Preparation and Performance of an Aging-Resistant Nanocomposite Film of Binary Natural Polymer—Graphene Oxide

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ABSTRACT: As one of the materials having a bionic structure, nacrelike layered composites, inspired by their natural hybrid structures, have been studied via a variety of approaches. Graphene oxide (GO), which differed from inert graphene, was used as a new building block because it could be readily chemically functionalized. Rather than natural polymers, synthetic polymers were most commonly used to fabricate nacrelike GO—polymer materials. However, naturally occurring polymers complied more easily with the requirements of biocompatibility, biodegradability, and nontoxicity. Here, a simple solution-casting method was used to mimic natural nacre and fabricate a self-assembled and aging-resistant binary natural polymer, (κ-carrageenan (κ-CAR)—Konjac glucomannan (KGM)—GO nanocomposites, with varying GO concentrations. The investigation results revealed that κ-CAR—KGM and GO mostly self-assemble via the formation of intermolecular hydrogen bonds to form a well-defined layered structure. The mechanical properties of the natural polymer—GO films were improved significantly compared to those of pure natural polymer films. With the addition of 7.5 wt % GO, the tensile strength (TS) and Young’s modulus were found to increase by 129.5 and 491.5%, respectively. In addition, the composite films demonstrated high reliability and aging resistance as well as a definite TS after cold and hot shock and ozone aging tests, especially showing a superior ozone resistance. The composite films can potentially be used as biomaterials or packing materials.

INTRODUCTION

Motivated by the in-depth studies on biological structure, materials with a bionic structure have recently become a popular topic of materials research. The shell of Phormosoma placenta, a natural nacre, is a typical example of this.† The excellent mechanical properties of the shell of P. placenta arise from their combined advantages of the orderly layered structure and the abundant area of the interface between the inorganic platelets and organic matrix.‡ Inspired by their natural hybrid structures and excellent mechanical properties, scientists have attempted to mimic natural nacre and construct nacrelike layered composites via a variety of approaches.§ Recently, flattened double-walled carbon nanotubes, Al₂O₃ platelets, graphene oxide (GO), as well as other materials have been used as new building blocks with a polymer to provide many options for the development of new high-performance artificial materials through the duplication of the orderly layered structure.¶ GO was used as a precursor for the production of chemically modified graphene for the synthesis of new materials.‖ Graphene composites have become a hot research topic because graphene has many advanced characteristics that are superior to those of all materials, with some reaching theoretically predicted limits. As graphene is highly inert, GO can be readily chemically functionalized.¶ Recently, it has been found that the specific penetration energy for multilayer graphene at a velocity of 600 m/s is ~10 times higher than that reported in the literature for macroscopic steel sheets.© Notably, GO nanosheets can be used as ideal inorganic building blocks for the assembly of nacrelike materials.§–‖ Nanoreinforced GO—polymer materials exhibited excellent mechanical properties. Currently, most scientists use synthetic rather than natural polymers for assembly with GO.‖ However, the raw materials for synthetic polymers, such as petroleum and coal, are nonrenewable. Therefore, the use of natural polymers for the synthesis of new materials with a superior performance is a necessary direction for materials science research.¶

Compared with synthetic polymers, naturally occurring polymers comply more easily with the requirements of biocompatibility, biodegradability, and nontoxicity.‖ Carra-geenan (CAR), a marine-derived polymer, is a kind of polysaccharide that is extracted from red seaweed and is composed of galactose and anhydrogalactose units linked by glycosidic bonds.© κ-CAR and i-CAR are two types of CARs with gel-forming ability. Compared with i-CAR, κ-CAR gels are...
more firm, elastic, and soft. Furthermore, Κ-CAR exhibits good film-forming characteristics. Owing to its good pharmacological and biological activities, Κ-CAR is the most widely used commercial CAR. It was found that GO can be functionalized by CAR. The resulting Go—CAR composite was further used as a substrate for biomimetic and cell-mediated mineralization of hydroxyapatite. It has been suggested that the Go—CAR hybrid is a promising material for bone regeneration and implantation. In addition to these advantages, Κ-CAR also displays fatal weaknesses of low viscosity, which makes it difficult to control the formation of films in solvent evaporates, and poor mechanical properties for use in Κ-CAR composite materials. Konjac glucomanann (KGM) is another natural polymer that possesses great advantages of gelling, film-forming ability (hard film), antibacterial action, and low caloric value. Therefore, a kind of composite polymer of Κ-CAR and KGM can be prepared as a promising component for the construction of ultrastrong materials with GO through hydrogen-bond interactions due to the abundance of hydroxyl groups in the polymer chains and GO nanosheet.

