used time-resolved ATR−FTIR to analyze the variation of function groups of RC/GO-ODA nanocomposites affected by water vapor molecules. Figure 6 shows the time-resolved FTIR in the range of 1200−1700 cm$^{-1}$ of RC and RC0.5 during water vapor permeation. As universally known, hydrogen bonding (interaction between cellulose and water) has been deemed as an important factor not only in physics and chemistry of cellulose but also in water vapor absorption of cellulose. Given the types of hydrogen bonding, there are three types of water in nanocomposite films, including free water, nonfreezing bound water and freezing bound water.47 RC and RC0.5 show the characteristic peaks at 1335 and 1470 cm$^{-1}$, which stem from the vibrations and in plane bending of −OH of cellulose chains. Both of the two peaks are sensitive to the bound water in the cellulose because of interruption of hydrogen bonding. Another dispersion peak appears at 1640 cm$^{-1}$ because of hydrogen bonding absorption of the weak interaction of OH$\cdots$OH, corresponding to the free water of free volume in cellulose.28−50 From Figure 6, the intensities of all FTIR peaks of RC and RC0.5 gradually increase as a function of time, indicating that the water vapor slowly passes through the film samples. Furthermore, 2D correlation analysis can distinguish the sequence of time-resolved FTIR changes, reflecting the microstructural variations affected by water vapor molecules in detail.

In 2D correlation analysis, synchronous ($\phi(v_1,v_2)$) and asynchronous correlation spectra ($\psi(v_1,v_2)$) indicate coordinate similarity of two separate spectral intensity variations and dissimilarity of the spectral intensity variation measured at different spectral variables, respectively. It provides the sequential order of intensity changes of peak $v_1$ and $v_2$. According to the Noda’s rule, when $\phi(v_1,v_2) > 0$, if $\psi(v_1,v_2) > 0$ (the red area in 2D correlation spectra map), the peak $v_1$ varies before the peak $v_2$, and if $\psi(v_1,v_2) < 0$ (the blue area in 2D correlation spectra map), the peak $v_1$ varies after the peak $v_2$. Besides, if $\phi(v_1,v_2) < 0$, the judgemental rule is just reversed. In 2D synchronous correlation spectra map of water vapor diffusion in the RC and RC0.5 films in the range of 1700−1200 cm$^{-1}$, $\phi(v_1,v_2) > 0$ (Figure 7a,b), which illustrates that all components in films gradually increase with the water vapor diffusion process. In the 2D asynchronous correlation spectra map, $\psi(1640,1470) < 0$ and $\psi(1640,1335) < 0$ of RC film (Figure 7c), suggesting that the peak 1640 cm$^{-1}$ varies after the peak at 1470 and 1335 cm$^{-1}$. Similar tendency is shown in the RC0.5 sample (Figure 7d). Therefore, the sequential order of the peak for water vapor diffusion in the
RC film is: 1335/1470 cm$^{-1}$ → 1640 cm$^{-1}$. The water vapor molecules interact with cellulose chains by formation of hydrogen bondings during diffusion. Subsequently, the free water (i.e. the cluster of water) forms with the increase of water content. The above results demonstrate that the water vapor diffusion paths in the cellulose matrix are altered by the addition of GO-ODA nanosheets, and the mechanism of water vapor diffusion is the same for both the samples.

