

High Performance of PVA Nanocomposite Reinforced by Janus-like Asymmetrically Oxidized Graphene: Synergetic Effect of H-bonding Interaction and Interfacial Crystallization

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Electronic Supplementary Information

Abstract Macromolecule nanocrystal network and strong interfacial interaction are always beneficial to enhance the mechanical property of polymer-based nanocomposites. Poly(vinyl alcohol) (PVA), a typical biocompatible semicrystalline polymer, is an ideal candidate for preparing high performance polymer-based nanocomposites. However, the rich hydrogen bonds between PVA matrix and graphene oxide (GO) can disrupt the formation of PVA nanocrystal network. Thus, it remains a great challenge to achieve both strong and tough PVA-GO nanocomposites. Herein, by introducing a novel Janus-like amphiphilic graphene oxide (JGO), both hydrogen bonding and interfacial crystallization have been constructed between JGO sheets and PVA matrix. Benefiting from amphiphilic interfacial interaction and the enhanced crystal network, both PVA-JGO dried films and their swollen hydrogel films show superior mechanical properties than those of traditional PVA-GO nanocomposites. PVA-JGO dried films exhibit a 264% improvement of toughness at a JGO loading of 1 wt%. Meanwhile, the corresponding PVA-JGO swollen hydrogel films display simultaneous improvement of nearly 8 times increase of tensile strength and 20 times increase of toughness compared to traditional PVA-GO nanocomposite. This work indicates multiple interfacial interactions and macromolecule crystal networks can be concurrent in PVA nanocomposites by innovative modification of nanofillers, providing a new strategy to construct PVA nanocomposites with high strength and high toughness. The integration of outstanding mechanical and swelling resistance properties on PVA-JGO nanocomposite films render their promising applications, such as packaging and toughening hydrogel materials.

Keywords Poly(vinyl alcohol); Janus-like graphene oxide; Hydrogen-bonding interactions; Interfacial crystallization; Amphiphilicity

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INTRODUCTION

The development of high-performance polymer-based composite is an important bridge between polymer physics and chemistry and engineering applications. In recent years, the nanocomposite strategy, especially composite with high aspect-ratio nanomaterials (graphene, graphene oxide, cellulose nanofiber,^[1] etc.), has attracted much attention as an effective reinforcing method for staple polymer composite. As an environment friendly and biocompatible polymer, poly(vinyl alcohol) (PVA) possesses good mechanical properties.^[2] It is also an excellent candidate for preparing physical gels with high mechanical strength due to the fact that its microcrystals can form physical cross-linking networks.^[3–5] Graphene oxide (GO)

prepared by traditional Hummers' method^[6,7] is often blended with PVA in aqueous phase to achieve high mechanical strength PVA-based nanocomposites.^[8] Good water dispersibility and interfacial interaction between PVA and GO can be facilitated by the high density of oxygen containing functional groups, including hydroxyl epoxide, and carboxyl groups on the basal planes and edges of GO.^[9] However, previous work revealed that GO only increased Young's modulus and strength, but resulted in a sharp decrease of tensile elongation and toughness of the composites.^[10–13] It might be due to the formation of strong hydrogen (H)-bonding interactions between GO and PVA have detriment to the inter-chain H-bonding among PVA and then disturb homogeneity of the crystalline network of PVA.

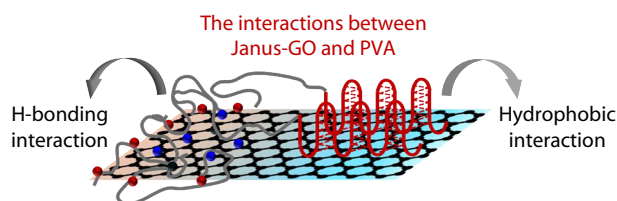
In contrast, graphene or reduced graphene oxide (RGO) with no or less oxygen-containing groups has been identified as a more promising filler for improving the strength and toughness of PVA nanocomposite than GO.^[14,15] Nevertheless, graphene or RGO sheets restack easily due to the strong

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π - π stacking interface. For avoiding the unfavored aggregations, various methods have been used to promote the dispersion of graphene nanosheets in PVA matrix, such as *in situ* reduction strategy by hydrazine hydrate and surfactant assisted dispersion.^[11,16–19] The procedures are cumbersome and additional toxic chemicals are required. Therefore, it is challenging to develop a simple and eco-friendly method that endows the graphene-based PVA nanocomposite with much improved strength and failure strain simultaneously. Is there a material that can combine the characteristics of GO and graphene to reinforce and toughen PVA materials by a convenient way? Recently, our group reported a novel Janus-like asymmetric graphene oxide (JGO)^[20] which has asymmetric oxidation structure along the sheet face with hydrophilicity on one end of the sheet and hydrophobicity on the other end. It is noteworthy that JGO has good water dispersion and should be able to disperse well in PVA aqueous solution. In addition, both JGO and PVA demonstrate the amphiphilic character,^[20–22] so that the multiple interactions including H-bonding and hydrophobic interaction could be constructed between JGO sheets and PVA chains. Moreover, hydrophobic interaction may promote the interface crystallization of PVA. This idea is illustrated in Scheme 1. We thus conjecture that JGO may combine the features of traditional GO and graphene sheets to achieve the simultaneous improvement of strength and toughness for PVA nanocomposite.



Scheme 1 Possible interface interaction between JGO sheet and PVA chains. Colorful spheres represent different oxygen containing functional groups, red curve lines represent possible interfacial crystallization.

In this study, both PVA-JGO and PVA-GO dried films were prepared by a simple solution casting and drying method, and their swollen hydrogel films were also fabricated for further investigating the effect of interface interaction and interface crystallization on the mechanical properties of prepared PVA nanocomposite. By this comparative study, we demonstrated that PVA-JGO dried films and their swollen hydrogel films showed remarkable improvement on both strength and toughness than those of PVA-GO films. It is very exciting that the tensile strength of hydrogel thin film is up to several megapascal level. The reinforcement mechanism for PVA-JGO nanocomposite was clarified by analyzing the microstructures of PVA-GO and PVA-JGO nanocomposite in this work by combining various characterization techniques, including Fourier transform infrared (FTIR), transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). It revealed that strong interfacial interactions and homogeneous macromolecule crystal networks played important roles on tailoring the mechanical properties of PVA nanocomposite.

EXPERIMENTAL

Materials

Natural flake graphite (180 mesh; purity >99%) was supplied by Qingdao Jinrilai Graphite Co., Ltd., (China). PVA powders produced by Kuraray Co., (molecular weight of 7.0×10^4 – 7.5×10^4 , hydrolysis 97%–99%), potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4 , 98%) and hydrogen peroxide (H_2O_2 , 30 wt%) were purchased from Qingdao Zhengye Reagent Co., Ltd., (China).