Herein, nacrelike GO—polymer materials were prepared using two low-cost natural polymers, Κ-CAR and KGM, which enhanced their respective advantages and maintained good pharmacological and biological activities, thereby improving the film-forming controllability and mechanical properties and expanding the range of possible uses of composite materials in biomedical applications. Therefore, films were prepared from binary blends of Κ-CAR and KGM by adding different amounts of GO nanosheets to them. The mechanical and functional properties of the films were analyzed, and the effects of cold and hot shock and ozone aging on their structural and functional properties were discussed to evaluate the reliability of the material in practical applications.

**RESULTS AND DISCUSSION**

The obtained Κ-CAR—KGM (CK) film was white and semitransparent (Figure S1a, Supporting Information). CK—GO (CKG), containing GO, formed a well-defined layered structure (Figure 1d). Upon addition of GO, the film became dark brown (Figure 1a). SEM images showed that GO was embedded in CK and a higher GO content led to more intense and larger embedding regions in the layered structure (Figure 1c,d). In this process, GO nanosheets are combined with CK through intermolecular hydrogen bonds (Figure 2b). Focusing on the composite areas, we observed that the surface was not smooth because of the agglomeration of GO sheets and the agglomeration was not completely contiguous and uniform (Figure 1b). The thicknesses of the CKG films were measured,
The surface morphology and cross section of the samples were analyzed by scanning electron microscopy (SEM). The surface morphology SEM images of CKG showed GO sheet agglomeration, and it was found that the agglomeration was not completely contiguous and uniform (Figure 1b). Representative cross-sectional SEM images of CKG nanocomposites with different GO concentrations are shown in Figure 1c–d. With an increase in the GO concentration, the cross section of the CKG nanocomposite films became rough, which was ascribed to their well-defined layered structure. Additionally, it was clearly observed that the shear fracture surfaces of the CK–GO–7.5 wt % (CKG7.5) film had typical ductile fracture characteristics (Figure 1d). To determine the effect of different GO concentrations on the properties of CKG composite materials, representative SEM images of the tensile fracture cross section of CKG were obtained and are shown in Figure 1e–i. It can be found that the mechanism of tensile fracture of CKG was ductile fracture. A rough fracture surface can be clearly observed, and the tensile fracture cross section showed a small connecting wire and deformation traces before the occurrence of the fracture. The most serious structural damage occurred on CKG7.5 after tensile fracture, which led to almost total damage of its well-defined layered structure. Moreover, CKG7.5 showed the maximum TS with increasing GO concentration.

