Sustainable, High-Performance, and Biodegradable Plastics Made from Chitin

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Cite This: ACS Appl. Mater. Interfaces 2022, 14, 46980−46993

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ABSTRACT: A high-performance biodegradable plastic was made from a chitin KOH/urea solution. The solution was transferred into a hydrogel by cross-linking using epichlorohydrin and ethanol immersion, and a chitin bioplastic was finally prepared by drying in a mold at 40 °C. The solution concentration positively impacts viscosity, crystallinity, and smoothness. A 4% chitin bioplastic exhibits high barrier properties, flame retardancy, high-temperature resistance, mechanical properties (tensile strength up to 107.1 MPa), and soil degradation properties. The chitin bioplastic can be completely degraded by microorganisms in 7 weeks. In addition, biosafety tests suggest that chitin is safe for cells and crops (wheat and mung beans). The chitin bioplastic was further applied to containers, straws, cups, and photoprotection, and it was found that the water resistance and transparency were comparable to those of commercial polypropylene plastics. Due to the excellent performance, safety, and sustainability of the chitin bioplastic, it is expected to become a good substitute for conventional fossil fuel-based plastics.

KEYWORDS: chitin, microstructure, flame retardancy, biodegradation, toxicity
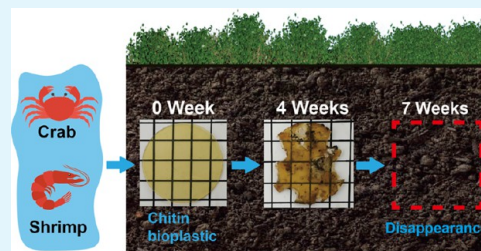
1. INTRODUCTION

At present, bioplastics are favored by researchers and industry as an alternative to traditional fossil fuel plastics.[1,2] According to the European Bioplastics Organization, bioplastics are either biobased, biodegradable, or features both properties.[3] Bioplastics have many benefits, including reducing greenhouse gas emissions, being able to biodegrade, etc., which make them an attractive invention for environmental sustainability that solves the problem of plastic pollution.[4,5] Bioplastics are usually made from natural and renewable raw materials and biomass sources such as vegetable oil,[6] cellulose,[7−9] starch,[10,11] and chitin.[12] There have been many advances in this area recently. For example, Xia et al. used a facile in situ lignin regeneration strategy to synthesize lignin bioplastics with high mechanical strength, degradability, and recyclability.[9] Ding et al. prepared monolayer chitin nanoribbons films and pipettes by filtering and drying using chitin as raw materials. It was supposed to be a candidate for partial replacement of petroleum-derived and hardly degradable plastic products.[13] A biodegradable film composed of palm oil-plasticized starch and chitosan was prepared by Hasan, and this film was promising for sustainable packaging applications due to its high stability and excellent biodegradability.[14] All of these studies show that bioplastics are a viable, green, sustainable material with far-reaching implications for ameliorating plastic pollution. Nevertheless, compared with various renewable resources, chitin has the characteristics of abundant reserves, biodegradability, film-forming properties, nontoxicity, biocompatibility, and bio-

chemical availability. Therefore, chitin is very attractive as a raw material for the preparation of bioplastics.[15−17]

Chitin is the second most abundant natural biomass resource. Chitin is found in ordered crystal structures in the shells of crustaceans (such as shrimp and crabs), the cell walls and secretions of bacteria and fungi, the epidermis of various insects, the endoskeletons of mollusks (such as squid), and the cell walls of algae. Among them, the shells of shrimps and crabs contain the most chitin.[12,18−20] However, due to the high crystallinity and strong inter-/intramolecular hydrogen bonds, the solubility of chitin in water and common organic solvents is poor, which limits their utilization.[21] The solvents of chitin are mainly halogenated organic solvents such as trifluoroethanol (TFE) and trichloroacetic acid (TCA), ionic liquids (such as 1-butyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazole chloride), and other strong polar organic solvents (such as an N,N-dimethylacetamide (DMAc)/LiCl system).[20,22] These organic solvents have disadvantages such as environmental and human toxicity, difficulty in recycling, and high price.[20] Although a NaOH/urea solution can dissolve chitin effectively, it must undergo multiple freeze−thaw cycles. All of these routines are difficult for large-scale industrial applications

for preparing chitin bioplastics due to the technique and cost reasons.[20,23]

Recently, an improved and fast solvent of a KOH/urea solution for dissolving chitin was realized by Cai.[24] This method for dissolving chitin can obtain a clear and transparent chitin solution, and the obtained chitin hydrogel and the chitin film have excellent mechanical properties.[25,26] Therefore, preparing bioplastics with chitin as a raw material have a good development prospect.[25] Chen et al. developed a chitin hydrogel with good transparency and toughness by dissolving chitin in a KOH/urea solution, and then using γ-(2,3-epoxypropoxy) propytrimethoxysilane (KH560) as a cross-linking agent and coagulating at low temperature in an ethanol solution.[26] Huang et al. dissolved chitin in a KOH/urea solution to make a chitin hydrogel, and finally evaporated the hydrogel to obtain a chitin film with good flexibility and excellent mechanical properties.[25] However, previous studies have rarely reported the relationship between the structure, degradable properties, and daily applications of chitin bioplastics made by the KOH/urea dissolving method.

In this study, different contents of chitin were dissolved in a KOH/urea solution, and epichlorohydrin (ECH) was used as a chemical cross-linking agent of the chitin solution and then immersed in ethanol to shrink the chitin molecular chain to form physical cross-linking bonds (hydrogen bonds) to prepare a double cross-linked chitin hydrogel. Subsequently, chitin bioplastics were successfully prepared by drying in a mold at 40 °C. The morphology and the structure of the chitin bioplastics were determined, and the mechanical properties, flame retardancy, reliability, degradability, and biosafety of the bioplastics were evaluated. Finally, the photoprotection of chitin bioplastics was compared with commercial polypropylene plastics. Furthermore, due to the excellent properties of the chitin, the prepared bioplastic was applied to straws, cups, and plastic seals. This work provides a routine for using ocean renewable resources in high-performance biodegradable plastics as a substitute for petrochemical plastics.

2. EXPERIMENTAL SECTION

2.1. Materials. Raw materials and chemical reagents were used without further treatment unless otherwise specified. Chitin was supplied by Weifang Dongxing Chitin Manufacturing Co., Ltd., China. Potassium hydroxide (KOH) was purchased from Tianjin Baishi Chemical Co., Ltd., China. Urea was obtained from Tianjin Damao Chemical Reagent Factory, China. ECH was acquired by Tianjin Fusheng Chemical Reagent Factory, China. Ethanol was provided by Tianjin Fuyu Fine Chemical Co., Ltd., China.

2.2. Preparation of Chitin Bioplastics. Chitin powder was dissolved in a KOH/urea solution at a low temperature according to the method in the literature.[27] First, a certain amount of chitin powder was uniformly dispersed in a KOH/urea solution according to the ratio of KOH/urea/distilled water = 20:4:76 to prepare 2, 3, and 4% chitin solutions. The well-stirred mixture was placed in a refrigerator at −70 °C for 8 h until the mixture was completely frozen. Then, the solution was thawed at room temperature. After the mixture was evenly stirred, the chitin solution was placed in the refrigerator at −70 °C for 8 h again. Then, the chitin solution was thawed out and obtained. Finally, the chitin solution was poured into 50 mL centrifuge tubes and centrifuged at 13,000 rpm for 15 min at 0 °C to remove air bubbles and impurities to obtain a clear chitin solution.

Subsequently, ECH was added dropwise to the chitin solution in an ice−water bath (0 °C) with a molar ratio of ECH to N-acetyl-D-glucosamine units as 1:1. After stirring evenly, the mixture solution was cast into the mold. The mold was sealed and placed in a 60 °C oven for 24 h. After that, the chitin hydrogel was soaked in a 75%

ethanol seal for 12 h and then washed with pure water to remove alkali and urea until the solution was neutral. The transparent chitin hydrogel was then placed between two glass sheets and clamped with a phoenix clip, and then placed in an oven at 40 °C for at least a week to be dried to obtain a chitin bioplastic.

