ChemSusChem
Research Article
doi.org/10.1002/cssc.202400512
Chemistry Europe
European Chemical Societies Publishing
www.chemsuschem.org

A Highly Sustainable Supramolecular Bioplastic Film with Superior Hydroplasticity and Biodegradability

Hongjun Jin+,*[a] Ziyan Wu+,[a] Weilin Lin,[a] Yiteng Cai,[b] Lianbo He,[c] Changlin Cao,[a] Xuejiao Wang,[c] Qingrong Qian,*[a] Qinghua Chen,[a] and Yun Yan[b]

Massive accumulation of postconsumer plastic waste in ecosystem has raised growing environmental concerns. Sustainable end-of-life managements of the indispensable plastic are highly demanding and challenging in modern society. To relieve the plastic menace, herein we present a full life cycle sustainable supramolecular bioplastic made from biomass-derived polyelectrolyte (chitosan quaternary ammonium salt, QCS) and natural sodium fatty acid (sodium laurate, SL) through solid-phase molecular self-assembly (SPMSA), by which the QCS-SL complexes, precipitated from mixing the aqueous solutions, self-assemble to form bioplastic film by mildly pressing at room temperature. The QCS-SL bioplastic films display superior hydroplasticity owing to the water-activated molecular rearrangement and electrostatic bond reconstruction, which allows facile self-healing and reprocessing at room temperature to significantly extend the service lifetime of both products and raw materials. With higher water content, the dynamic electrostatic interactions and precipitation-dissolution equilibrium endow the QCS-SL bioplastic films with considerable solubility in water, which is promising to mitigate the plastic accumulation in aquatic environment. Because both QCS and SL are biocompatible and biodegradable, the dissolved QCS-SL films are nontoxic and environmentally friendly. Thus, this novel supramolecular bioplastic is highly sustainable throughout the whole life cycle, which is expected to open a new vista in sustainable plastic materials.

1. Introduction

Plastics are ubiquitous and dispensable in modern society. The world annual production of plastics has exponentially grown since 1950s, which reached 359 million metric tons in 2018, generated from various areas such as packaging, constructions, textiles and electronics.[1,2] However, the vast majority of commodity plastics are petrochemical, which are non-degradable and challenging to recycle. A large proportion of the plastics enduringly accumulate as waste in the environment, resulting in serious plastic pollution and ecological concerns.[3–7] At present, plastic recycling and biodegradation are the main approaches to relive the environmental concerns.[8,9] Comparing to the traditional mechanical recycling which is down-cycle to low-value commodities, chemical recycling is potentially upcycle to high-performing materials and valuable products.[10–13] However, the state-of-the-art techniques for chemical recycling generally need hash conditions and expensive catalysts.[14] Meanwhile, current commercialized biodegradable plastics such as poly(lactic acid) (PLA) and poly(butyleneadipate-co-terephthalate) (PBAT) can be biodegraded in compost settings under specific humidity, temperature and microbes conditions, but the degradation in the diverse natural environment remains challenges.[15]

To mitigate plastic pollution, novel plastic alternatives that are easy to recycle and biodegrade in natural environment are of great significance. Within the past decades, many efforts have focused on the renewable biomass-based materials, such as starch,[16,17] cellulose[18]/lignocellulose[19] and chitosan,[20,21] which are biocompatible and biodegradable in natural environment. Such bioplastics can reduce the reliance on non-renewable fossil resources and decrease the plastic accumulation in eco-system. In recent years, supramolecular bioplastics with reversible interactions such as electrostatic interaction, hydrogen bonding and dynamic covalent bonding are delicately designed to endow the bioplastics with self-healability and reprocessability.[22–26] These supramolecular bioplastics are highly expected to extend service lifetime and enhance resource utilization. However, manufacturing of the reported bioplastics generally needs hot pressing,[27,28] freezing drying[22,29] or solvent casting,[25,26,30] which is neither high energy consuming nor toxic. Even so, hot pressing, which allows massive production, is a main manufacturing approach for both bioplastics and petrochemical plastics. Thus, a room-temperature pressing strategy for supramolecular bioplastics is crucial for advancing the full life cycle sustainability.