The unique feature of composite materials is their ability to combine properties that are in contrast to each other. Nacre is an excellent example of such a composite, obtained using layering. To understand the chemistry of κ-CAR, KGM, and GO interactions, we characterized κ-CAR, KGM, the CK composite, and the CKG nanocomposite using FTIR spectra (Figure 2a,b). Comparison of the spectra of pure κ-CAR,22 pure KGM,23,24 and CK composite films shows that the following changes occurred in the composite films. The bands of −OH, the C−H stretching vibration, and the bending vibrations of saccharide, C−O, and C6−OH groups were weakened and red-shifted to 3426, 2927, 1403, 1634, and 1075 cm$^{-1}$, respectively, indicating the formation of strong intermolecular hydrogen bonds between κ-CAR and KGM. These changes were caused by the anionic electrolyte generated by the half-ester sulfate groups on κ-CAR residues after the formation of the compound and the intermolecular hydrogen bond between O−SO$_3^−$ in κ-CAR and KGM. The existence of hydrogen bonds played a very important role in the increase in the efficiency of the ligand glue system (CK composite). Furthermore, the spectrum of the CK composite was similar to that of κ-CAR and only showed some notable differences within the fingerprint area. It can be speculated that the ligand glue system formed the main κ-CAR network structure, in which a core of κ-CAR chains aggregated with KGM chains attached to the surface. Here, KGM played an important role in improving the elastic and viscous properties of the ligand glue system.25–27 For GO, characteristic peaks appeared for carboxylic acids and carbonyl group C=O (1730 cm$^{-1}$), aromatic C=CC (1622 cm$^{-1}$), carboxy C−O (1414 cm$^{-1}$), epoxy C−O (1228 cm$^{-1}$), C−O (1116 cm$^{-1}$), and C−O−C (1035 cm$^{-1}$).28 Comparison of the spectra of pure GO, CK composite films, and CKG nanocomposite films shows that the following changes occurred in the spectra of the CKG nanocomposite films. The vibration bands of the −OH, C−O, C−H, and C6−OH groups were weakened and shifted to 3426, 1635, 1401, and 1069 cm$^{-1}$, respectively, because of the presence of strong intermolecular hydrogen bonds between GO and the CK composite.29 The vibration bands of carboxylic

Figure 2. (a, b) Fourier transform infrared (FTIR) spectra of κ-CAR, KGM, CK, GO, and CKG-7.5 wt % nanocomposite films. Rheological properties of CKG solutions: (c) moduli dependent on GO concentration in the form of linear coordinates.
acids and carbonyl group C=O (1730 cm\(^{-1}\)), aromatic C=C (1622 cm\(^{-1}\)), epoxy C–O (1228 cm\(^{-1}\)), and C–O–C (1035 cm\(^{-1}\)) cannot be observed clearly. This is most likely due to the vibration bands of the small amount of GO being overlapped by the spectrum of the CK composite. No new vibration bands were observed, indicating that with the exception of intermolecular hydrogen bonds no new chemical bonds are present. Such confirmed interactions in the assembled films would provide a solid foundation, resulting in enhanced mechanical properties.

To further elucidate the CK–GO interactions, we investigated the rheological properties of CKG solutions with different GO concentrations used for film casting (Figure 2c). We found that both the storage modulus, \(G'\), and the loss modulus, \(G''\), increased with increasing GO concentration up to 7.5 wt%; however, they declined dramatically at 10 wt%, which was most probably caused by the interactions between GO and CK, which are also beneficial for enhancing the mechanical properties of the as-prepared nanocomposites.\(^{11,30}\)

Moreover, the changes in the storage modulus, \(G'\), and loss modulus, \(G''\), were consistent with the change in the TS. With increasing GO concentration, the slope of the storage modulus plotted against the GO concentration of CKG solutions was much steeper than that of the loss modulus. For example, relative to those of the pure CK, the \(G'\) of CKG7.5 is significantly increased by 227.2%, whereas the \(G''\) is improved by 133.3%. Furthermore, it was found that the storage modulus, \(G'\), and loss modulus, \(G''\), of pristine GO are very low, indicating that the effect of GO concentration on the modulus of the suspensions was slight.\(^{23}\) This indicated the existence of strong interactions of GO with the molecular chains of CK and restricted mobility of CK molecules.

The dependence of the rheological properties of the CKG composites on the GO concentration was quantified using the analyses discussed above. These experiments also demonstrated that the properties of CK can be controlled by incorporation of different GO concentrations, which strongly indicated the intense interactions between the CK molecules and GO nanosheets.