Preparation of JGO and GO

JGO suspension was prepared by a method of low-dose oxidant peroxidation and strong sonication, and the detailed procedures were listed in our previous study.^[20] In briefly, KMnO_4 (2 g) and graphite (1 g) were added to concentrated H_2SO_4 (40 mL, 98%) in ice water bath. After 6 h, the mixture was slowly added into ice water followed by adding H_2O_2 to stop the reaction, and the wet powder was filtrated and washed until reaching a neutral pH. Then, the powder was added to deionized (DI) water (400 mL) and adjusted pH to 11 using ammonia water. Next, the suspension was sonicated by using an ultrasonic homogenizer with an output power of 180 W for 5 min. Finally, the suspension was diluted and centrifuged at 8000 r/min for 10 min. The GO was prepared from natural graphite using the modified Hummers' method according to a well-established protocol.^[6] KMnO_4 (3 g) and graphite (1 g) were added to concentrated H_2SO_4 (60 mL, 98%), the mixture stirred at 0 °C for 2 h, and heated at 50 °C for 6 h. Then the mixture was slowly poured into 200 mL of deionized water, followed by adding H_2O_2 to stop the reaction. The GO suspension was centrifuged and washed by deionized water until pH value reached 7. Both the JGO and GO suspensions were dialyzed to pH=7, and the concentration was adjusted to 2 mg/mL for use.

Preparation of PVA Nanocomposite

To prepare PVA-JGO (GO) nanocomposite films, PVA was first dissolved in deionized water at 90 °C in a beaker with mechanical stirring to form a transparent aqueous solution (10 wt%). Then, a certain amount of JGO (GO) aqueous suspension was slowly added into the PVA solution and subsequently stirred at room temperature for 12 h. Finally, the solution was cast onto PTFE petri-dish and dried at room temperature for 2 days to form flat films which were peeled off and further kept at 40 °C vacuum oven for 24 h to remove residual water and dried films were obtained. PVA-JGO and PVA-GO hydrogel films were fabricated by soaking dry films in DI water to reach swollen equilibrium. Both the dried films (thickness= 150 ± 20 μm) and the hydrogel films (thickness= 200 ± 20 μm) were cut into specimens with certain species sizes for measurements. The as-prepared films were marked as PVA-JGO (GO) 0.1, 0.5, 1.0, 1.5, where the specific numbers represented the weight percentage (wt%) of JGO and GO in the composites.

Characterization

The morphology and size of GO and JGO were characterized by atomic force microscopy (AFM) (BRUKER) with Peak Force Tapping mode. Raman mappings were carried out using an InVia Series Laser Confocal Micro Raman Spectrometer (RENISHAW) with the following settings: 1 pixel $\times$ 1 pixel, 100 $\times$

objective, 532 nm laser with 5% power, diffraction grating of 1800 gr/mm, 3 s of exposure time, 1 accumulation. The surface chemical elements of the GO and JGO were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi Thermo Fisher).

The hydrated diameters of PVA, PVA-JGO and PVA-GO with 0.05 wt% concentration solution were determined by dynamic light scattering (DLS, BI-2005M) with a laser wavelength of 532 nm. The adsorption behavior of the JGO and GO on PVA substrate was studied by a Quartz Crystal Microbalance (QCM) with admittance analysis (QCM-A DBY-17, Hangzhou Longqin Advanced Materials Sci&Tech Co., Ltd., Hangzhou, China) controlled by a “QCM-DBY” program, which was written by Prof. Binyang Du, Zhejiang University, Hangzhou, China. The adsorbed quality of material on the gold electrodes can be calculated according to the following equation:^[23,24]

$$\Delta f/f_0 = \omega m_f / \pi Z_q \quad (1)$$

where, Δf is the difference of resonant frequencies, $\omega = 2\pi f$, ($f = 15$ MHz) is the measured resonant angular frequency of quartz crystal and m_f is the quantity of the substance adsorbed on unit area of the quartz crystal, and Z_q is the impedance of the gold electrodes ($Z_q = 8.8 \times 10^6 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$). The quartz crystals were AT-cut with a fundamental resonant frequency f_0 of 5 MHz and gold electrodes covered with a polyethyleneimine (PEI) film. The concentrations of PVA and suspensions (GO, JGO) were all diluted to $1 \text{ mg} \cdot \text{mL}^{-1}$ at a pH of 7, severally.

SAXS measurements were carried out at the BL16B1 beam-line in Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of X-ray radiation was 0.124 nm. Two-dimensional SAXS patterns were collected using a DECTRIS FLATUS838-900K, having resolution of $981 \text{ pixel} \times 1043 \text{ pixel}$. The sample to detector distance was 1938 mm for SAXS. The collection time for each image was 30 s. TEM images of the NC films were conducted on a JEOL JEM-2200 FS instrument at 200 kV. The specimens were obtained via a Leica EM UC7 ultramicrotome. Flash differential scanning calorimetry (Flash DSC) analysis was performed on a Mettler Toledo DSC2+ at heating rates of 50, 100, 200, 300, 400, $\sim 1000 \text{ K/S}$ from 40°C to 240°C . FTIR spectra were recorded on a Bruker tensor 70 spectrometer equipped with a DTG detector using a spectral width ranging from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} .

Mechanical properties of PVA nanocomposite were measured by Instron 5943. The NC films were cut into dumbbell-shaped with length of 75 mm and width of 4 mm and the tensile rate was $10 \text{ mm} \cdot \text{min}^{-1}$, and at least 5 specimens were measured for each sample. To study the water-swelling resistance of nanocomposite, the samples (same to mechanical property test) were completely submerged in distilled water for 48 h. The samples were moved out of the water and removed the excess water on the outer surface by a clean tissue paper, and then were weighed. The 48 h swelling ratio was calculated for each nanocomposite film sample by the following equation: Swelling ratio = $(W_s - W_d)/W_d$. In this equation, W_s and W_d are the weights was swollen and dried samples, respectively. Gas permeability was tested by gas permeability tester (VAC-V3, JiNanLanGuang), using the relevant method in ISO255.