2.3. Characterization of Chitin Bioplastics. The viscosity, storage modulus (G'), and loss modulus (G'') of a chitin solution and a hydrogel were tested by a rheometer (Discovery HR-20, TA Instruments). The surface morphology was characterized by scanning electron microscopy (SEM, SU1000, HITACHI, Japan) at a voltage of 15 kV. The three-dimensional (3D) surface morphology was observed by atomic force microscopy (AFM, Bioscope Catalyst Nano scope-V, Bruker Instruments Ltd.), and the surface roughness was analyzed. The crystal phase structure was determined by X-ray diffraction analysis (XRD, Rigaku Group, Japan) using Cu Kα radiation (λ = 1.5418 Å). The molecular structure was tested by a Fourier transform infrared spectrometer (FTIR, Nicolet iS50, Thermo Fisher Scientific Co. Ltd.), with a scanning range of 400−4000 cm^{-1}. The water and oil (peanut oil) contact angle was measured with a contact angle tester (DSA 100, KRUSS, Germany). The thermogravimetric analysis (TGA) was tested by a thermogravimetric instrument (Mettler, Toledo, Switzerland) using a heating rate of 10 °C/min from 30 to 700 °C under a nitrogen atmosphere. The temperature of thermal degradation was detected by a differential scanning calorimeter (DSC, Q20, TA Instruments) under a nitrogen atmosphere (50 cm^3/min) in a temperature range of 30−400 °C with a heating rate of 10 °C/min. The tensile properties were determined by an electric universal testing system (AGS-X, Shimadzu, Japan), and the stretching rate was placed at 5 mm/min.

2.4. Water Vapor Permeability (WVP) and the Oxygen Transmission Rate (OTR). The WVP of chitin bioplastics was determined gravimetrically at 25 °C. The bioplastic was tightly covered on a weighing bottle containing about 16 g of a predried anhydrous silica gel. After weighing, it was placed in a sealed desiccator controlled at a 44% relative humidity for adsorption balance. Then, the total weight of the device was weighed after 48 h. The parallel test was done 3 times.

The WVP of the chitin bioplastic can be calculated by

$$\text{WVP} = \frac{\Delta m \times d}{\Delta t \times A \times \Delta P} \tag{1}$$

where $\Delta m / \Delta t$ is the weight gain of the weighing bottle per unit time (g/s), d is the thickness of the film (m), A is the effective area of the film (m^2), and ΔP is the water vapor pressure difference across the membrane at 25 °C (1753.55 Pa).

The OTR of chitin bioplastics was evaluated using an oxygen transmission rate test system (PERME OX2/230, Labthink, China). It was measured at 25 ± 2 °C, 50% ± 5 relative humidity (RH) following the ASTM D-3985 standard method. The results were the mean of at least three replicate measurements. The unit of the OTR was used as barrer, which was equal to 7.5005 × 10^{-18} m^2 s^{-1} Pa^{-1}.

2.5. Optical Transmittance and Swelling Properties. The optical transmittance of the chitin bioplastic was obtained by testing its light transmittance in an optical wavelength range of 200−800 nm with a ultraviolet (UV) light photometer (TU-1810SPC, Beijing Puxi General Instrument Co., Ltd., China). The parallel test was done 3 times.

The swelling properties of the chitin bioplastic in a water phase and an oil phase were tested. The chitin bioplastic (a round piece with a diameter of 2 cm) was soaked in distilled water and peanut oil at room temperature for 6, 12, 24, 36, 48, 60, and 72 h, and the weight before and after the sample was recorded, respectively. The parallel test was done 3 times. Then, the swelling rate of the chitin bioplastic was calculated by the following equation

$$\text{swelling rate} = \frac{S_b - S_a}{S_a} \times 100\% \tag{2}$$

where S_a and S_b are the weights of the bioplastic before and after immersion in the water phase or the oil phase, respectively.
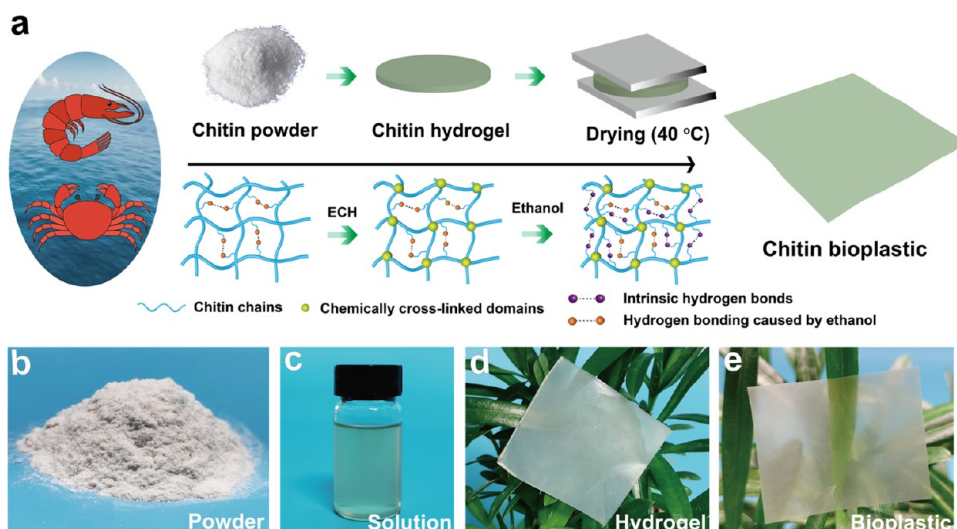
Figure 1. Preparation of the high-performance chitin bioplastic. The schematic demonstrating the preparation of the chitin bioplastic (a). The appearance of chitin powder (b), solution (c), hydrogel (d), and bioplastic (e).
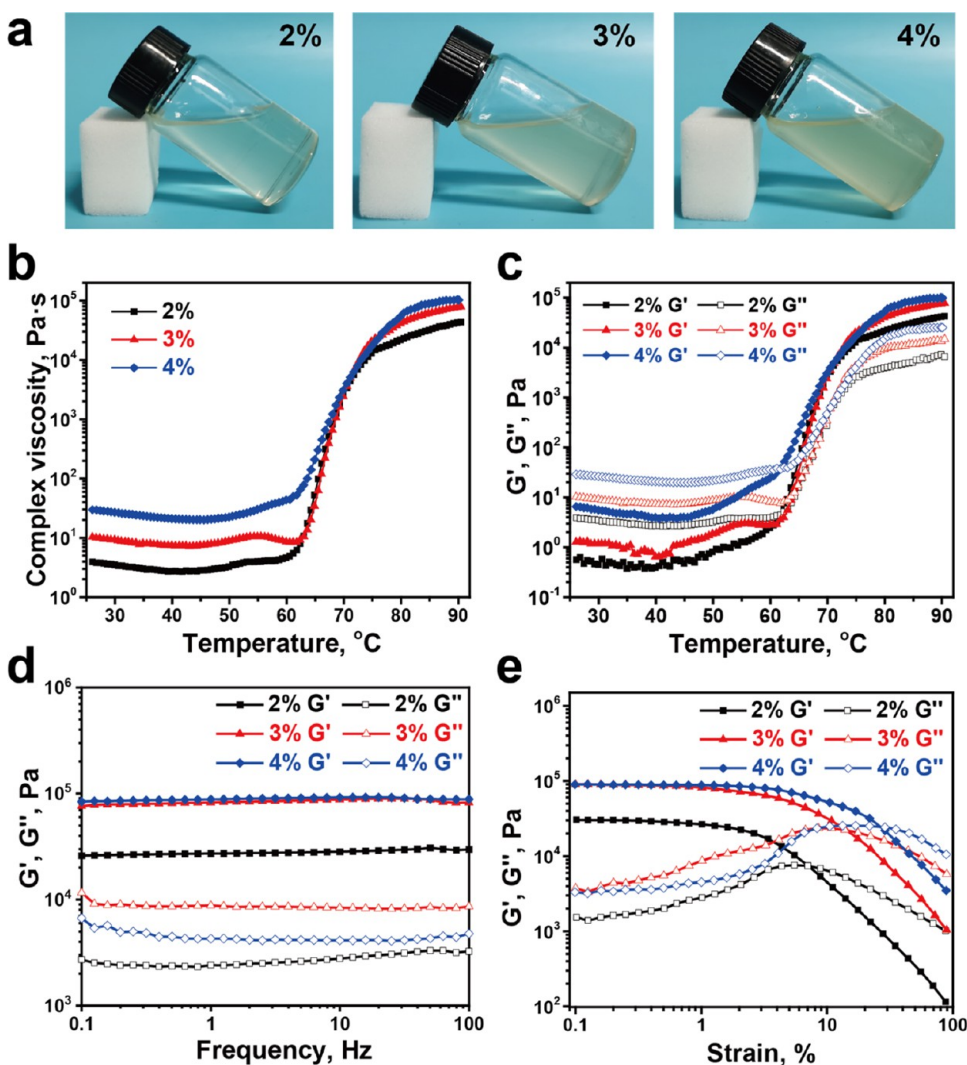

Figure 2. Rheological properties of the chitin solution and the chitin hydrogel. The appearance of chitin solutions in different concentrations (a). The relationship between viscosity and temperature of the chitin solution (b). Curves of G' and G'' of the chitin solution versus temperature (c). Curves of the chitin hydrogel G' and G'' vs frequency (d). G' and G'' vs strain relationship of the chitin hydrogel (e).