Recently, we developed a solid-phase molecular self-assembly (SPMSA) strategy to massively fabricate

---

[a] Engineering Research Center of Polymer Green Recycling of Ministry of Education, College of Environmental and Resource Sciences, College of Carbon Neutral Modern Industry, Fujian Normal University, Fuzhou, Fujian, China
[b] Beijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry and Molecular Engineering, Peking University, Beijing, China
[c] Fujian Provincial University Engineering Research Center of Industrial Biocatalysis, College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, China

Correspondence: Dr. Hongjun Jin and Prof. Qingrong Qian, Engineering Research Center of Polymer Green Recycling of Ministry of Education, College of Environmental and Resource Sciences, College of Carbon Neutral Modern Industry, Fujian Normal University, Fuzhou, Fujian 350007, China. Email: hongjunjin@fjnu.edu.cn and qrqian@fjnu.edu.cn

[+] contributed equally to this work.

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cssc.202400512

supramolecular films by mildly pressing the electrostatic complexes of polyelectrolytes (PE) and oppositely charged surfactants (SA).[31–35] Such room-temperature pressing strategy is a green process without organic solvents usage and high-energy consumption. We expect that if SPMSA is applied to fabricate supramolecular bioplastics, the full life cycle sustainability will be effectively achieved. Thus, in this work we report a highly sustainable supramolecular bioplastic made from renewable biomass-derived polyelectrolyte (chitosan quaternary ammonium salt, QCS) and natural surfactant (sodium laurate, SL) through SPMSA, which involves an aqueous self-assembling to QCS-SL precipitates, followed by a room-temperature pressing to transparent films (Figure 1a). QCS is derived from the second most abundant natural polymer, chitin, presenting mainly in fungi and exoskeleton of crustaceans.[36] SL is the sodium salt of lauric acid, which is a saturated fatty acid and a main component of vegetable oil such as coconut oil and palm oil.[37,38] Thus, the QCS-SL bioplastic films are renewable and sustainable from the source. Besides, QCS-SL films display superior hydroplasticity owing to the water-activated electrostatic bond reconstruction and rapid molecular rearrangement. When damage occurs during use, the QCS-SL films show remarkable self-healability with the aid of water, which is expected to significantly extend the service lifetime. The self-healing efficiency has been significantly improved from about 60 % to 100 % comparing to our previous works. After use, the QCS-SL films can be facilely reprocessed at room temperature without fatigue even after multiple recycling. For the end-of-life options, comparing to our previously reported PE-SA films which are insoluble in water, the QCS-SL films display considerable solubility due to the superior hydroplasticity. The dissolved QCS-SL films are supposed to have little impact on eco-system, because both QCS and SL are highly biocompatible and biodegradable. Such water-soluble bioplastics are expected to mitigate the plastic pollution in aquatic environment, which is vital to ecological security. We anticipate this novel supramolecular bioplastic will open a new vista in sustainable materials.

2. Results and Discussion

The QCS-SL bioplastic films were prepared by our previously reported solid-phase molecular self-assembly (SPMSA) strategy, which was successfully used to fabricate supramolecular films with commercial polyelectrolytes and oppositely charged surfactants.[31,33,35] Figure 1a shows the schematic process of the SPMSA with QCS and SL. As a biomass-derived cationic polyelectrolyte, QCS interacts with the natural anionic surfactant, SL, in aqueous solution to form vesicles at low concentration, and the vesicles become highly cross-linked when the concentration of SL reaches 25 mM (Figure S1). Turbidity of the mixed solutions of QCS and SL at different molar ratios and concentrations were tested using a turbidimeter. Figure 1b-c shows the turbidity reaches maximum at charge balancing ratio, indicating the formation of QCS-SL precipitates are mainly driven by electrostatic interactions. Meanwhile, the turbidity drastically increases with the concentration. When the concentration increased to above 7 mM at charge balancing ratio, obvious precipitates formed after centrifuging at 10000 rpm.