RESULTS AND DISCUSSION

Structure of GO/JGO and Compounding with PVA

Clarifying the microstructure of nanosheets is very critical to illustrate the interfacial behavior between nanoparticles and PVA. AFM (Figs. 1a and 1b) show the lateral sizes of GO and JGO particles distributed in range of $1\text{--}2 \mu\text{m}$ and the thickness of $1\text{--}1.2 \text{ nm}$ (Fig. S1 in the electronic supplementary information, ESI), confirming a typical monolayer GO.^[25,26] Raman spectra based on D and G band intensity ratio can visualize the distribution of oxygen-containing functional groups on GO and JGO nanosheets. Comparing Fig. 1(c) and Fig. 1(d), it can be found that JGO has a lower I_D/I_G ratio (~ 0.86) in the blue area (low oxidation) and a higher I_D/I_G ratio (~ 1.02) in the red area (high oxidation). While GO shows a uniform color, in which I_D/I_G ratio of GO is about 1 for the whole area. The deconvoluted C1s spectra from XPS (Fig. S2 in ESI) demonstrate the difference in functional groups between JGO and GO. The full-width at half-maximum (FWHM) of the $\text{sp}^2\text{-C}$ bond peak decreases, which confirm the presence of more ordered $\text{sp}^2\text{-C}$ structures in JGO.^[25] The content ratio of O to C increases from 0.66 in JGO to 1.23 in GO (Fig. S2c in ESI), which indicates higher oxygen content in GO.

According to the above characterizations, the microscopic models of GO and JGO are depicted in Figs. 1(e) and 1(f), respectively. The asymmetric oxidation structure endows JGO with oxygen functional groups at one end and remains graphene domain at the other end. Benefiting from the oxygen functional groups, JGO also has the good water dispersibility as GO (Fig. S3 in ESI). Fig. 1(g) illustrates the preparation process of PVA-JGO/GO dried film and swollen hydrogen film. Both PVA-JGO and PVA-GO can form uniform and stable compound solution (Fig. S4 in ESI). After defoaming, the mixed solution was casted into a disc-shaped mold and water evaporate slowly to form flat dried films. The dried films were further swollen in deionized water to prepare hydrogel films. As is seen from Fig. 1(g), only swelling happened and no dissolving is observed in PVA-JGO and PVA-GO films after immersing in water, suggesting that a crystalline crosslinking network may have been formed in matrix providing the water resistance. It should be mentioned that there is difference in dimension (Fig. S5 in ESI) between PVA-JGO and PVA-GO gel films after swelling. The swollen PVA-JGO hydrogel film exhibited smaller dimensions than PVA-GO. This observation indicates denser crystalline network structure in the PVA-JGO matrix.

Interactions between PVA and JGO/GO Nanosheet

It is interesting to note that the subtle difference between JGO and GO can cause much obvious differences in PVA nanocomposite properties. Various interfacial interrelations lead to different adhesions of PVA chains to the nanosheets. The particle size distribution of neat PVA, PVA-GO and PVA-JGO in water was tested by dynamic light scattering (DLS) test as shown in Fig. 2(a). It can be clearly observed that pure PVA aqueous solution has a unimodal distribution with a maximum at around 200 nm, corresponding to the hydrated radius of PVA coils. Nevertheless, the particle size of PVA-GO dilute solution has bimodal distribution, one peak at around 200 nm is similar to the location of PVA coils, and the other around 1500 nm is

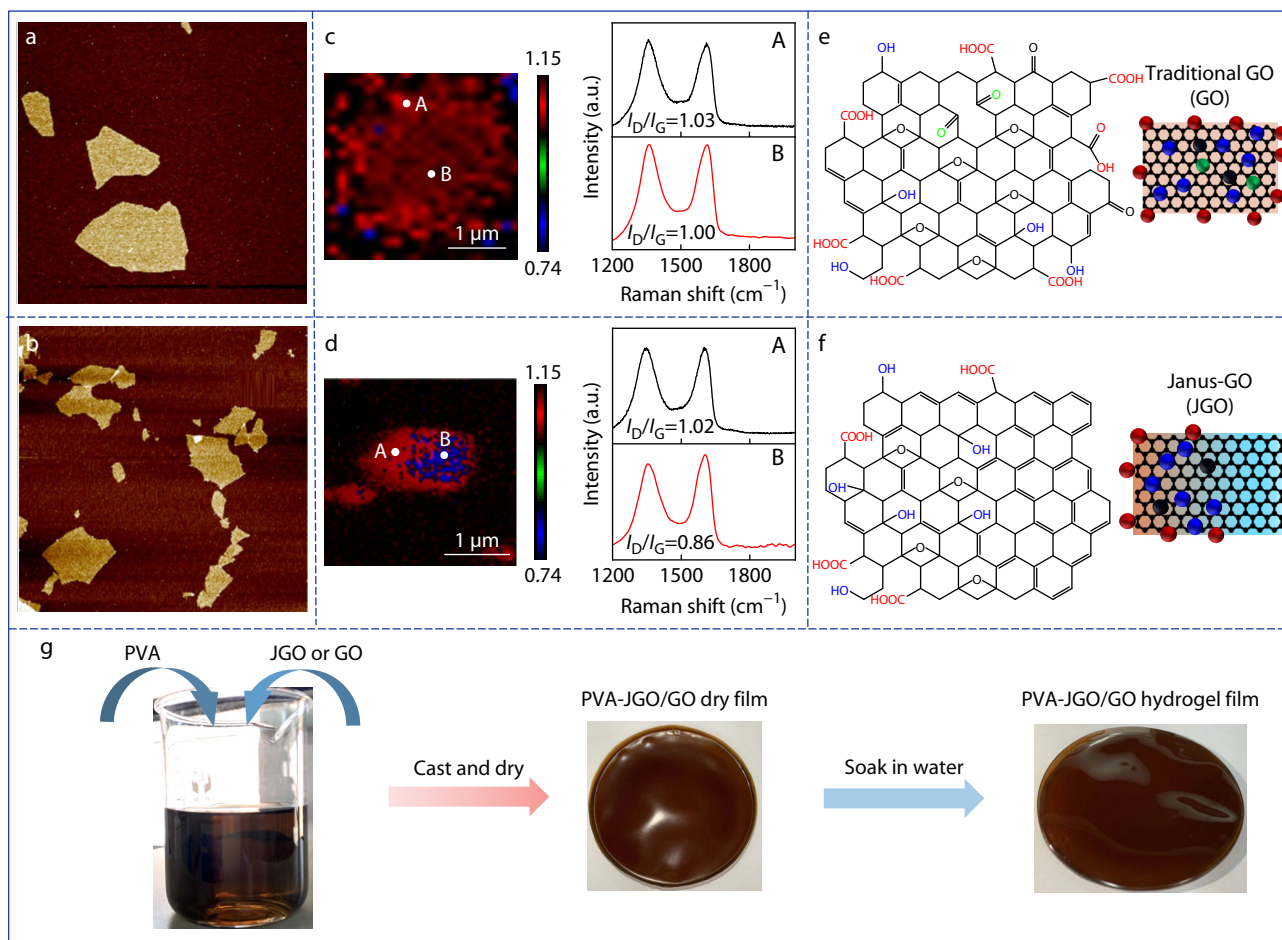


Fig. 1 Morphology comparison of GO and JGO, and the sampling process of PVA nanocomposites. AFM photographs of (a) GO nanosheets and (b) JGO nanosheets, the image size is $10\ \mu\text{m} \times 10\ \mu\text{m}$. Raman mapping of (c) GO and (d) JGO using the I_D/I_G ratio from the corresponding Raman spectra. (e, f) Sketch maps for GO and JGO, respectively. The colorful balls drawn on nanosheets correspond to the same colorful functional groups. (g) Preparation of PVA-JGO/GO nanocomposite dry films and hydrogel films.

attributed to GO or GO/PVA hybrids. This indicates the limited miscibility of GO and PVA in water environment. In contrast, the aggregated micelles in PVA-JGO solution present a unimodal distribution, demonstrating the good miscibility between JGO and PVA in water.