2.6. Flame-Retardant Properties and High-Temperature Resistance. The chitin bioplastic (0.8 cm × 5 cm) was tilted at an angle of 45°, and the process from ignition to natural extinction was recorded after igniting one side of the sample to test the flame retardancy of chitin bioplastic. The parallel test was done three times.

The cup-shaped chitin bioplastic containing water and peanut oil was placed on the asbestos net, and an alcohol lamp was lit under the asbestos net to test the high-temperature resistance of chitin bioplastic. The parallel test was done three times.

2.7. Degradation Test in the Soil. A chitin bioplastic disk (2 cm in diameter) was buried in the soil at room temperature. The bioplastic was taken out at a fixed time every week, and the soil pH value was determined. Then, the taken samples were gently rinsed with distilled water and placed in an oven at 50 °C for drying for testing.

2.8. Biocompatibility. Wheat and mung bean seeds were soaked in distilled water for 24 h, and then the seeds were transferred to a container containing a chitin bioplastic for germination and growth. The germination rates of different groups were calculated. In addition, after 10 days of culture, the average root length of each group was counted. The group without chitin was used as the control group, and each group was tested three times in parallel. In addition, the liquid extract of the chitin bioplastic was used to culture mouse fibroblast L929, and the cytotoxicity of the material was evaluated by the cell counting kit 8 (CCK-8). L929 cells (3×10^4 cells/mL) were seeded (100 μL/well) in a 96-well plate (3599, Corning), and the plates were preincubated in a humidified incubator for 24 h to allow cells to adhere to the well walls. The sterile chitin bioplastic was soaked in a cell growth medium (2 mL of the medium containing 1 cm^2 of the sample) for 24 h, and then the extract and the cell culture solution were mixed at 0:5, 1:4, 2:3, 3:2, and 4:1 ratios to prepare a new cell growth medium. After 24 or 48 h of treatment, each well's absorbance at 450 nm was measured using a microplate reader (Bio-Tek, Hercules). Each group was tested three times in parallel, and cell viability was estimated.

Acridine orange (AO) (living cell/green) and ethidium bromide (EB) (dead cell/red) kits were used to detect the fluorescent staining of live/dead cells. L929 cells (3×10^4 cells/mL, 1 mL/well) were inoculated in a 24-well plate (3524, Corning) and treated with different proportions of extracts. The morphology of cells was observed under a fluorescence microscope (XDY-2, Guangzhou Liss Optical Instrument Co., Ltd., China). At 24 and 48 h, L929 cells were injected with 5 μL of Annexin-V-FITC and propidium iodide (PI) to distinguish cells in different apoptosis cycles. After incubation for 10 min, flow cytometry (BDFACSCantoII, BD Bioscience) was used to analyze the treated cells.[28] The parallel test was done three times, and the final results were analyzed by flowjo 10.0.2 software (BD Biosciences).[29]

3. RESULTS AND DISCUSSION

3.1. Preparation of Chitin Bioplastics and Rheology Properties of a Chitin Solution and a Chitin Hydrogel. Raw chitin derived from crab can be easily dissolved in a KOH/urea solution by a freeze−thaw method twice. The clear and transparent chitin solution was then transferred into a hydrogel by chemical cross-linking by ECH and physical cross-linking by immersing in an ethanol solution. Finally, the chitin hydrogel was dried between two plates at 40 °C to form a thin film (the thickness is about 100 μm). The preparation process of the chitin bioplastic and the appearance of the product are illustrated in Figure 1. It can be seen the prepared chitin bioplastic was self-standing and semitransparent with certain flexibility. The influence of the chitin solution concentration on the structure and properties of the bioplastic was investigated in detail.

Chitin powder was mixed with a KOH/urea solution at a different concentration by stirring, and the chitin powder was dissolved by a low-temperature freeze−thaw method to obtain a clear and transparent chitin solution (Figure 2a). While the solution concentration is beyond 4%, the high viscosity limits the preparation of the hydrogel. To determine the solution− hydrogel transfer temperature of the chitin solution, the relationship between the viscosity of the chitin solution and temperature was studied by a rheometer. Figure 2b shows the relationship curve of the viscosity of the chitin solution with different concentrations as a function of temperature, which shows the process of the chitin solution transforming into a chitin hydrogel. It can be seen that the viscosity of the chitin solution at different concentrations showed a gradual decrease at first due to the heating and then increased rapidly with the increase in temperature. The complex viscosity of 2 and 3% chitin solutions increased rapidly after 64 °C, and the complex viscosity of the 4% chitin solution increased rapidly after 62 °C, indicating that the chitin solution was changing to a hydrogel in this temperature range. The viscosity of the solution and the hydrogel increased with solution concentration since more polymer chains were in the solution. To further explore the influence of the chitin concentration and temperature on solution stability, the relationship between the G' and G'' of the chitin solution and temperature was studied. G' represents the elasticity of the solution and G'' represents the viscosity of the solution. When G' intersects G'', the corresponding temperature is considered the gelation temperature of the solution. The gelation temperature of 2 and 3% chitin solutions was 64 °C, and the gelation temperature of the 4% chitin solution was 62 °C (Figure 2c). Before becoming a hydrogel, the G' of the chitin solution with three concentrations was much lower than that of G''. At this time, the solution had fluidity. When the temperature was close to the gelation temperature, G' increased sharply. Then, G' equals G'' and continued to increase and reach its peak value, so the chitin solution was completely gelatinization and stabilized. The reason that the chitin solution became a hydrogel upon heating is that the aggregation and entanglement of chitin chains were driven by the hydrophobic interaction during the process of temperature increase.[30] Notably, the sudden increase in G' over a very narrow temperature range indicated that the solution−hydrogel transition was fast and strict. In addition, in previous literature reports,[12,31,32] the reaction temperature of ECH as a cross-linking agent with a chitin solution can be 4 °C, room temperature, or 60 °C. Based on these results, to promote cross-linking, 60 °C was chosen in this work, which is close to the gelation temperature of the chitin solution.