To prove that the existence of strong CK–GO interactions contributes to the enhanced mechanical properties of their macroscopic assemblies, tensile stress–strain curves were plotted for CK and CKG composite films with different weight ratios of GO to CK, as shown in Figure 3. Here, the pure CKG goes to the CKG without dispose. For pure CKG, Young’s modulus and the TS of the CKG composite were significantly enhanced with increasing GO concentrations relative to those for CK (Figure 3a). For a GO concentration of 7.5 wt%, Young’s modulus and the TS of the CKG composite increased by 491.5 and 129.5%, achieving the best performance of 14.6 GPa and 126.9 MPa, respectively. With an increase in the GO concentration up to 7.5 wt%, the TS and Young’s modulus also increased, but the ultimate strain (US) decreased (Figure 3b,c). These changes were in accordance with the linear rule. Upon further increase of the GO concentration to 10 wt%, the TS and Young’s modulus decreased drastically. The high viscosity of the CKG composite caused by the strong interactions of GO with the molecular chains of CK damaged the uniform dispersion of GO at high GO concentration, resulting in the aggregation that gave rise to the observed attenuation of the mechanical properties. The aggregation was revealed by the appearance of the characteristic GO diffraction peak at 9.3° and graphite diffraction peak at 28° in the X-ray diffraction (XRD) pattern of the CKG-10 wt % film (Figure S3).\(^{31}\) The small-angle XRD pattern clearly showed the very obvious GO characteristic peak with an increase in concentration. By FTIR spectroscopy analysis, we showed that with the exception of intermolecular hydrogen bonds, no new chemical bonds are formed among \(\kappa\)-CAR, KGM, and GO. As GO nanosheets increased the toughness of CK, we can deduce that when the GO concentration reached the critical value the number and interactions of hydrogen bonds formed among the three
components, κ-CAR, KGM, and GO, were the largest and strongest, leading to optimal mechanical properties. When the GO concentration continued to increase, the distance between the GO nanosheets became smaller, caused by the molecular interatomic forces, leading to aggregation of the GO nanosheets. Interlayer sliding between the gathered GO layers would weaken the strengthening effect on the mechanical properties of the film. For pure CKG, we found that the critical value of GO concentration was 7.5 wt %.

To evaluate the reliability of CKG in practical applications, cold and hot shock and ozone aging resistance tests were used to manipulate the films. The mechanical properties of the films were evaluated to investigate the effect of cold and hot shock and ozone aging on the film. In this article, cold and hot shock

Figure 4. Mechanical properties of CKG films. (a, b) Stress–strain curves of CK and CKG7.5 nanocomposite films before (CK and CKG7.5) and after cold and hot shock (10 and 30 min) and ozone aging (50, 100, and 150 ppm) tests.

Figure 5. Mechanical properties of CKG films. (a) Stress–strain curves of cold and hot shock CKG nanocomposite films at 10 and 30 min, respectively. (b) TS of pure CKG and cold and hot shock CKG (at 10 and 30 min) nanocomposite films at different GO concentrations.

Figure 6. Mechanical properties of CKG films. (a) Stress–strain curves of the ozone aging CKG nanocomposite films at 50, 100, and 150 ppm. (b) TS of the pure CKG and ozone aging CKG (50, 100, and 150 ppm) nanocomposite films at different GO concentrations.
CKG and ozone aging CKG represent CKG subjected to cold and hot shock and ozone aging tests, respectively. For cold and hot shock CKG and ozone aging CKG, Young’s modulus and the TS were significantly enhanced with increasing GO concentration relative to those of CK and significantly reduced relative to those of pure CKG (Figure 4a,b).

**Effect of Cold and Hot Shock on CKG Films.** Cold and hot shock CKG showed results different from those for pure CKG (Figure 5a,b). At a GO concentration of 5 wt %, the best Young’s modulus and TS of the 10 min test were increased by 31.1 and 60.9%, yielding 1.42 GPa and 65.4 MPa, respectively, and the 30 min test showed a higher decrease than that in the 10 min test. The decrease in the TS of CKG was much higher than that for CK, pure CKG, and pure CK. This can be due to the more serious destruction of the interaction between the GO and CK than the interaction between κ-CAR and KGM.