Generally, layered filler with large aspect ratio can act as impermeable nanoplatelets to intensify the tortuosity of the penetration paths for diffusing molecules.$^{53-56}$ Moreover, it is found that oriented filler from hot pressure drying of RC/nanofiller is an effective method to further prolong paths of gas molecule permeability and finally to improve barrier property.$^{55}$ In this work, it shows that the hydrophobicity of oriented filler and interfacial interactions are important factors.
in determining the water vapor barrier properties of the RC film. Combining with 2D correlation analysis of time-resolved FTIR, we propose a preliminary mechanism of water vapor diffusion into RC and RC/GO-ODA films, as schematically drawn in Figure 8. For RC films, the water molecules tend to form H-bond interaction with cellulose chains probably in the amorphous or at the surface of the crystalline phase of RC because of abundant crystal of cellulose II to form bounded water. Then, water vapor diffuses into the amorphous phase of RC forming nonfreezing bound water. Finally, the water vapor spreads to free volume to form water clusters (free water) in cellulose network and subsequently escapes out of the cellulose film. In the water vapor diffusion process of RC, although high crystallinity is presented, the low aspect ratio and nonoriented crystalline structure of cellulose crystal cannot effectively serve as impermeable nanoplatelets to improve the barrier property. On the other hand, superhydrophilic RC is an absorber of water vapor, which would result in poor water vapor barrier property. Addition of hydrophobic GO-ODA results in low water vapor permeability (WVP). Three factors are considered to account for the result. First, the water vapor molecules tend to diffuse in the vicinity of weakened interface, but the diffusion rate is immediately reduced because of high hydrophobicity of GO-ODA, which prevents the formation of hydrogen bonding between H$_2$O and GO. Moreover, the hydrophobic GO-ODA nanosheets are an effective hamper to restrict the water vapor diffusion. Eventually, if the water vapor forms hydrogen bonding with the other side of cellulose chains for diffusion, it is necessary to bypass the GO-ODA nanosheets with high aspect ratio, leading to low WVP.

CONCLUSIONS

In this work, we successfully synthesized the hydrophobic GO via grafting of ODA, which was proved to be an effective water barrier filler of the RC film. The RC/GO-ODA nanocomposite film was easily fabricated via an environmentally friendly method to dissolve nature cellulose incorporating with GO-ODA in NaOH/urea aqueous solution. Compared to the neat RC film, the tensile strength and Young’s modulus were also increased with the loading of GO-ODA (Figure S3). Combined with 2D FTIR correlation spectra for water vapor diffusion into film specimen, it is found that the water vapor molecules tend to form hydrogen bond interaction with cellulose chains to form bounded water, and then water vapor diffuses into free volume to form water clusters (free water) in the cellulose network and subsequently escape out of the cellulose film. GO-ODA can retard this process by disruption of hydrogen bonding and creation of tortuous path for diffusion. The promising hydrophobicity of GO-ODA effectively retards the formation of hydrogen bonding at the relatively weakened interface of GO and RC, compensating for the diffusion at the interface; on the other hand, the GO-ODA nanosheets can orient and exfoliate in RC during the hot pressure drying, creating a tortuous pathway for diffusion of water vapor molecules. These results and insights can provide valuable reference for widening cellulose application in the area of encapsulation, package, and so forth.

EXPERIMENTAL SECTION

Materials. The cotton line of cellulose was friendly supplied by Hubei Jinhuang Co. Ltd. (Xiangfan, China), and the degree of polymerization was 500 ± 50. Expandable graphite with an expansion rate of 200 mL/g was used to fabricate GO, which was provided by Haida Graphite Co., Ltd. (Qingdao, China). The concentrated sulfuric acid (H$_2$SO$_4$), hydrochloric acid (HCl), potassium permanganate (KMnO$_4$), hydrogen peroxide (H$_2$O$_2$), ethanol, octadecyl amine (ODA), cetyltrimethyl ammonium bromide (CTAB), deionized water, urea, and NaOH were purchased from Kelong Chemical Reagent Factory (Chengdu, China). All reagents were used as received without further purification.

Preparation of ODA-Grafted GO (GO-ODA) from Expandable Graphite. First, GO was obtained from expandable graphite through the modified “Hummers” method. The details are described in the Supporting Information. 0.6 g GO powder was dispersed in 300 mL deionized water under ultrasonication for 0.5 h. Subsequently, the suspension was mixed with 90 mL ODA/anhydrous ethanol solution (0.01 g/mL) under vigorous stirring. The resultant mixture was refluxed 24 h for grafting at 70 ºC. After the end of chemical grafting, the product was separated by filtration, followed by washing with large amounts of ethanol and filtering repeatedly to remove the physically absorbed ODA chains. Finally, the resulting products were dried in a vacuum oven at 50 ºC for 24 h to evaporate the residual ethanol.