Furthermore, the relationship of the angular frequency of different concentrations of a physically/chemically double cross-linked chitin hydrogel was investigated, as shown in Figure 2d. It can be seen that with the increase in angular frequency, the G' corresponding to different concentrations of the chitin hydrogel was always greater than its corresponding G'', which indicates that the chitin hydrogel with different concentrations in the angular frequency range shows a solid state. The dynamic viscoelasticity of different concentrations of the chitin hydrogel was tested by a rheometer under a dynamic stress environment to further understand the effect of concentration on the mechanical properties of the chitin hydrogel. In Figure 2e, the G' of the chitin hydrogel with different concentrations decreased with the increase in strain, and the lower the concentration, the faster the decrease. When G' of the hydrogel was higher than G'', the chitin hydrogel also presented a solid-like state, which can maintain good elasticity
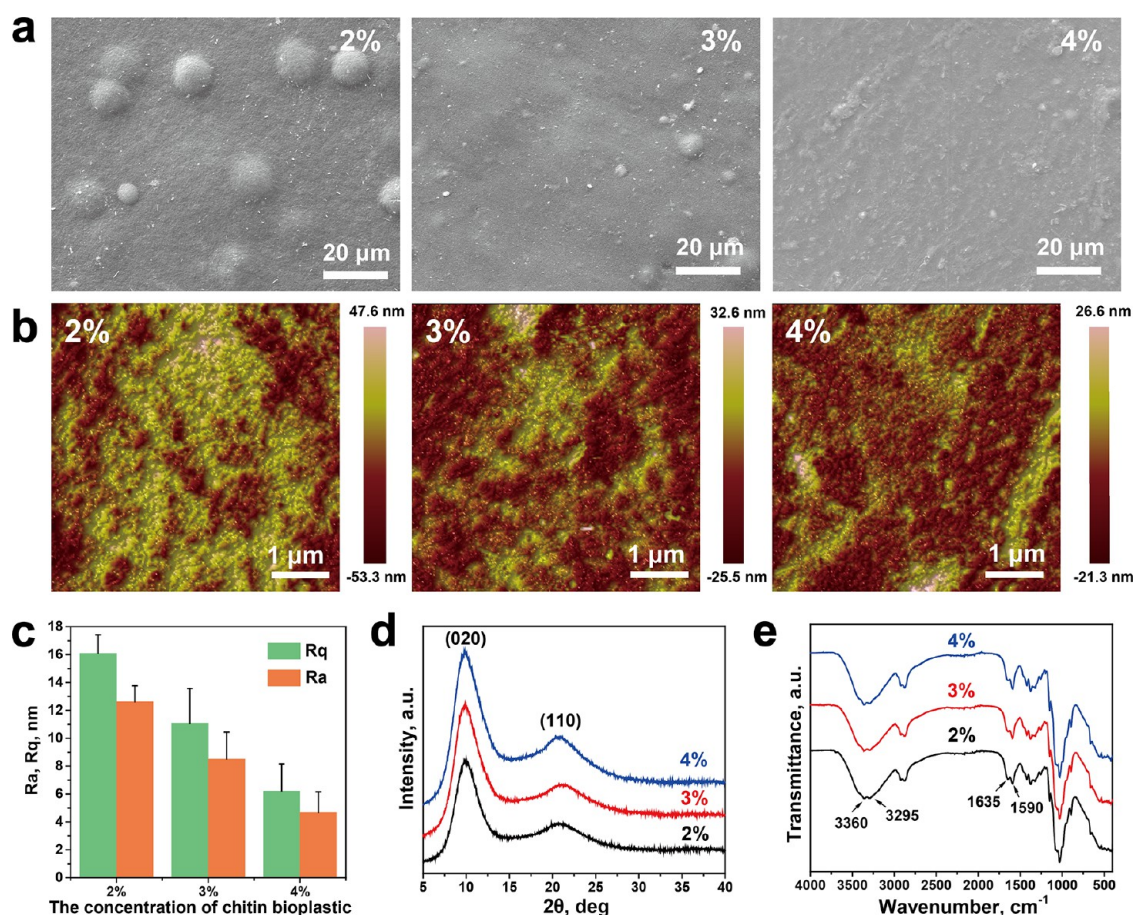
Figure 3. Characterization of the chitin bioplastic. SEM image (a), AFM image (b), roughness (c), XRD patterns (d), and FTIR spectra (e) of the chitin bioplastic.
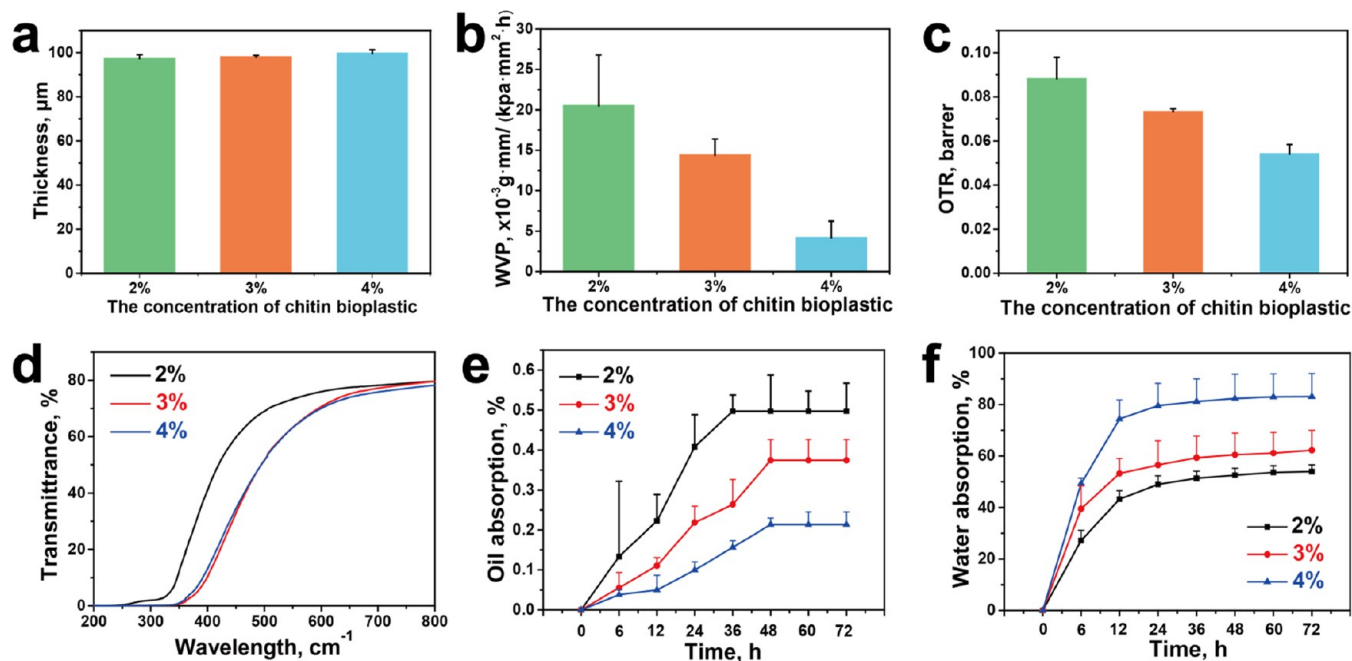

Figure 4. Barrier properties and the swelling rate of chitin bioplastic. The thickness (a), WVP (b), OTR (c), optical transmittance (d), peanut oil (e), and water (f) absorption of the chitin bioplastic.

and deformation resilience, while when G' was lower than G'', the solid-like state of the chitin hydrogel was destroyed due to

the high stress breaking down the polymer network of the entangled chitin hydrogel. Therefore, the 4% hydrogel can
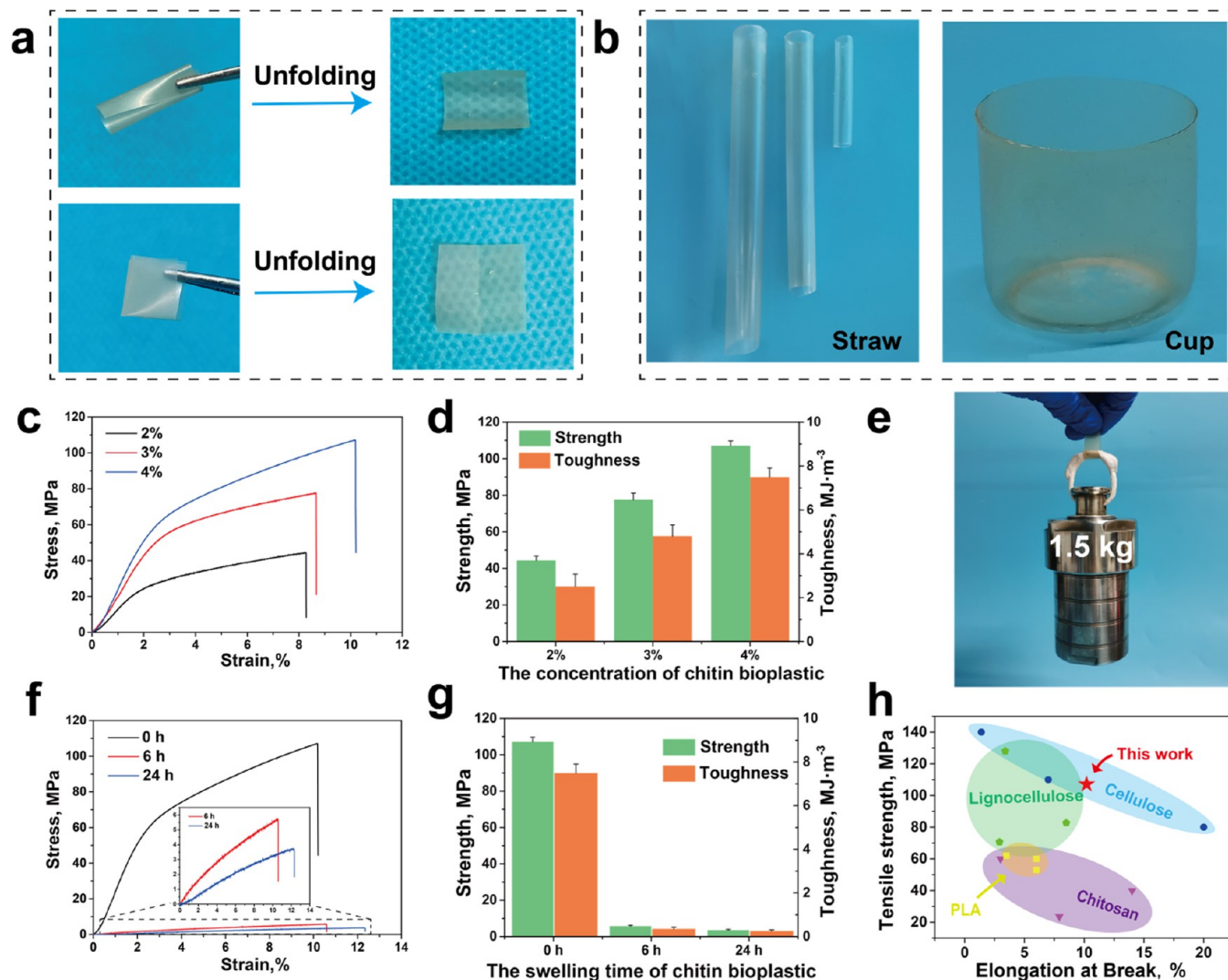
Figure 5. Mechanical properties of the chitin bioplastic. Crimping and folding of the chitin bioplastic (a). Straw and cup made with the chitin bioplastic (b). The tensile stress−strain curves (c) and the calculated strength and toughness (d) of the chitin bioplastic with different concentrations. A 1.5 kg weight hanging from the 4% chitin bioplastic strip (with a 7 mm width and 0.1 mm thickness) (e). The tensile stress−strain curves (f) and the calculated strength and toughness (g) of the chitin bioplastic with different swelling times in water. A comparison of the tensile strength and elongation at break of the bioplastic prepared in this study with those of biobased plastics reported previously (h).