**Effects of Ozone Aging on CKG Films.** The ozone aging CKG was the same as that of the pure CKG when the ozone concentration at 50 ppm, Young’s modulus and TS of the composite at the GO concentration of 7.5 wt % were increased by 181.6 and 440.1%, achieving 3.34 GPa and 80.0 MPa, respectively. With an increase in the ozone concentration to 100 and 150 ppm, the performance of the mechanical properties decreased, and the best value was obtained at a GO concentration of 5 wt % (Figure 6a,b). On the basis of the dramatic decline in the TS of CK, it can be suggested that GO played an important role in resisting ozone aging, owing to its full oxidation, and interaction among the three components resulted in better performance at a lower GO concentration. The reaction between ozone and the polymer resulted in a serious reduction in the mechanical strength of CK, indicating that ozone is an effective agent for the modification of polymers through many chemical reactions, such as the formation of hydroperoxide and peroxide groups, chain scissions, and intramolecular rearrangements. Because only intermolecular hydrogen bonds were present in CKG, it can be indicated that ozone destroyed these bonds by reacting with the polymers.

In this work, we found that the critical values of GO concentrations for pure CKG, cold and hot shock CKG, and ozone aging CKG are 7.5, 5, and 7.5 wt % (50 ppm) or 5 wt % (100 and 150 ppm), respectively. For cold and hot shock CKG, the difference can be due to the much more severe destruction of the interaction between GO and CK. Owing to the reaction between ozone and the polymer, the interaction between κ-CAR and KGM was destroyed, resulting in a change in the critical value of GO concentration with a change in the ozone concentration. The above two analyses were confirmed by FTIR spectroscopy on cold and hot shock CKG and ozone aging CKG, indicating that the vibration bands of −OH and C–H at 3426 and 2927 cm⁻¹ were weakened (Figure 7a,b).

**Comparison of the different GO concentrations and post-processing of the obtained CKG results showed that CKG7.5 showed the best comprehensive performance, on the basis of the results presented in Figures 8 and 9. In general, the CKG films maintained a definite TS after cold and hot shock and ozone aging and demonstrated their high reliability, making them favorable for practical applications.**

As plotted in Figure 10, compared with the reported composite films, the CKG7.5 film presented in our work exhibited remarkable mechanical properties. Its TS was of the same order of magnitude as that of the previous GO-based nanocomposite films and that reported in previous papers, for example, 1.58 times higher than that of the synthesized polymer–GO films (PVA–GO film, 80.2 MPa) and close to the values for natural polymer–GO mixture films (GO–chitosan film, 137.5 MPa). Although CKG did not exhibit the best TS, its US was higher than that of the other films.
previous GO-based nanocomposite films, which had a higher TS. CKG films showed outstanding toughness.

**EXPERIMENTAL SECTION**

**Materials and Methods.** Food-quality κ-CAR was obtained from Aladdin Co., Ltd. (Shanghai, China); KGM was provided by Mianyang Haomao Konjac Food Co. Ltd. (Sichuan, China); and GO nanosheets were obtained from flake graphite (<30 μm, Qingdao, China) using the modified Hummers’ method.41

**Preparation of CKG Films.** CKG films were obtained by evaporation-induced self-assembly after solubilization of film-forming substances. For solubilization of film-forming substances, κ-CAR and KGM powder should first be mixed in a ratio of 5.5:4.5, determined by the preliminary experiment (Figure S2, Table S1). Then, the mixed powder should be added into 200 mL of GO solution after ultrasonic treatment for 30 min. Thereafter, the reactant was reacted at 353 K for 30 min under magnetic stirring at 450 rpm, followed by ultrasonication for 30 min. The added GO amounts were set as 0, 2.5, 5, 7.5, and 10 wt %. The proportions of the reactants for the CKG films are presented in Table S2. The film-forming solution was poured into a plate mold slowly to form a flat solution membrane layer by flow-casting; it was then dried at 303 K, followed by careful peeling of the dried film after keeping it at room temperature for 2 h. Figure 1a illustrates the self-assembly based, efficient, and scalable preparation procedure for CK–GO nanocomposite films using GO as the nanoscale building block and natural polymers κ-CAR and KGM as organic adhesion agents.