The cartoon pictures in Fig. 2 depict PVA coils and the various complexation of PVA chains with GO or JGO in water. It illustrates that there is a better miscibility in PVA/JGO than that of PVA/GO aqueous solution. A bimodal distribution of DLS in PVA-GO dilute solution is attributed to too much oxygen-containing groups coated on GO basal planes and edges, which make GO readily interact with water. As we know, hydrogen bonds own the character of saturation. Some GO maintain weak H-bonding interaction with amphiphilic PVA in water environment due to the influence of water molecules. The inhomogeneity leads to bimodal distribution. Amphiphilic nature of PVA makes it widely used as the steric stabilizer^[27,28] in dispersing and emulsifying applications. As we reported earlier,^[20] JGO with a hydrophobic structure at one end and a hydrophilic domain structure at the other of the lamella also exhibited amphiphilic properties and can be used for oil-water emulsification. The amphiphilic adsorption between

PVA and protein has been reported by Yu *et al.*^[29] It is reasonable to believe that amphiphilicity-driven including H-bonding^[20,30] interactions and hydrophobic interactions make the PVA chains and JGO nanoparticles integrate into a whole and homogeneous microscopic distribution.

To evaluate the interactions between PVA and nanosheets quantitatively, the adsorption behavior between PVA and JGO/GO in aqueous medium was further investigated by QCM. As shown in Fig. 2(b), the adsorption capacity of PVA for JGO is 12 times higher than that of PVA for GO. This higher adsorption capacity indicates that the interaction between PVA and JGO is stronger than that of PVA-GO. However, the existence of both hydrophobic and hydrophilic (H-bonding) interactions between amphiphilic PVA and JGO contribute to the larger adsorption capacity. In fact, the hydrophobic-hydrophobic interactions exist commonly for PVA, for example, PVA can be strongly adsorbed on hydrophobic substrates such as PDMS,^[31] polystyrene^[32] and gold^[33] substrates by the "hydrophobic interactions" due to the amphiphilicity of PVA. But at present, we cannot decouple the effects of H-bonding and hydrophobic-hydrophobic interaction between PVA and JGO.

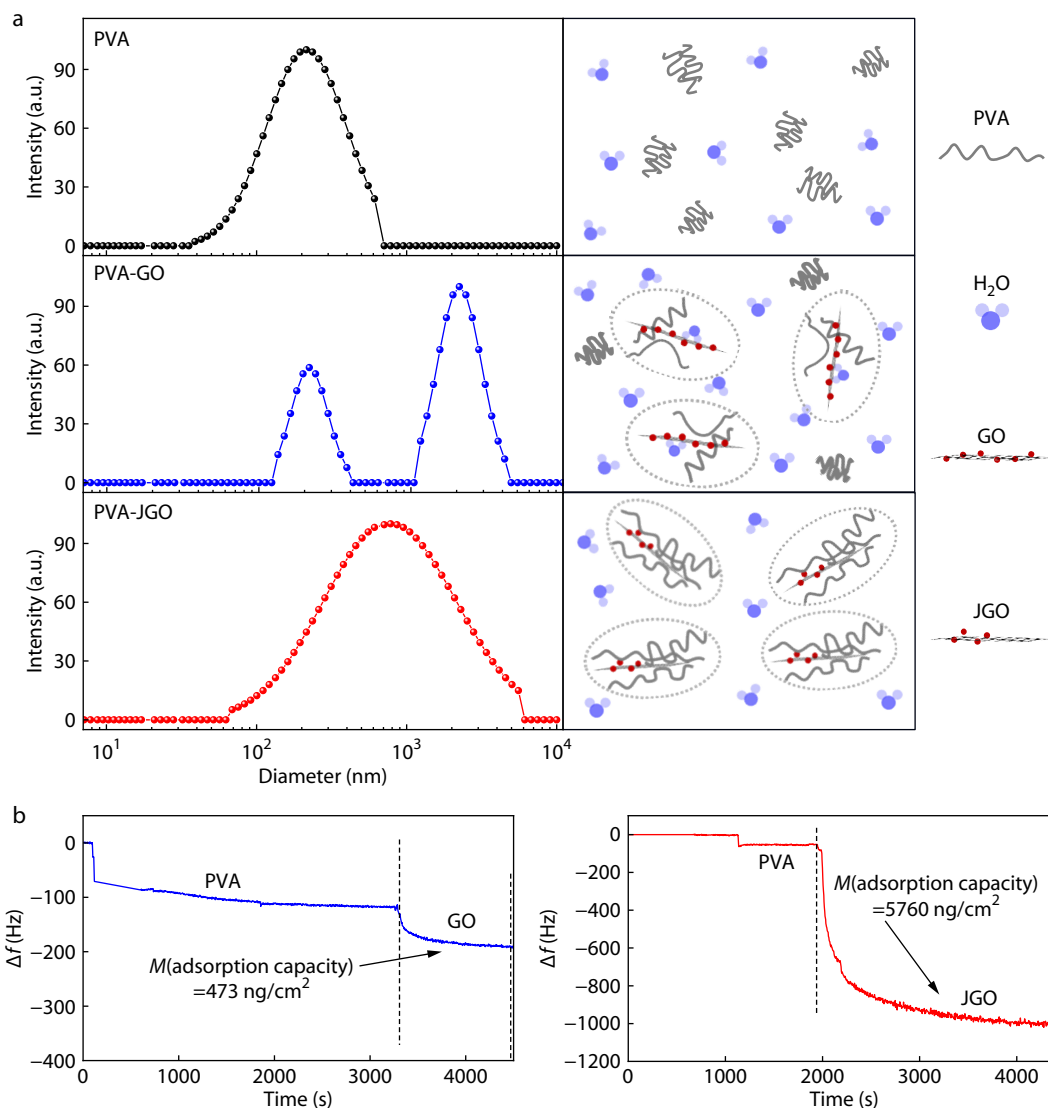


Fig. 2 Molecular interaction between PVA and GO/JGO nanosheets in solution. (a) Aggregation micelle diameter distribution curves of PVA, PVA-GO and PVA-JGO solution detected by DLS. The cartoons graphically explain the relationship of interaction in solution. (b) QCM results of the GO and JGO adsorbed on the PVA thin film.