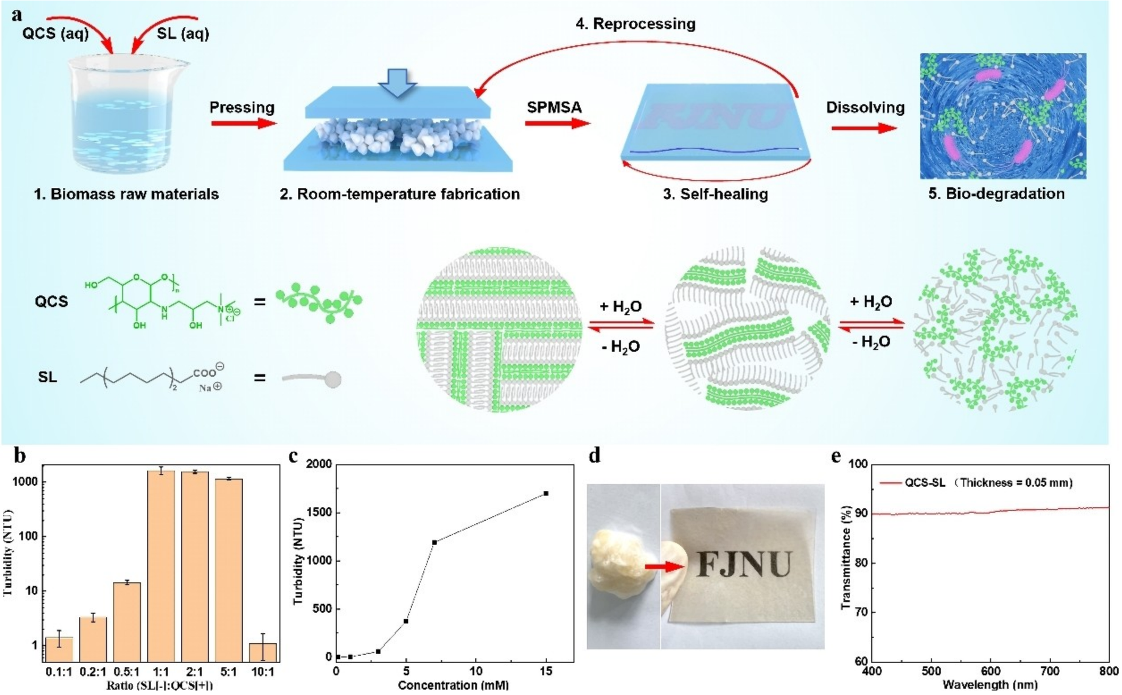


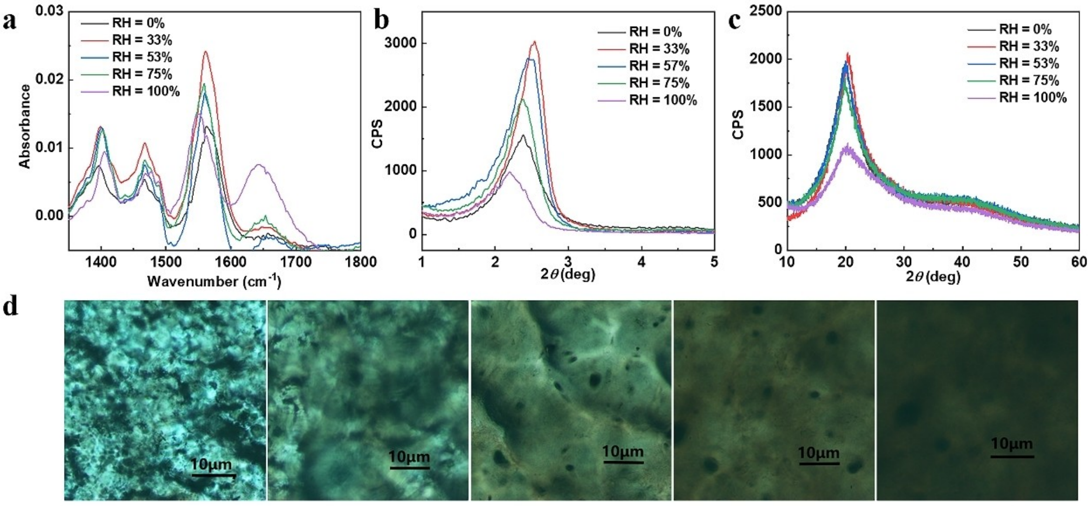
Figure 1. Solid phase molecular self-assembly (SPMSA) of chitosan quaternary ammonium-sodium laurate (QCS-SL). (a) The schematic illustration of the SPMSA process of the full-life-cycle sustainable QCS-SL bioplastic film and the molecular mechanism of hydroplasticity. (b) Turbidity of QCS-SL aqueous suspension at different SL[−]: QCS[+] ratio (QCS[+] = 10 mM). (c) Turbidity of QCS-SL aqueous suspension at different concentration (SL[−]: QCS[+] = 1 : 1). (d) Digital images of the fresh QCS-SL precipitate and film. (e) UV-Vis transmission spectra of the QCS-SL film.