**Characterization.** A digital micrometer (CHY-C 2; Languang, China) was used to measure the film thickness, with an accuracy of 0.1 μm. The structural characteristics of the samples were studied by XRD (Panalytical X’Pert Pro) using Cu Kα radiation. The surface morphologies and cross sections of the samples were analyzed by SEM (JSM-6390 LV; JEOL Ltd., Tokyo, Japan). The surface of the film was coated with gold particles (Bio-Rad type SC 502; JEOL Ltd., Japan) by sputtering for 60 s, allowing surface visualization using an accelerating voltage of 30 kV, followed by observation at a magnification of 2000–20 000×. The FTIR spectra of the films were recorded using pressed KBr pellets (Aldrich, 99%, analytical reagent), scanned from 4000 to 400 cm⁻¹ using a Nicolet 8700 FTIR spectrometer at room temperature. All film samples were preconditioned in a constant-temperature humidity chamber set at 298 K and 50% RH for at least 48 h before further testing. In the rheological measurements, the storage modulus (\(G^\prime\)) and loss modulus (\(G^\prime\)) were measured using a HAAKE RS 6000 Rotational Rheometer (Germany) at 298 ± 0.05 K.

**Measurement of Mechanical Properties.** The mechanical properties of the films, including the TS, US, and elasticity modulus (\(E\)), were determined according to the standard GB-T 1040.3 2006 method, using an MTS Testing Machine (CMT 5305; MTS Industrial Systems (China) Co., Ltd., Shenzhen, China) equipped with a 0.25 kN load cell. Rectangular strips (150 × 10 mm²) were cut from the individually prepared films. The initial grip separation was set at 50 mm and the cross-head speed was set at 5 mm/min. Five samples for each type of film were replicated.

**Cold and Hot Shock Test.** The cold and hot shock test was used to evaluate the reliability of the films in practical applications. The mechanical properties were measured after five cycles of cold and hot shock at a low temperature (\(T_L\)) of 243 K and a high temperature (\(T_H\)) of 353 K, with a test duration of 10 or 30 min according to the GB/T 2423 standard, using programmable hot and cold impact test cases (GT-CHT-2 S; Gotech Testing Machines Inc. Co., Ltd., China).

**Ozone Aging Resistance Test.** The ozone aging resistance test was also used to evaluate the reliability of the films in practical applications. The mechanical properties were tested by conducting ozone aging resistance tests at ozone concentrations of 50, 100, and 150 ppm at 313 K for 48 h according to the standard GB/T 7762-2003 method using an economical ozone resistance tester (OZ-0200-AC; Huasheng instrument (China) Co., Ltd., China). The reliability of the films in practical applications was evaluated by comparing their mechanical properties before and after disposal (cold and hot shock and ozone aging).

**CONCLUSIONS**

In summary, we have demonstrated a self-assembly based, simple, efficient, and scalable method to prepare CK–GO nanocomposite films with a well-defined layered structure. The synthesis was carried out on the basis of the strong hydrogen-bonding interactions between GO nanosheets and the κ-CAR and KGM molecules, with GO being the nanoscale building block.
block and the naturally occurring polymers, κ-CAR and KGM, being organic adhesion agents. The obtained CKG7.5 composite film exhibited excellent mechanical properties, with the same order of magnitude as that of previously investigated GO-based nanocomposite films and that in previous papers. Significantly, the CKG films maintained a definite TS after cold and hot shock and ozone aging and demonstrated good reliability in practical applications, especially superior ozone resistance. This natural polymer–GO composite film with excellent properties showed promise for a wide range of applications in diverse fields, such as food packaging, tissue engineering, and biological devices (Figure S6).

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00291.

Digital photos of CK and CKG7.5, mechanical properties of C (short for pure κ-CAR) and CK with different ratios of κ-CAR to KGM, XRD patterns and small-angle XRD patterns of CKG with different GO concentrations, typical tapping-mode AFM and TEM images of GO nanosheets, cytotoxicity test result of CKG, and data on reactant proportions and thicknesses of the CKG films (PDF)

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**Notes**

The authors declare no competing financial interest.

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