Mechanical Properties of PVA-JGO/GO Nanocomposites

As stated in the introduction, GO can improve strength of PVA nanocomposite but greatly reduce fracture toughness. To develop graphene-based PVA nanocomposite with simultaneously high strength and high toughness by an eco-friendly method is still a great challenge. In this subsection, we focus on the mechanical properties of PVA-JGO nanocomposite. At the same time, the differences in the properties of PVA-GO and PVA-JGO materials are compared. The mechanical properties of both dry films and hydrogel films are investigated comprehensively. The strain-stress curves with various nanosheets loadings are all shown in Fig. S6 (in ESI). The nanocomposites with 1 wt% nanoparticle have better performance and are therefore chosen as representative curves with optimum performance for comparison (all the following nanocomposites for comparison according to this content except for specified instruction). The typical tensile stress-strain comparative curves of dry films with

GO and JGO are shown in Fig. 3(a). The data clearly reveal that both JGO and GO can improve strength of PVA. However, the elongation at break of dry PVA-JGO nanocomposite is significantly higher than that of dry PVA-GO nanocomposite. The fracture toughness^[30] defined as the area under the stress-strain curve is depicted in Fig. 3(b). The toughness of dry PVA-JGO nanocomposite with various JGO loadings is remarkably higher than that of dry PVA-GO nanocomposite. The toughness of PVA-JGO dry film reaches 49.5 MJ/m³, which is 3.5 times higher than that of PVA-GO films with loading 1 wt%, and improves 172% compared with that of neat PVA. The mechanical properties of hydrogel films are shown in Figs. 3(c) and 3(d). A remarkable improvement in both ultimate stress and strain of hydrogel films is observed for PVA-JGO system. Of note, PVA-JGO hydrogel films with thickness of only 0.2 mm achieve ultimate stress of 3.5 MPa, strain of 380%, toughness of 4.2 MJ/m³. The hydrogel fracture toughness displays more than 20 times higher than PVA-GO, and 14 times higher than

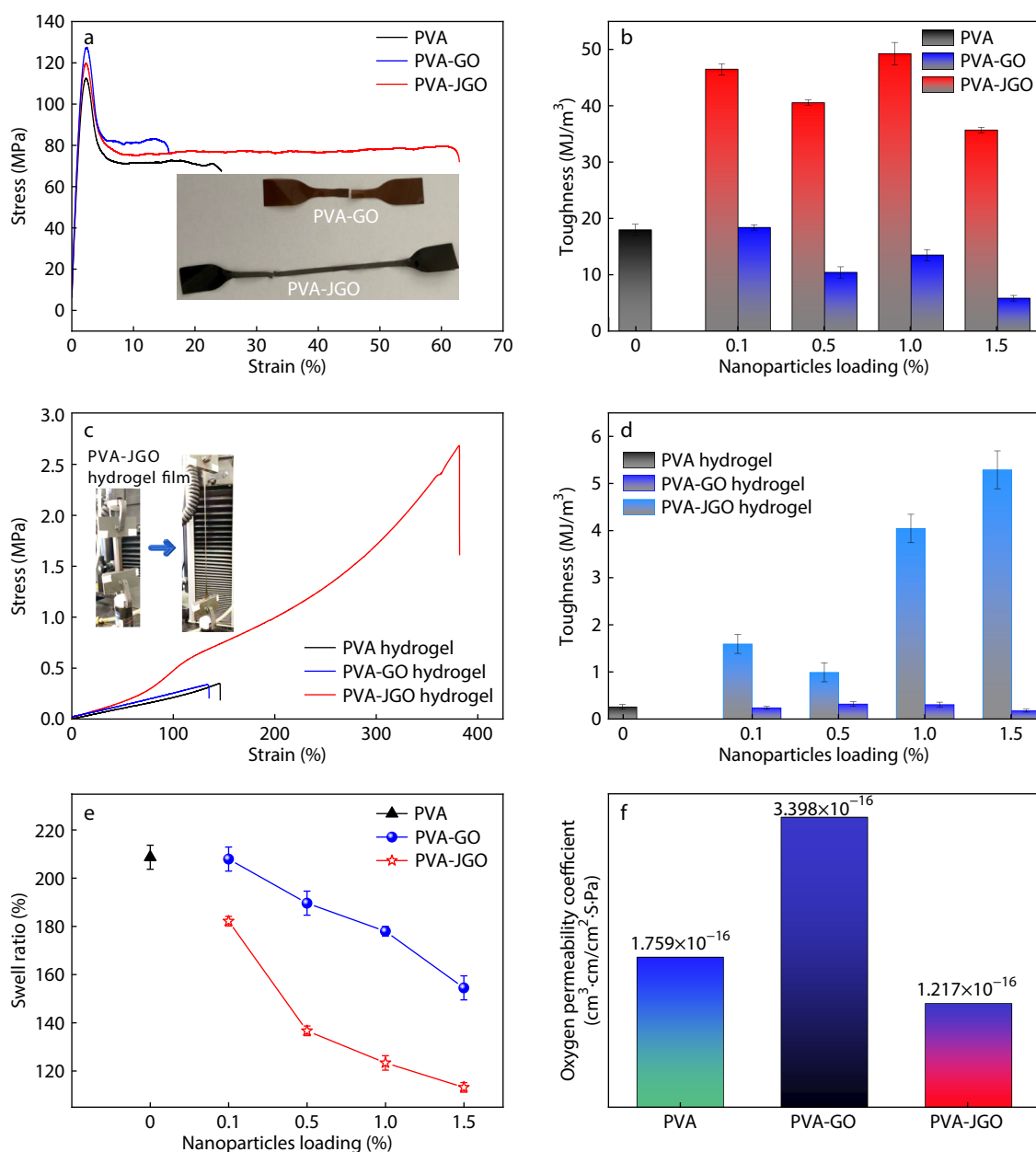


Fig. 3 Properties of the neat PVA and the nanocomposites filled with JGO or GO. (a) Cast-Dry films representative stress-strain curves (nanoparticles loading 1.0 wt%), Insets: Photo of the PVA-GO and PVA-JGO composite before and after uniaxial tension; (b) Toughness of CD films with different nanoparticles loadings; (c) Swell equilibrium wet hydrogel films stress-strain curves; (d) Wet hydrogel films toughness with different nanoparticle loadings. Insets: Photo initiate and ultimate stretched state of PVA-JGO gel; (e) The performance of water swelling resistance of neat PVA, PVA-JGO, PVA-GO, nanoparticles (the error bars represent standard deviation; sample size $n=5$); (f) Oxygen permeability coefficient of neat PVA, PVA-JGO, PVA-GO.

neat PVA gel. These results suggest that JGO nanoparticles concurrently reinforce and toughen both dry and hydrogel PVA nanocomposite films.