tolerate higher stress and maintain the hydrogel state at high frequencies and strain than the other two hydrogels.[33]

3.2. Characterization of Chitin Bioplastics. The surface morphology of the chitin bioplastic with different concentrations was analyzed by SEM and AFM (Figure 3a,b). It can be seen from the SEM images that the surface of the chitin bioplastic was uneven. However, the surface flatness and smoothness of the bioplastic became better with the increase in chitin concentration. The surface roughness of a 2% concentration was larger, the surface roughness of a 3% concentration was reduced, and the surface of a 4% concentration was very flat and smooth. AFM pictures also prove this conclusion. The higher the concentration, the smaller the fluctuation of the surface height of the chitin bioplastic, and the surface was smooth and flat. The histogram of the surface roughness of the chitin membrane measured by AFM is shown in Figure 3c. It can be known that with the increase in chitin concentration, the R_a and R_q will also decrease. These results indicated that the concentration of chitin will affect the surface smoothness of the chitin bioplastic.

It is considered that the higher the concentration of chitin, the greater the density of molecules in the bioplastic, resulting in a tighter arrangement of molecules and smaller gaps.[34] Therefore, the higher the concentration, the smoother and tidier the membrane surface will be.

The XRD patterns of 2, 3, and 4% chitin bioplastics are illustrated in Figure 3d. There are diffraction peaks at about 10 and 20.8°, respectively, representing the (020) and (110) crystal planes, respectively.[27,35] With the increase in chitin concentration, the diffraction peak of the chitin bioplastic became higher and sharper, which is because there are more crystalline phase transitions in the chitin bioplastic with increased concentration.[36] In addition, the FTIR spectra of the chitin bioplastic are also compared in Figure 3e. The characteristic peaks of 2, 3, and 4% chitin bioplastics were 3360 cm^{-1} (O−H stretching), 3295 cm^{-1} (N−H stretching), 1635 cm^{-1} (amide I), and 1590 cm^{-1} (amide II), indicating that the chitin bioplastic is a typical α-chitin structure.[37] No new peak of the cross-linked chitin bioplastic was observed due to the small amount of the cross-linking bond in the whole
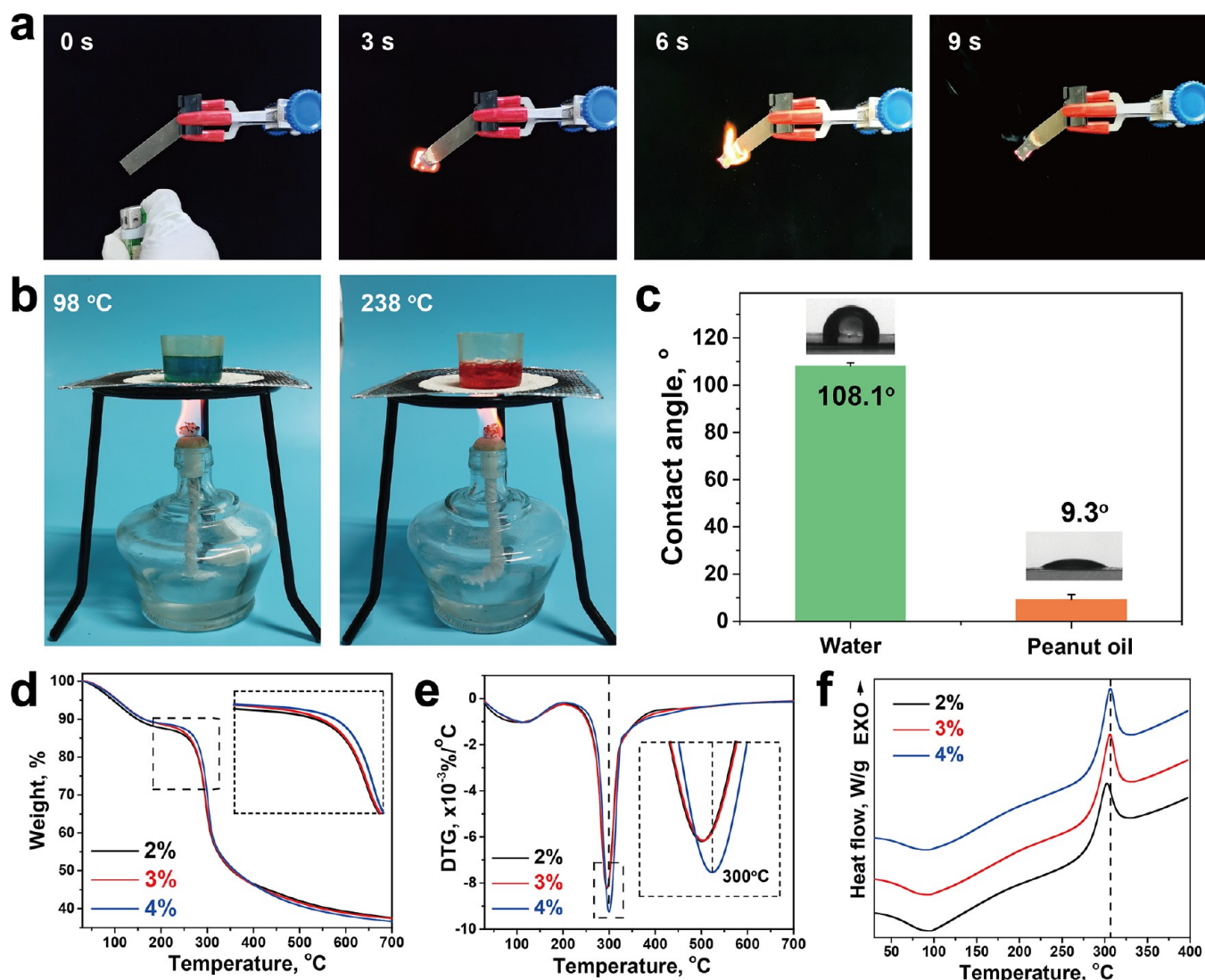
Figure 6. Flame retardancy and high-temperature resistance. Burning of the chitin bioplastic (a). Hold boiling water (dyed by methylene blue) and oil (dyed by Sudan III) in the cup-shaped chitin bioplastic (b). The contact angle of peanut oil and water at different temperatures of the 4% chitin bioplastic (c). The TG (d), DTG (e), and DSC (f) curves of 2, 3, and 4% chitin bioplastics.

system. The characteristic peaks of the chitin bioplastic with a 4% concentration were relatively stronger than those of the plastic with a relatively low concentration.

3.3. Properties of the Chitin Bioplastic. After drying in a mold, the thickness of 2, 3, and 4% chitin bioplastics was approximately 100 μm, and the weight loss rate was close to 90% (Figures 4a and S1). To understand the barrier properties of the chitin bioplastic, the WVP and OTR tests were carried out (Figure 4b,c). The results show that the WVP and OTR of the chitin bioplastic decreased with concentration increase. This is because as the concentration increased, the chitin's polymer network formed became denser, and the free volume became lower. Hence, the amount of water vapor and oxygen passing through the bioplastic per unit time was also reduced.[38] Surprisingly, the OTR of the chitin bioplastic was comparable to or better than that of commonly used packaging films made of other polymer materials, such as polypropylene (PP) and polyethylene (PE) (the OTR of PP and PE are 0.75−1.52 barrer and 0.75−1.04 barrer, respectively).[39,40] This facilitates the application of the chitin bioplastic in food packaging. Figure 4d shows the light transmittance test of

different concentrations of the chitin bioplastic at 200−800 nm. The maximum light transmittance of the chitin bioplastic was 80%, and the light transmittance decreased a little with the increase in concentration. The light transmittance of a 2% concentration was significantly different from that of 3 and 4%, which may be due to the looser polymer chains in the 2% concentration. The slightly different transparency has little effect on the application of the chitin bioplastic in packaging.[41] Furthermore, when the chitin concentration exceeded 3%, more alkyl groups undergo n−π* electronic transitions under the action of NH$_2$ and hydroxyl auxiliaries, which made the chitin bioplastic exhibit UV absorption in the UV region.[42] The chitin bioplastic shows excellent barrier performance and anti-UV irradiation functions, showing great potential in food package materials.