Fabrication of RC/GO-ODA Nanocomposite Films. RC nanocomposite films with the GO-ODA loading of 0.5, 1.0, 2.0, and 5.0 wt % were fabricated via an environmentally friendly method to dissolve nature cellulose followed by drying under a certain pressure. Taking the 0.5 wt % GO-ODA as an example, first, 25.78 mg of dried GO-ODA powder soaked in 1.0 g of anhydrous ethanol for 60 min to promote the dispersion. Then, the soaked GO-ODA was dispersed into 162.0 g of deionized water uniformly with the aid of surfactant CTAB (the mass ratio of CTAB to GO-ODA was 4/5) via an ultrasonication for 2 h. The resulting suspension directly mixed with 24 g urea and 14 g NaOH, and the suspension was precooled to −12.0 ºC for dissolution of nature cellulose. 5.13 g of cellulose was immediately added into precooled suspension with vigorous mechanical stirring (3000 rpm) for 5 min at ambient temperature. The resultant solution with a cellulose concentration of 2.5 wt % was centrifuged at 8000 rpm for 2 min to degas. Subsequently, 25 g of homogeneous cellulose solution was placed into a 10 × 10 cm$^2$ rectangular glass holder at 20 ºC for 12 h to gel. After gelation, the sample was immersed in fresh water to remove urea, CTAB, and NaOH at ambient temperature until the pH of wash water was ca. 7. Finally, the RC/GO-ODA nanocomposite hydrogel was hot dried under 2 MPa pressure at 150 ºC for 10 min. The dried RC/GO-ODA nanocomposite films with a thickness of about 80 μm were coded as RCx, where the x is the mass concentration of GO-ODA. For comparison, the fabrication process of neat RC was the same as RC/GO-ODA nanocomposite films.

FTIR Spectroscopy. To determine the chemical structure of GO-ODA, FTIR was performed on a Nicolet 6700 FTIR spectrometer (Thermal Scientific, USA) in the transmission mode. The GO and GO-ODA were ground with potassium bromide (KBr) followed by pressing into KBr disks for FTIR characterization. For each FTIR measurement, the scanning range was 4000–500 cm$^{-1}$ and, on average, 16 scans were collected at a resolution of 2 cm$^{-1}$.

To detect the interaction of GO-ODA and RC, ATR–FTIR was carried out on a Nicolet 6700 FTIR spectrometer.
(Thermal Scientific, USA). For each FTIR measurement, on average 32 scans were collected at a resolution of 2 cm\(^{-1}\). Besides, time-resolved ATR–FTIR was performed at 29 °C to reveal the water diffusion process in RC/GO-ODA nanocomposite films. As shown in Figure S1 in the Supporting Information, the single-reflection ATR crystal accessory was covered by an 80 µm thickness of film specimen with a rectangular film (15.0 × 15.0 mm\(^2\)), and overlaid three layers of filter paper with the same size. Then, 0.5 mL of water was injected into the filter paper during the data acquisition. For each film specimen, 32 scans were added together to obtain the spectrum signal at 2 cm\(^{-1}\) resolution in the scan range of 1700–1200 cm\(^{-1}\). 2D correlation analysis via a “2DCS Professional” software established by Dr. Tao Zhou (Sichuan University, China) was used to analyze the series of time-resolved FTIR spectra. In the 2D correlation spectra, blue regions and red regions indicate negative and positive correlation intensities, respectively.

X-ray Diffraction. The GO and GO-ODA samples were used for XRD characterization on a DX-1000 diffractometer with Cu Kα irradiation at 40 kV to characterize the layer-to-layer distance. For each XRD measurement, the scanning wavelength, scanning rate, and scanning 2θ range were 0.154 nm, 3.6°/min, and 2–30°, respectively.

Thermal Gravimetric Analysis. TGA was performed on a 209F1 instrument (Netzsch, Germany) under a N\(_2\) atmosphere. Mass change of the sample (about 5.0 mg) in the alumina pan was recorded at the temperature range from 40 to 800 °C with a heating rate of 10 °C/min.

Field-Emission Scanning Electron Microscopy. The morphology of RC/GO-ODA films was observed by field-emission scanning electron microscopy (SEM) (Nova NanoSEM450, FEI, USA) at an accelerated voltage of 5 kV. Before measurement, the sample was frozen for 30 min in liquid nitrogen and then cryo-fractured. Subsequently, the cross-section of samples was sprayed a thin layer of gold.