We also investigated the water swelling resistance and oxygen barrier properties of the dry films, and the results were listed in Figs. 3(e) and 3(f) respectively. Composites with both types of nanoparticles show better water resistance than neat PVA, and the swelling rate decreases gradually with the increase of particle content. PVA-JGO films render the best swelling resistance. PVA-JGO dry films also show better oxygen barrier properties. This observation indicates that

JGO may act as the nucleation agent and promote the formation of denser crystal network during the cast-drying process. We will discuss this point in next section.

Morphology and Structure of PVA-JGO/GO Nanocomposites

Numerous work revealed that the properties of the nanocomposites were dominated heavily by the interfacial effects between the polymer and the inorganic nanoparticles.^[34–36] It is noteworthy that most of the studies mainly focused on the effect of H-bonding interactions on the properties of PVA,^[10]

while the crystalline morphology and distribution of micro-crystal network of PVA usually are neglected. Obvious differences in interfacial morphologies of PVA-GO and PVA-JGO are revealed by TEM as shown in Figs. 4(a) and 4(b), respectively. It can be seen that the interfaces between PVA and GO are blurred. While observing PVA-JGO, the boundary layer of PVA-JGO shows a worm-like morphology which is similar to the interfacial crystallization morphology reported in the literature.^[37] Flash DSC (FDSC) with heating rate tens of times higher than normal DSC is used to investigate the crystallization of graphene based PVA nanocomposite. It can effectively avoid the influence of the heating process on material, especially to avoid the structure change caused by the reduction of GO in heating process by general DSC testing, thus can detect the original sample information more truly. The heating rate used in Fig. 4(c) is 1000 K/min. Notably, we discover that the melting point shifts to higher temperature for PVA-JGO nanocomposite, indicating the effect of JGO on improving the lamella thickness. Meanwhile the melting peak width of PVA-JGO is obviously wider than that of PVA-GO. This phenomenon suggests differences in lamellar thickness distributions of crystallite. Interfacial crystallization tends to cause an increase in lamella thickness and multiscale distribution of crystalline size.^[36] Other data of different heating rates are shown in Figs. S9(a) and S9(b) (in ESI), exhibiting the same trend.

If crystallization is formed on the surface of JGO, the crystallinity will be significantly increased. FTIR is used to further confirm the crystallinity of the nanocomposite. The absorb-

ance at 1142 cm^{-1} is considered to depend on the degree of crystallinity.^[38,39] Both absorbances are normalized to the band 1330 cm^{-1} to calibrate different thicknesses of each sample. Comparing the FTIR spectra of the nanocomposite films (Fig. 4d), the crystalline sensitive band at 1142 cm^{-1} in PVA-JGO is more pronounced than that in PVA-GO. This indicates that JGO nanoparticles are easier to induce PVA crystallization with higher crystallinity.

To explore the crystal morphology in a quantitative way, synchrotron radiation SAXS was investigated to research the regular stacking cycle of lamellar crystals and the 2D SAXS patterns of PVA-GO and PVA-JGO are shown in Figs. 5(a) and 5(b). Circular scattering pattern with a homogeneous intensity distribution along the circle is observed in both two kinds of nanocomposites. Nevertheless, there is a remarkable difference in diffraction density. Lorentz-corrected SAXS intensity profiles are calculated through a small-angle arc integral by the Fit2d software package and listed in Fig. 5(c). Generally, the peaks are suggestive of the ordered structures in the samples. According to the peak intensity in Fig. 5(c), we can conclude the lamellar of PVA-JGO stack more orderly than that of PVA-GO nanocomposite conspicuously, and one obvious effect of GO is to reduce stacks regularly of the crystalline lamellar. The data are Lorentz-corrected by multiplying the intensity data by q^2 . The correlation function $K(z)$ can be directly obtained by applying the inverse Fourier transformation:

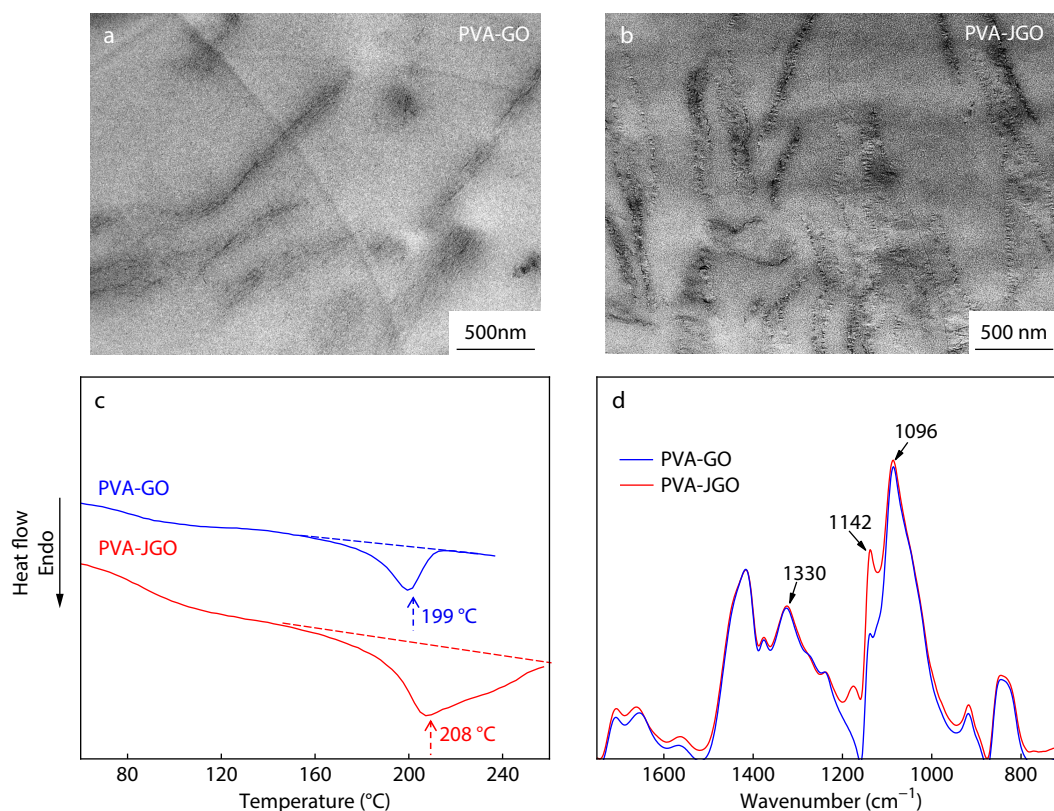


Fig. 4 TEM images of (a) PVA-GO and (b) PVA-JGO; (c) Flash DSC curves of PVA-GO, PVA-JGO at heating rates of 1000 K/s; (d) FTIR spectra of the PVA-GO and PVA-JGO nanocomposite films after normalized to the band 1330 cm^{-1} , the band 1142 cm^{-1} associated with crystallization.