The swelling behavior of the chitin bioplastic was studied with distilled water and peanut oil. Figure 4e shows the absorption curve of the chitin bioplastic to peanut oil within 72 h. The figure shows that the chitin bioplastic with lower concentration has a higher oil absorption rate per unit time. However, the absorption rate of peanut oil by the chitin

bioplastic with these three concentrations was not high (<0.6%). Figure 4f shows the absorption curve of the chitin bioplastic to water within 72 h, indicating that the chitin bioplastic with a higher concentration had higher water absorption per unit time. The results of water adsorption and WVP are not consistent. This is because there is an osmotic driving force in water; when chitin swelled, the hydrophilic groups on the chitin molecular chain were fully hydrated, and the hydrophobic groups generated hydrophobic bound water until the swelling equilibrium was reached. However, for the WVP of the chitin bioplastic, since the sample was not immersed in water, the main factor affecting the WVP was the compactness of the molecular structure of the chitin bioplastic.[43]

For application as package materials, the bioplastic must exhibit good mechanical properties. The chitin bioplastic (1.5 cm ×1.5 cm) can be curled and folded arbitrarily (Figure 5a). Also, the chitin bioplastic can not be damaged after curling and folding, which indicates that the chitin bioplastic will have good plasticity. Therefore, the chitin bioplastic in the shape of a cup and straw was then prepared (Figure 5b). Recently. Chen et al. prepared high-performance chitin straws with the method of suction filtration of the chitin slurry, but it took a longer preparation time than the method used in this work.[44] Similar to chitin straws prepared by Chen, the straw-shaped chitin bioplastic of this work also can suck up solutions under suction and can be used in different drinks (Figure S2 and Movie S1), and the straw-shaped chitin with various colors can also be prepared by immersing the hydrogel in dye solutions according to preference (Figure S3). In addition, the cup-shaped chitin bioplastic can also hold different solutions, such as water, peanut oil, milk, and coffee. Moreover, the stress−strain curves of the chitin bioplastic with different concentrations were tested (Figure 5c). With the increase in chitin concentration, the tensile strength and elongation at the break of the chitin bioplastic significantly improved. Figure 5d shows the maximum tensile strength and toughness calculated from the stress−strain curves. It can be seen that when the concentration increased, the maximum tensile strength and toughness of the chitin bioplastic gradually improved, and the tensile strength and elongation at break of the 4% chitin bioplastic reached 107.1 MPa and 10.2%, respectively. The 4% chitin bioplastic strip with a width of 7 mm and a thickness of 0.1 mm can support a weight of 1.5 kg and exhibit excellent mechanical properties (Figure 5e). The aggregation, entanglement, and interaction between rigid chains of chitin increase with the increase in concentration, which contributes to the improvement of the strength.[25] The flexibility of the chitin bioplastic will be increased after soaking in an aqueous solution, which can be employed as a toughening method. Therefore, by testing the 4% chitin bioplastic at a different soaking time, the stress−strain curves after swelling in water were calculated by a universal testing machine (Figure 5f). It can be observed that although the chitin bioplastic soaked in water for a period of time can increase its elongation at break, its tensile strength and modulus were greatly reduced (Figure 5g). This indicates that water molecules enter the rigid chains of chitin and disrupt interchain aggregation and interchain entanglement, resulting in a dramatic decrease in strength and toughness.[45] Therefore, in the use of packaging, the chitin bioplastic should be avoided in contact with water for too long time. Furthermore, the chitin bioplastic was compared with the mechanical properties of other biobased plastics such as

cellulose,[46−48] lignocellulose,[9,49,50] chitosan,[51−53] and poly-lactic acid (PLA).[54] From Figure 5h, it is known that the mechanical properties of tensile strength and elongation at the break of the chitin bioplastic in this work are better than those of these commonly used bioplastics. Through our test, no matter how long it takes, the chitin water cup can still hold a certain amount of water without breaking and water leakage, and the chitin straw can still be used for as long as 6 h. This proves that the mechanical properties of the chitin bioplastic are sufficient for daily life applications.

The properties of flame retardancy and high-temperature resistance are essential properties for evaluating packaging materials. A combustion test was conducted to determine the flame retardancy of chitin bioplastic. The chitin bioplastic sample was ignited by a lighter (Figure 6a and Movie S2). The results show that the chitin bioplastic sample took only 9 s from ignition to extinction, which means that the chitin bioplastic has good flame retardancy. This may be because the chains of chitin are rich in nitrogen.

When ammonia is generated during combustion, nitrogen has inherent flame retardancy.[55] Moveover, the cup-shaped chitin bioplastic was filled with water or peanut oil and heated with an alcohol lamp to further investigate the heat resistance. During this process, the water and oil temperature gradually increased until it boiled. Interestingly, the chitin bioplastic cup was still able to withstand this temperature without being damaged within 2 min surprisingly (Figure 6b). To explore why chitin can withstand the high temperature, TGA and DSC of the chitin bioplastic were tested. Figure 6d,e shows the TG and differential thermogravimetry (DTG) curves of chitin bioplastic, respectively. The slight weight loss around 100 °C was attributed to the water release related to the hydrophilic character of chitin. At 200−400 °C, the chitin bioplastic loses weight seriously, with a weight loss rate of 55%. This is due to the depolymerization and decomposition of the polymer chain through deacetylation and glycosidic bond cleavage, which is also the main process of thermal degradation of chitin. At the same time, according to the DTG test, the thermal decomposition temperatures of 2, 3, and 4% chitin bioplastic were 296, 296.5, and 300 °C, respectively. DSC curves in Figure 6f also support the high thermal stability of the chitin bioplastic below 300 °C. Therefore, the chitin bioplastic can hold boiling water and peanut oil (boiling point below 290 °C). Most applications associated with such bioplastics, such as packaging and containers, typically operate at temperatures ranging from room temperature to just over 100 °C. These operating temperatures are well below what the chitin bioplastic of this work can withstand.[56] In addition, the contact angle of the chitin bioplastic to water and peanut oil was explored (Figure 6c). The contact angle of the chitin bioplastic with water was larger than that of peanut oil, suggesting its surface hydrophobicity. This is mainly because the fact that the cross-linking of chitin with epichlorohydrin reduces the number of surface hydroxyl groups, and the physical cross-linking makes the chitin molecule more dense.[57,58] Thus, the flame retardancy and high-temperature resistance tests demonstrate that the chitin bioplastic can be used in packaging and containers.