Wide Angle X-ray Diffraction. 2D WAXD images of films were acquired on 15U (\(\lambda = 0.124 \) nm) at Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China) to obtain the crystal structure and crystallinity (\(X_c\)) of cellulose. The distance between detector and samples was 160 mm. The \(X_c\) of film can be calculated as follows (eq 1).

\[
X_c = \frac{\sum A_{\text{cryst}}}{\sum A_{\text{cryst}} + \sum A_{\text{amorp}}} \tag{1}
\]

where the \(A_{\text{amorp}}\) and \(A_{\text{cryst}}\) are the fitted area of amorphous phase and crystalline phase, respectively.

Mechanical Testing. According to the ASTM standard (D638), the mechanical properties of the rectangular strips of RC/GO-ODA films with a width of about 10 mm and a length of 40 mm were measured on an universal tensile testing machine (model SS76, Instron Instrument, USA) with a 20 mm span length at a tensile speed of 1.0 mm/min. Before measurement, the thickness of samples was measured separately for at least five times. The parameters of mechanical properties were evaluated from at least 5 samples for each group.

Water Vapor Permeability. WVP of RC/GO-ODA films was measured gravimetrically on a W3/031 WVP test machine (Jinan Languang Mechanical and Electrical Technology Co., Ltd., China) at 38 °C and 90% relative humidity. A water transmission container was divided by films into the dry chamber and the chamber with a constant saturated vapor pressure. During the water vapor passing the dry chamber through films, the weight of deionized water in water transmission container was continuously monitored in real-time. Finally, the coefficient of WVP (\(P_{\text{H2O}}\)) was calculated by the following equation

\[
P_{\text{H2O}} = \frac{\Delta m \cdot d}{A \cdot t \cdot P_v} \tag{2}
\]

where \(\Delta m\) is the weight variation of water transmission container in a certain time span (\(t\)); \(d\) and \(A\) are the thickness and the water vapor transmission area of film specimen, respectively; \(P_v\) is the partial pressure of water vapor.

**Water Contact Angle.** GO and GO-ODA films were tested on optical contact angle (DSA30KRPSS, Germany) to measure WCA to evaluate the effect of chemical grafted ODA on GO. 1.0 mg of GO and GO-ODA was dissolved in deionized water and dichloromethane, respectively, coating on the polyethylene terephthalate film after ultrasonic dispersion for 30 min. After this, the resulting film was dried in a vacuum oven at 50 °C for WCA measurement.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02866.

Schematic illustration of the ATR–FTIR experiment, 2D-WAXD patterns of RC and its GO-ODA nanocomposite films, and typical stress-strain curves (A) and mechanical properties (B) of RC and its GO-ODA nanocomposite films (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: ganji.zhong@scu.edu.cn (G.-J.Z.).
*E-mail: zml@scu.edu.cn (Z.-M.L.).

**ORCID**

Jia-Zhuang Xu: 0000-0001-9888-7014
Gan-Ji Zhong: 0000-0002-8540-7293
Zhong-Ming Li: 0000-0001-7203-1453

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors are grateful for the financial support from the National Natural Science Foundation of China (21776186, 51533004, 51573147 and 51673135), the Youth Foundation of Science & Technology Department of Sichuan Province (grant no. 2017JQ0017), the Programme of Introducing Talents of Discipline to Universities (B13040), and the Fundamental Research Funds for the Central Universities (2012017Jysy102). We also thank Beamline BL16B and BL15U in Shanghai Synchrotron Radiation Facility (SSRF) for supporting the X-ray measurement.

**REFERENCES**

(1) Klemm, D.; Heublein, B.; Fink, H.-P.; Bohn, A. Cellulose: Fascinating Biopolymer and Sustainable Raw Material. Angew. Chem., Int. Ed. 2005, 44, 3358–3393.
ethylene nanocomposite films by incorporating hydrophobic graphene oxide nanosheets. RSC Adv. 2015, 5, 80739–80748.

(25) Lin, Z.; Liu, Y.; Wong, C.-p. Facile Fabrication of Super-hydrophobic Octadecylamine-Functionalized Graphite Oxide Film. Langmuir 2010, 26, 16110–16114.