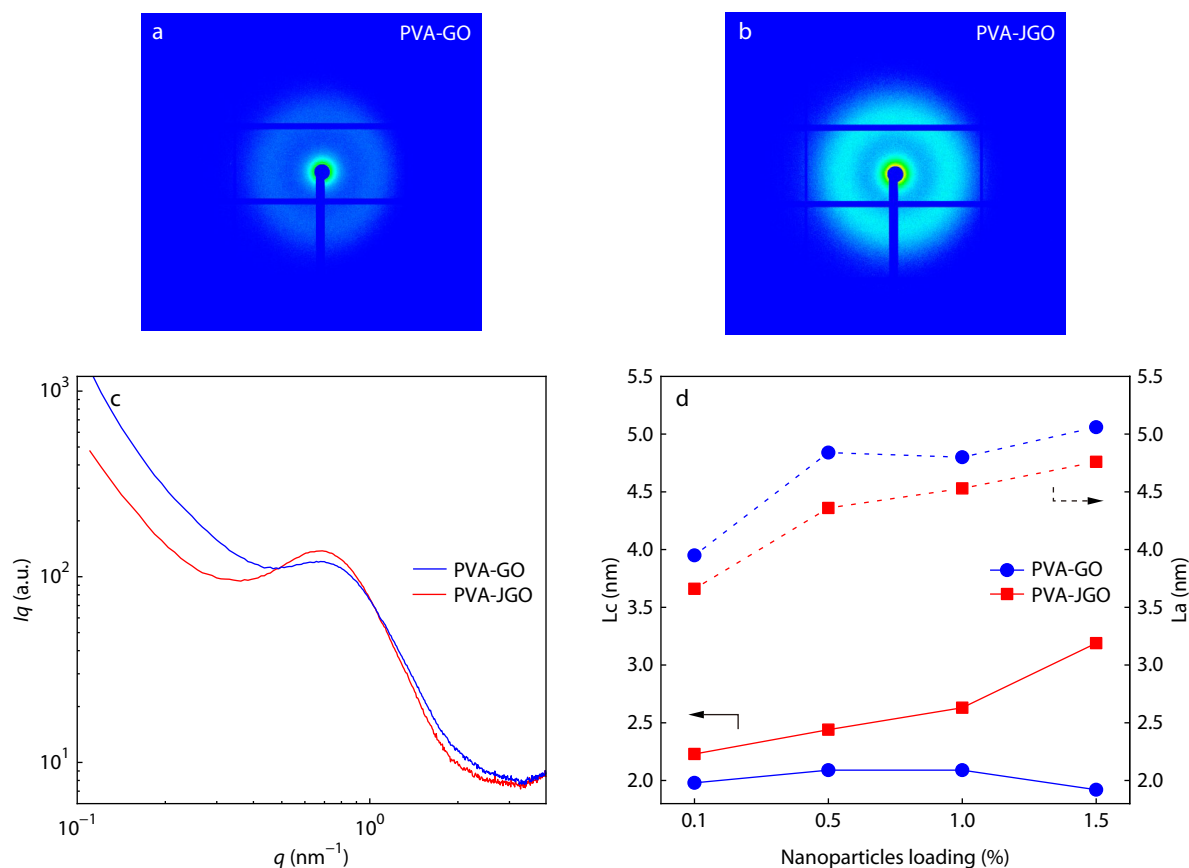


Fig. 5 Synchrotron 2D-SAXS patterns of (a) PVA-GO1.0 and (b) PVA-JGO1.0 nanocomposites by synchrotron radiation respectively. (c) Lorentz-corrected SAXS intensity profiles one-dimensional integral curve. (d) Thicknesses of crystalline lamellae (Lc), amorphous layers (La), calculated by Lorentz-corrected from one-dimensional electron density correlation function $K(z)$ estimated from the SAXS pattern of PVA-JGO and PVA-GO nanocomposite with different nanoparticles loading.

$$K(z) = \frac{\int_0^\infty I(q) q^2 \cos(qz) dq}{\int_0^\infty I(q) q^2 dq} \quad (2)$$

which is used for computing the thicknesses of crystalline lamellae (Lc), amorphous layers (La), and the long period (L) of the samples composed of layer-like system.^[38,40] Where z is perpendicular to the loading direction and $I(q)$ is obtained by integrating along the equator. The resultant $K(z)$ curves of PVA-GO and PVA-JGO with different loading samples are shown in Figs. S11(a) and S11(b) (in ESI), respectively. Corresponding curves of La and Lc are listed in Fig. 5(d). With increasing nanoparticles loading, the Lc value for PVA-JGO is conspicuously higher than that for PVA-GO, from 2.23 nm to 3.19 nm; PVA-GO has much lower Lc value from 2.08 nm to 1.92 nm. Additionally, compared with PVA-GO samples, the PVA-JGO samples show a relatively lower La, resulting from the denser crystallization structure of PVA-JGO samples promoted by JGO. These results indicate that JGO induces PVA to form thicker lamella crystalline and denser crystallization network and the results are consistent with the FDSC data.

On the origin for the interface crystallization in PVA-JGO system, there are two possible mechanisms: (1) Epitaxial crystallization; PVA has a monoclinic unit cell consisting of two molecules with lattice parameters of $a=0.781$ nm, $b=0.252$ nm, $c=0.551$ nm,^[41] while crystallographic parameter of the

graphene spacing is 0.246 nm,^[9] which can afford crystallographic match with PVA parameters of b crystal according to the fact that 10%–15% lattice mismatch rate is the upper limit of epitaxy.^[42] Therefore, it is speculated that such interfacial crystallization should be a kind of epitaxial crystallization. We do not discuss this point furtherly in this study. (2) Hydrophobic-hydrophobic interaction driven crystallization; The previous studies^[31,43,44] showed the similar phenomenon that the adsorption of PVA on the surface of hydrophobic material is driven by crystallization which was attributed to "hydrophobic interaction". During the release of water molecules from the solid-liquid interface, the subsequent crystallization of PVA polymer chains occurs at the nanosheet interface. Here, the hydrophobic graphite domains on JGO should provide the sites for interfacial crystallization of PVA.