3.4. Degradation Test in the Soil. As a product to replace traditional plastic, the test of degradation performance in the environment is essential. Therefore, the biodegradation test of the chitin bioplastic was examined.[9,59] Chitin bioplastic discs (2 cm in diameter) were buried in the soil with a pH of
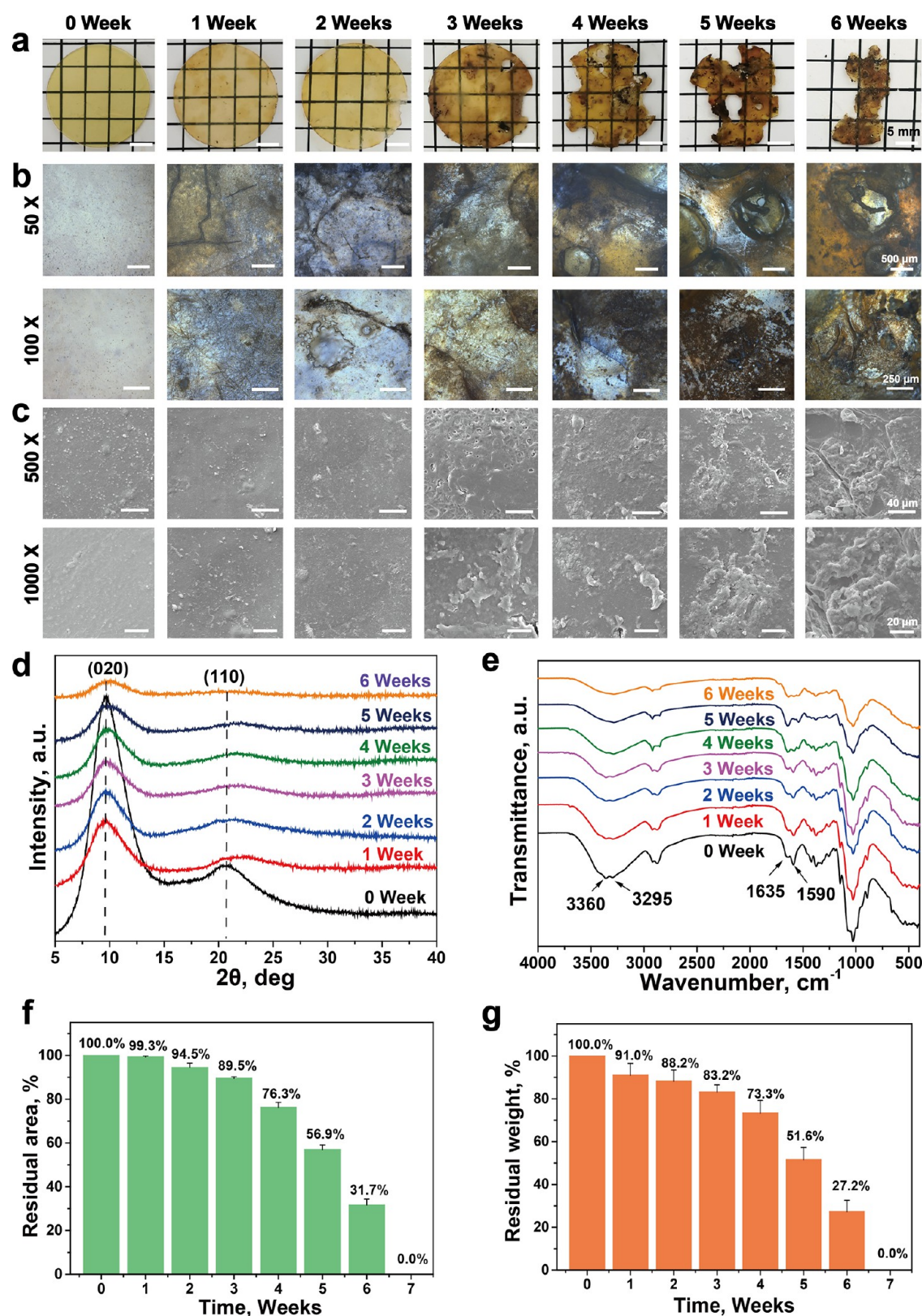
Figure 7. Degradation test of the chitin bioplastic in the soil. Digital images (a), optical microscopy images (b), SEM images (c), XRD patterns (d), FTIR spectra (e), residual area (f), and weight (g) of the 4% chitin bioplastic within the degradation period of 7 weeks.

about 5.6 at room temperature. The surface of the chitin bioplastic was gradually eroded with the increase in the soil burial time until the degradation ended (Figure 7a), indicating that the microorganisms (for example, bacteria and fungi) in the soil could directly degrade the chitin bioplastic.[9,59] At the same time, through optical microscopy observation, it can be seen that the chitin bioplastic forms a surface with an uneven surface and cracks from a flat surface (Figure 7b), which was
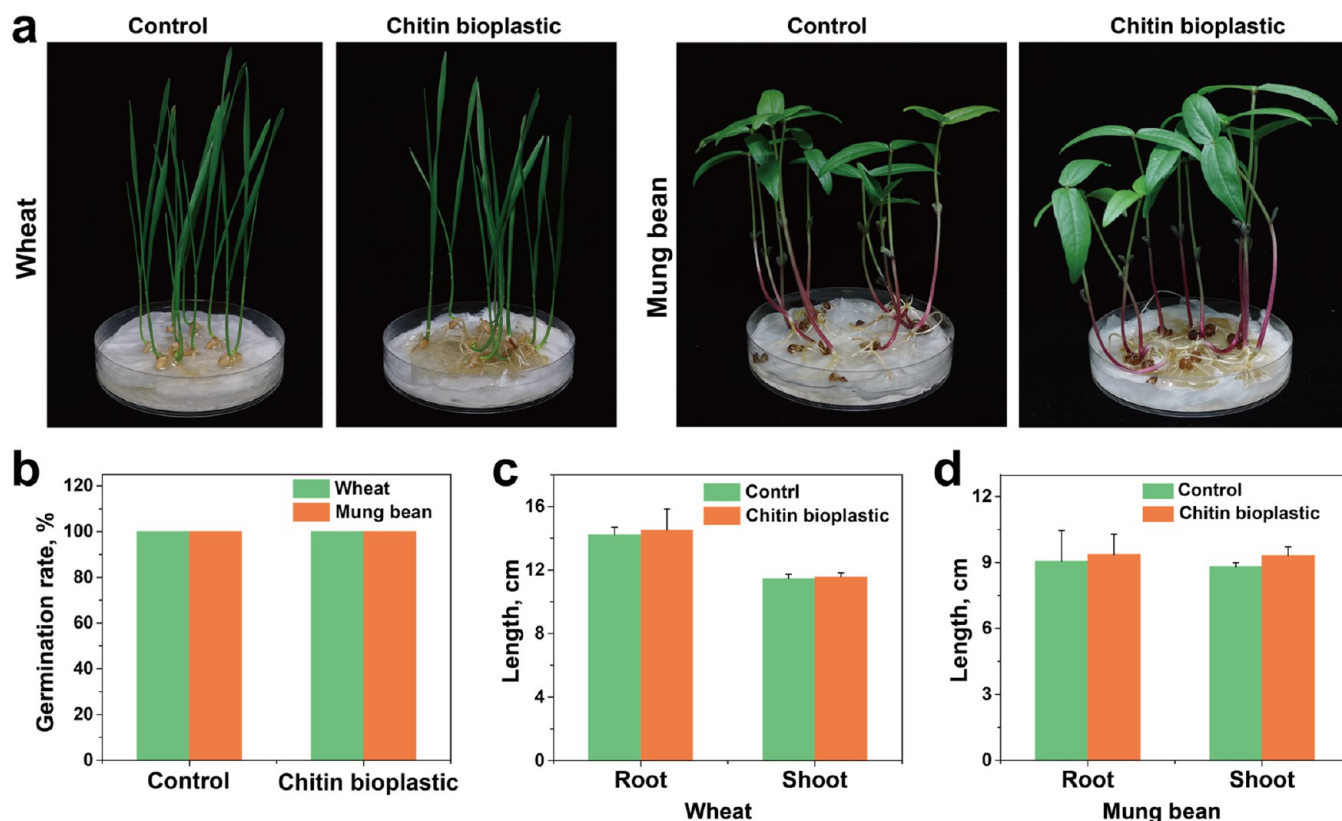
Figure 8. Biotoxicity of the chitin bioplastic (day 10). The growth situation (a) and the germination rate (b) of the wheat and mung bean. The root and shoot lengths of the wheat (c) and mung bean (d).

further confirmed by the SEM image, which indicates that the microorganisms in the soil can degrade the chitin bioplastic directly. To study the transformation of the structure and crystal phase of the chitin bioplastic during degradation, the chitin bioplastic degraded every week was tested by FTIR and XRD (Figure 7d,e). Through the test, it can be known that the intensity of the characteristic peaks of the chitin bioplastic gradually weakened, and the characteristic functional groups were gradually destroyed. This proves that the crystalline phase and functional groups of the chitin bioplastic were gradually destroyed by microorganisms. The chitin bioplastic was completely degraded by microorganisms over a period of 7 weeks. The incompletely degraded fragments of the chitin bioplastic were collected with care. The residual area calculated by ImageJ software and the residual weight of the chitin bioplastic every week were compared (Figure 7f,g). It was found that the degradation rate of the chitin bioplastic increased quickly from the 3rd week to the end of the 7th week. The degradation test shows that the chitin bioplastic has good biodegradability.

3.5. Biocompatibility and Practical Application. Traditional plastics have certain negative impacts on the environment.[60] Free ECH in the chitin bioplastic may be left in the environment or transferred to crops after degradation. To explore the biosafety of the chitin bioplastic, two common crop models, wheat and mung bean, were used to evaluate the ecotoxicity of the chitin bioplastic. Wheat and mung bean seeds were put into distilled water for seed germination and then transferred into containers containing the chitin bioplastic for cultivation. Figure 8a displays the growth of wheat and mung beans, respectively. By counting the germination rate,

root, and shoot length (Figure 8b−d), it was found that the germination rates of wheat and mung beans in the chitin bioplastic were both 100% as well as of the control group. The root and shoot length of the two plants after 10 days of growth was almost no different from that of the control group. Therefore, it can be concluded that chitin bioplastic has little harm to the germination and growth of plants, and the chitin bioplastic has good biological safety. The result can be understood by the fact that the etherification between chitin and ECH occurred easily in alkaline conditions, and the cross-linking reaction was completed. No chlorine is included in the molecular chain of the cross-linked chitin.