(26) Kuila, T.; Bose, S.; Hong, C. E.; Uddin, M. E.; Khanra, P.; Kim, N. H.; Lee, J. H. Preparation of functionalized graphene/linear low density polyethylene composites by a solution mixing method. Carbon 2011, 49, 1033–1037.

(27) Kuila, T.; Bose, S.; Mishra, A. K.; Khanra, P.; Kim, N. H.; Lee, J. H. Effect of functionalized graphene on the physical properties of linear low density polyethylene nanocomposites. Polym. Test. 2012, 31, 31–38.

(28) Cotugno, S.; Larobina, D.; Mensitieri, G.; Musto, P.; Ragosta, G. A novel spectroscopic approach to investigate transport processes in polymers: the case of water–epoxy system. Polymer 2001, 42, 6431–6438.

(29) Maréchal, Y.; Chamel, A. Water in a biomembrane by infrared spectroscopy. J. Phys. Chem. 1996, 100, 8551–8555.

(30) Noda, I. Two-dimensional infrared spectroscopy. J. Am. Chem. Soc. 1989, 111, 8116–8118.

(31) Murayama, K.; Wu, Y.; Czarnik-Matusewicz, B.; Ozaki, Y. Two-dimensional/attenuated total reflection infrared correlation spectroscopy studies on secondary structural changes in human serum albumin in aqueous solutions: pH-dependent structural changes in the secondary structures and in the hydrogen bonds of side chains. J. Phys. Chem. B 2001, 105, 4763–4769.

(32) Hummers, W. S.; Offeman, R. E. Preparation of graphitic oxide. J. Am. Chem. Soc. 1958, 80, 1339.

(33) Xu, X.-Z.; Zhang, Z.-J.; Xu, H.; Chen, J.-B.; Ran, L.; Li, Z.-M. Highly Enhanced Crystallization Kinetics of Poly(l-lactic acid) by Poly(ethylene glycol) Grafted Graphene Oxide Simultaneously as Heterogenous Nucleation Agent and Chain Mobility Promoter. Macromolecules 2015, 48, 4891–4900.

(34) Zhang, S.; Xiong, P.; Yang, X.; Wang, X. Novel PEG Functionalized Graphene Nanosheets: Enhancement of Dispensibility and Thermal Stability. Nanoscale 2011, 3, 2169–2174.

(35) Niyogi, S.; Bekyarova, E.; Itkis, M. E.; McWilliams, J. L.; Hamon, M. A.; Haddad, R. C. Solution properties of graphene and graphite. J. Am. Chem. Soc. 2006, 128, 7720–7721.

(36) Huang, H.-D.; Ren, P.-G.; Chen, J.; Zhang, W.-Q.; Ji, X.; Li, Z.-M. High Barrier Graphene Nanosheets/Poly(vinyl alcohol) Nanocomposite Films. J. Mater. Sci. 2012, 40, 410–416, 156–163.

(37) Choudhary, S.; Mungse, H. P.; Khatri, O. P. Dispersion of alkylated graphene in organic solvents and its potential for lubrication applications. J. Mater. Chem. 2012, 22, 21032–21039.

(38) Liang, J.; Huang, Y.; Zhang, L.; Wang, Y.; Ma, Y.; Guo, T.; Chen, Y. Molecular-level dispersion of graphene into poly(vinyl alcohol) and effective reinforcement of their nanocomposites. Adv. Funct. Mater. 2009, 19, 2297–2302.

(39) Gupta, P. K.; Uniyal, V.; Naithani, S. Polymeric transformation of cellulose I to cellulose II by alkali pretreatment and urea as an additive. Carbohydr. Polymer 2013, 94, 843–849.

(40) Liu, C.-Y.; Zhong, G.-J.; Huang, H.-D.; Li, Z.-M. Phase Assembly-Induced Transition of Three Dimensional Nanofibril-to-Sheet-Networks in Porous Cellulose with Tunable Properties. Cellulose 2013, 21, 383–394.

(41) Liu, C.-Y.; Zhong, G.-J.; Huang, H.-D.; Li, Z.-M. Confined Crystallization of Poly(butylene succinate) InterCalated Into Organoclay: Role of Surfactant Polarity. RSC Adv. 2016, 6, 68072–68080.