Structural Model for PVA-JGO/PVA-GO Nanocomposite

On the basis of the above results and analysis, we can conclude structural model of the two nanocomposites, as shown in Fig. 6. As for PVA-GO, some researches^[45,46] have reported that PVA is adsorbed on the surface of oxidized silicon wafer due to the strong H-bonding interactions, and the interfacial layer is fully amorphous. Similarly, PVA chains close to the GO layer are greatly bound by GO, forming a "dead layer", as a large number of oxygen functional groups are distributed evenly on the

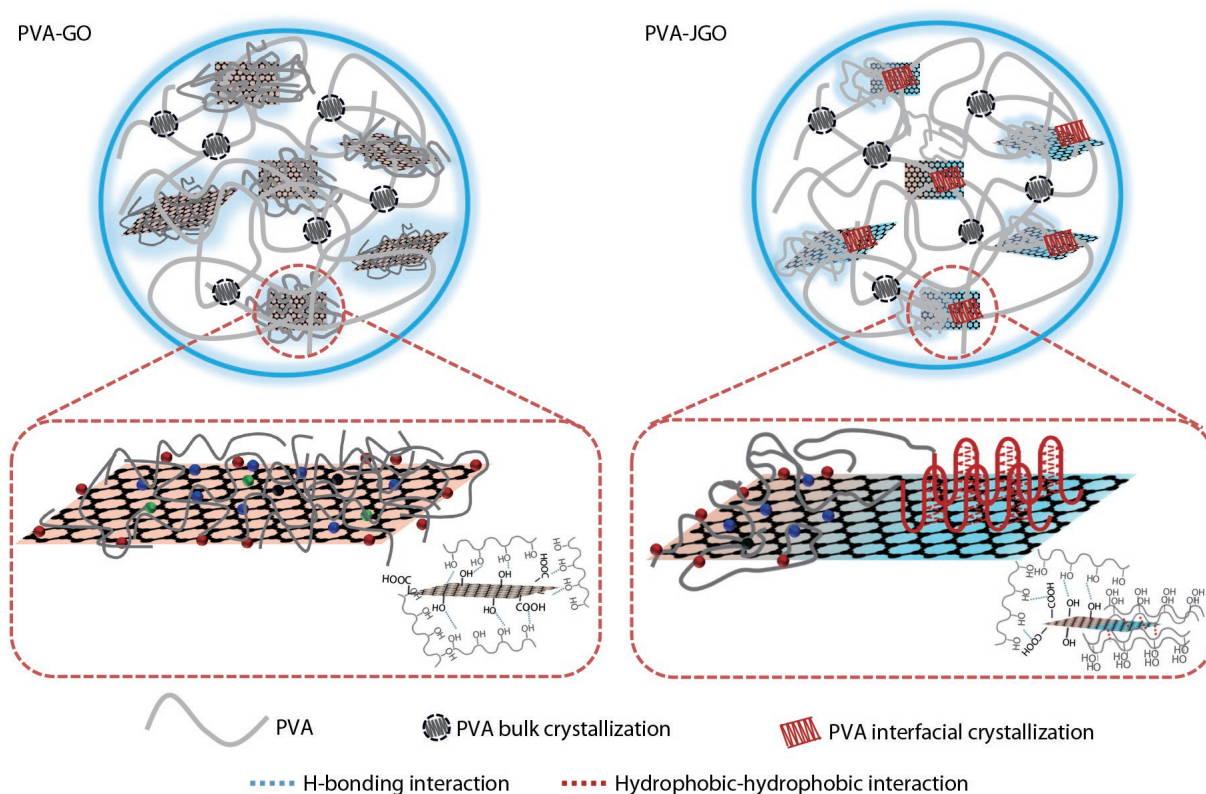


Fig. 6 Schematic representation of structural model for PVA-GO and PVA-JGO nanocomposite.

surface and edge of GO sheets. Crystallinity in PVA stems from double hydrogen bonds of hydroxyl groups in each monoclinic unit cell.^[41] Any influence on the intramolecular H-bonds of PVA will affect the PVA crystallization. The interfacial PVA chains around GO cannot take part in the crystallization of PVA matrix due to the confinement of the H-bonding effect. This also results in structural inhomogeneity. Whereas for PVA-JGO, the oxygen-containing functional group at one end of the JGO lamellae interacts with the hydroxyl group of PVA. In addition, the graphite domain structure at the other end of JGO is favorable for interfacial crystal growth of PVA by hydrophobic-hydrophobic effect. Interfacial crystallization in cooperation with bulk crystallization is beneficial to form more homogeneous crystallization network.

So far, several reasons have been proposed to explain why PVA-graphene or PVA-RGO materials show better reinforcing effect than PVA-GO composites: (1) Graphene or RGO has a higher intrinsic strength than GO for effective stress loads transfer to improve strength;^[19] (2) Graphene could act as a nucleating agent and thus improve crystallinity of PVA, leading to the enhanced mechanical performance;^[11,19] (3) Interfacial bonds of RGO are only distributed at the RGO sheet edges, causing RGO to align in the plane of the polymer film during stretching.^[15] Until now, no consensus is reached regarding this question. According to the above analysis, simultaneous improvement of strength and toughness for PVA-JGO should be attributed to favorable interaction for more uniform dispersion of JGO in PVA. What is more, the interfa-

cial crystalline layers formed by proper H-bonding interaction between PVA and JGO play positive roles in improving load transfer efficiency. That is, structural difference results in significant differences in performance between PVA-JGO and PVA-GO.

CONCLUSIONS

In summary, strong and tough PVA-graphene nanocomposites have been constructed by using the novel amphiphilic JGO nanofiller. The amphiphilic JGO surface with coexisting hydrophilic and hydrophobic domains facilitates the formation of strong H-hydrogen bonding and hydrophobic-hydrophobic interactions with amphiphilic PVA chains. As a result, the homogenous dispersion of JGO in PVA aqueous solution was easily achieved. Moreover, the hydrophobic interactions between JGO and PVA induced the interface crystallization of PVA during the subsequently drying process. The interface crystallization contributes to the formation of more dense and homogeneous PVA nanocrystal network. At the same time, the H-bonding interaction between JGO sheets and PVA matrix is beneficial to the stress transfer at the interface. Therefore, the synergetic effect of hydrogen bonding interaction and interfacial crystallization leads to a significant improvement in mechanical properties of both dry PVA nanocomposite films and their swollen hydrogel films. This study suggests that amphiphilic nanofiller is a promising candidate for reinforcing PVA to fabricate high-performance nanocomposites by tailoring both the macromolecule nanocrystal network and strong interfacial interaction.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

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