As a frequently used daily necessity, plastics will inevitably have indirect or direct contact with human skin. Here, L929 cells were used as a model for testing cytocompatibility. L929 cells were cultured with a control group and the gradient chitin bioplastic leaching solution for 24 and 48 h. After cocultivation, the cell viability was detected with a CCK-8 detection kit, and the toxicity of the chitin bioplastic was evaluated by comparison. As shown in Figure 9a, no matter whether it was cultured for 24 or 48 h, there was no significant difference between the groups cultured with the chitin bioplastic extract and the control group, and the cell viability for all of the groups exceeded 90.0%. This suggests that the chitin bioplastic has negligible toxicity to cells.[59]

To further test the cytocompatibility of the chitin bioplastic, L929 cells were stained with an AO/EB staining solution and observed using a fluorescence microscope. AO can enter living cells, staining the nucleus to glow green, and EB can cause cells in the late stages of death and apoptosis to glow red. Thus, under fluorescence microscopy, living cells appear green with
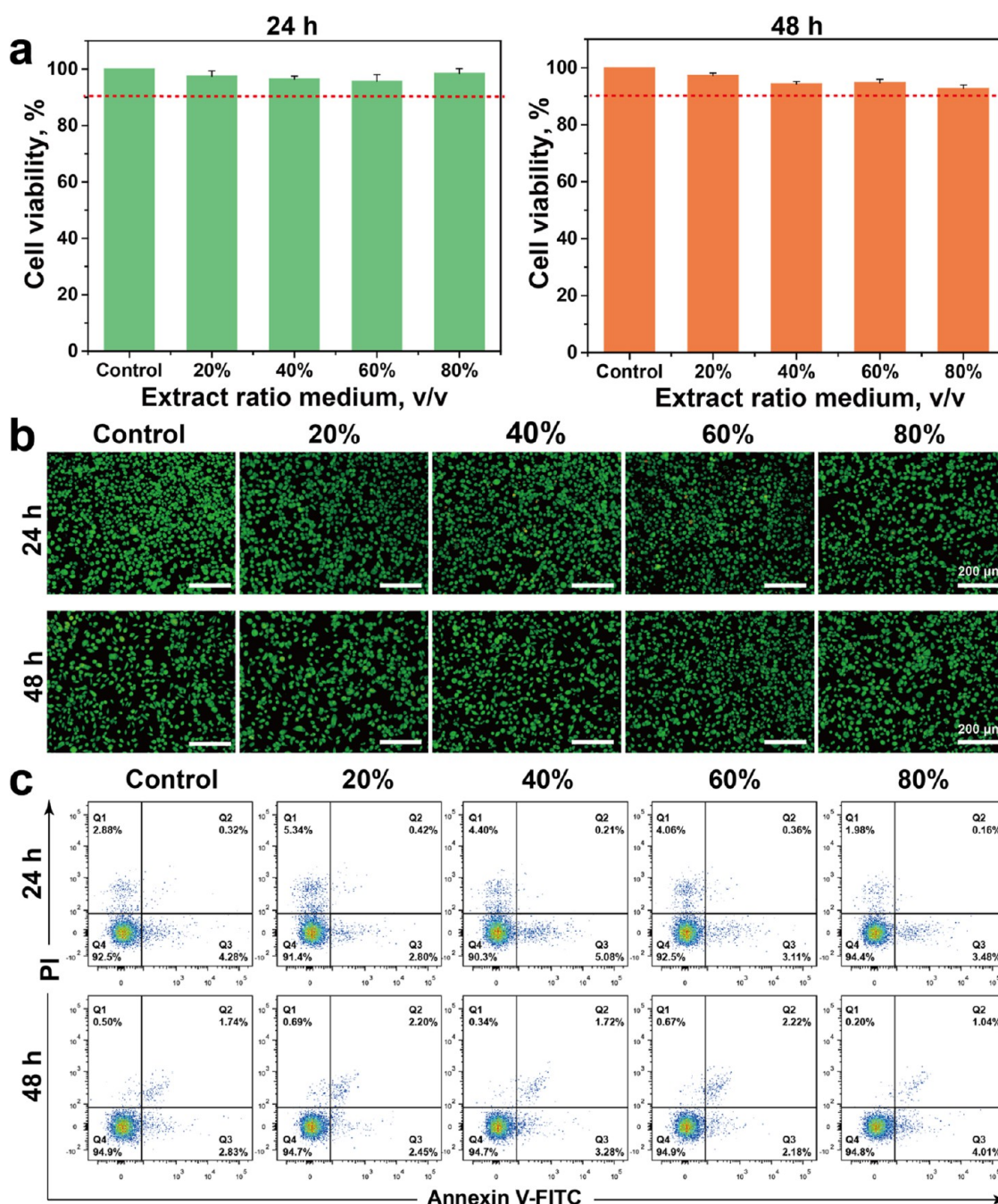
Figure 9. Cytocompatibility of the chitin bioplastic. Viability of L929 cells in culture media containing different concentrations of the chitin bioplastic extracts by the CCK-8 method (a). AO/EB live/dead staining images of L929 cells cultured for 24 and 48 h (b). Apoptosis and necrosis results of L929 cells in the culture media containing different concentrations of the chitin bioplastic extracts by flow cytometry (c).

intact round nuclei, and cells in the late stages of death and apoptosis appear red with condensed or fragmented nuclei. Figure 9b shows that the fluorescence microscopy images of both the control group and the gradient chitin bioplastic leaching solution group maintained a large area of green fluorescence, while the red fluorescence only existed in a small amount.[29,59]

Flow cytometry was also used to investigate the cytocompatibility of the chitin bioplastic. The cells in Q1 are necrotic cells, and there may be a few late apoptotic cells, even mechanically damaged cells. The cells in Q2, Q3, and Q4 regions are late apoptotic cells, early apoptotic cells, and living cells, respectively. Figure 9c shows that after incubating with

the gradient chitin bioplastic extract for 24 and 48 h, the number of living cells in the chitin bioplastic extract group was above 90% as that in the control group, which further proves that the chitin bioplastic has excellent cellular compatibility.[28] According to the crop toxicity and cytotoxicity evaluation of the chitin bioplastic, it can be believed that the chitin bioplastic has high biosafety.

Finally, because the chitin bioplastic has excellent comprehensive properties, it can be used in photoprotection. The properties were compared with the commercial photo-protecting membrane of biaxially oriented polypropylene (BOPP). As shown in Figure S4a, water was dropped on the photo sealed by the BOPP plastic and the photo sealed by the

chitin bioplastic to verify its water resistance. It could be found that after 5 min, there was no obvious change in the two water droplets. Thus, the ability to protect photos of the chitin bioplastic was comparable to commercial PP. Through the contact angle test, it was found that their contact angle was similar to the contact angle just after the drop and 5 min later (Figure S4b). To verify the force of direct binding of the chitin bioplastic with photo, XRD, and FTIR tests with raw chitin and the raw cellulose of photo (Figure S4c,d) were conducted. It was found that no new crystallization peaks and groups appeared in the chitin and cellulose composites, and there was no reaction between chitin and cellulose. Therefore, the chitin adhered to the photo by physical interactions such as hydrogen bonding. This simple application demonstrated the ability to protect photos of the chitin bioplastic was comparable to commercial PP plastics.

4. CONCLUSIONS

In this work, chitin, the second abundant natural biomass resource, was used as a raw material for preparing biodegradable plastics. After dissolving chitin in a KOH/urea solution, a double cross-linked chitin hydrogel was prepared using ECH as a chemical cross-linking agent and then immersed in ethanol to form a physical cross-linking bond (hydrogen bond). Subsequently, the chitin bioplastic was prepared by drying in a mold at 40 °C. The higher content of chitin is beneficial to the smooth surface topography and high crystallinity. The 4% chitin bioplastic exhibits an excellent barrier, flame-retardant, high-temperature resistance, mechanical properties (tensile strength up to 107.1 MPa), and soil degradation properties. Biosafety tests showed that the chitin bioplastic is a safe product for different crops, and no obvious cytotoxicity can be detected. The chitin bioplastic can be made into straws, cups, containers, and a photoprotecting film. The ability to protect photos of the chitin bioplastic is comparable to commercial PP. Due to its excellent performance and safety, the chitin bioplastic has great potential as a substitute for petrochemical plastics in the future.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c12764.

> Weight loss rate after drying in a mold of the chitin hydrogel with different concentrations; picture of the straw-shaped chitin bioplastic in different colors, and reliability and application of the chitin bioplastic (PDF)
> Suction test of straw-shaped chitin bioplastics (MP4)
> Flame retardancy of chitin bioplastics (MP4)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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