(42) Ji, X.; Chen, J.-B.; Zhong, G.-J.; Li, Z.-M.; Lei, J. Nonisothermal crystallization of isotactic polypropylene in carbon nanotube networks: The interplay of heterogeneous nucleation and confinement effect. J. Thermoplast. Compos. Mater. 2014, 29, 1352–1368.

(43) Suzuki, H.; Zhang, L.; Liu, C.-Y.; Zhong, G.-J.; Li, Z.-M. Functionalized Graphene Nanosheets: Enhancement of Dispersibility and Thermal Stability. Nanoscale 2011, 3, 2169–2174.
Dinand, E.; Vignon, M.; Chanzy, H.; Heux, L. Mercerization of primary wall cellulose and its implication for the conversion of cellulose I → cellulose II. *Cellulose* 2002, 9, 7–18.

Liu, Z.; Wang, H.; Li, Z.; Lu, X.; Zhang, X.; Zhang, S.; Zhou, K. Characterization of the regenerated cellulose films in ionic liquids and rheological properties of the solutions. *Mater. Chem. Phys.* 2011, 128, 220–227.

Jin, A. X.; Ren, J. L.; Peng, F.; Xu, F.; Zhou, G. Y.; Sun, R. C.; Kennedy, J. F. Comparative characterization of degraded and non-degradative hemicelluloses from barley straw and maize stems: Composition, structure, and thermal properties. *Carbohydr. Polym.* 2009, 78, 609–619.

Nakamura, K.; Hatakeyama, T.; Hatakeyama, H. Studies on Bound Water of Cellulose by Differential Scanning Calorimetry. *Text. Res. J.* 1981, 51, 607–613.

Watanabe, A.; Morita, S.; Kokot, S.; Matsubara, M.; Fukai, K.; Ozaki, Y. Drying process of microcrystalline cellulose studied by attenuated total reflection IR spectroscopy with two-dimensional correlation spectroscopy and principal component analysis. *J. Mol. Struct.* 2006, 799, 102–110.

Carrillo, F.; Colom, X.; Suñol, J. J.; Saurina, J. Structural FTIR analysis and thermal characterisation of lyocell and viscose-type fibres. *Eur. Polym. J.* 2004, 40, 2229–2234.

Zhou, S.; Tashiro, K.; Hongo, T.; Shirataki, H.; Yamane, C.; Li, T. Influence of water on structure and mechanical properties of regenerated cellulose studied by an organized combination of infrared spectra, X-ray diffraction, and dynamic viscoelastica data measured as functions of temperature and humidity. *Macromolecules* 2001, 34, 1274–1280.

Jin, Y.; Wang, W.; Su, Z. Spectroscopic Study on Water Diffusion in Poly(l-lactide)–Poly(ethylene glycol) Diblock Copolymer Film. *Macromolecules* 2011, 44, 2132–2139.

Jin, Y.; Wang, W.; Su, Z. Spectroscopic study on water diffusion in poly(lactic acid) film. *Polym. Chem.* 2012, 3, 2430–2435.

Nielsen, L. E. Models for the Permeability of Filled Polymer Systems. *J. Macromol. Sci., Part A: Pure Appl. Chem.* 1967, 1, 929–942.

Farmahini-Farahani, M.; Bedane, A. H.; Pan, Y.; Xiao, H.; Eic, M.; Chibante, F. Cellulose/nanoclay composite films with high water vapor resistance and mechanical strength. *Cellulose* 2015, 22, 3941–3953.

Bharadwaj, R. K. Modeling the barrier properties of polymer-layered silicate nanocomposites. *Macromolecules* 2001, 34, 9189–9192.

Zhou, S.-Y.; Huang, H.-D.; Ji, X.; Yan, D.-X.; Zhong, G.-J.; Hsiao, B. S.; Li, Z.-M. Super-Robust Polylactide Barrier Films by Building Densely Oriented Lamellae Incorporated with Ductile in Situ Nanofibrils of Poly(butylene adipate-co-terephthalate). *ACS Appl. Mater. Interfaces* 2016, 8, 8096–8109.