The wet precipitates were collected and forced to form a compact cake, which gradually transformed into a transparent film within 1 h at room temperature. This film was further pressed repeatedly with a household noodle machine to reduce bubbles and defects (Figure 1d). UV-Vis spectrum manifests the film is highly transparent in visible range (Figure 1e). Thermal stability of the film was characterized by TGA, DSC and DMA (Figure S2). The thermal decomposition temperature is about 166 °C and no obvious glass transition was found upon heating.

Owing to the presence of abundant polar groups, the QCS-SL film can be reversibly hydrated and dehydrated (Figure S3). The rigid dry plastic film become soft and viscous when wetted, revealing the film can be markedly plasticized by water. Because the water content is positively correlated with the environmental relative humidity (RH) (Figure S4), the films were equilibrated under different RH for at least 24 hours before further tests. The hydroplasticity of QCS-SL film is derived from the water-activated reversibility of electrostatic interactions and molecular rearrangement, which was manifested by Fourier transform infrared (FT-IR) spectra, X-ray diffraction (XRD) spectra and polarizing microscope (POM) images. Figure 2a shows the characteristic vibrations of the symmetrical stretching vibration (ν_s) and asymmetric stretching vibration (ν_{as}) for COO$^-$ of SL, which are around 1400 cm^{-1} and 1600 cm^{-1}, respectively. For the dehydrated film (RH = 0), the COO$^-$ is tightly bonded to the quaternary ammonium (N$^+$) of QCS, resulting a lower vibrational frequency for COO$^-$ v_s. Under higher RH, the COO$^-$ and N$^+$ groups are hydrated with water, which weakens the electrostatic bindings between COO$^-$ and N$^+$, leading to a blue shift for COO$^-$ v_s and an opposite change for COO$^-$ v_{as}[35,39] (Ta]ble S1). XRD patterns show that distinct diffractions occur at $2\theta = 2.22° – 2.54°$ under different RH (Figure 2b). The corresponding d values (3.98 nm–3.48 nm) are shorter than twice the extending length of SL molecules (2.25 nm), indicating the SL molecules form ordered lamellar phase with staggered alkyl chains. The broad diffraction peaks around 20° in Figure 2c indicate the QCS chains form amorphous phase with partial orientation between the SL bilayers by electrostatic binding. Under higher RH, the absorbed water molecules insert between the charged groups of QCS and SL, leading to an increasing d value (Table S2). Besides, the decreasing intensity of the diffraction peaks in Figure 2b-c demonstrates both the lamellar phase and the chain orientation gradually gets disordered with the increasing water content. The molecular arrangement change is showed in Figure 1a. It worth noting that the dry film shows an exceptive diffraction with high d value and low intensity, which should be ascribed to the absence of driving force of hydrophobic effect for SL in the dehydrating environment, failing to form highly ordered and tightly packed lamellar phase. POM images also reveal the water-activated molecular rearrangement. The dry film displays strong birefringence due to the well-defined anisotropic structure, which gets disordered when wetted by a drop of water, verified by the disappearance of birefringence over time (Figure 2d).

The hydroplasticity was further clarified by the mechanical property and viscoelasticity change with RH (Figure 3). Stress-strain curves show the breaking stress and the Young's modulus of the QCS-SL films dramatically decrease with the increasing RH, while the breaking strain significantly increases (Figure 3a-b). Figure 3c-d shows the G′ and G″ change with RH. Frequency sweeps show the G′ which represents elasticity of the dry film is 4.5 times larger than the G″ representing viscosity, demonstrating the dry film is semi-solid. For hydrated films, G′, G″ and the gap between G′ and G″ all dramatically decrease with the increasing RH. When RH reaches 100 %, the G′ and G″ become nearly identical, indicating the semi-solid film transforms to be semi-fluid.[40] The abnormal increase of G′ with frequency for the 100 % RH film (Figure 3c, red line, filled data points) is attribute to the water loss via evaporation during test, because the ambient humidity (~70 %) was much lower than 100 %.

This superior hydroplasticity endows the QCS-SL film with excellent room-temperature self-healability and recyclability. To



Dry film 1 min 2 min 3 min 5 min

Figure 2. Mechanism of the hydroplasticity. (a) FT-IR spectra and (b–c) XRD patterns of the QCS-SL films under different RH. (d) POM images of the QCS-SL film showing birefringence change with different wetting time.

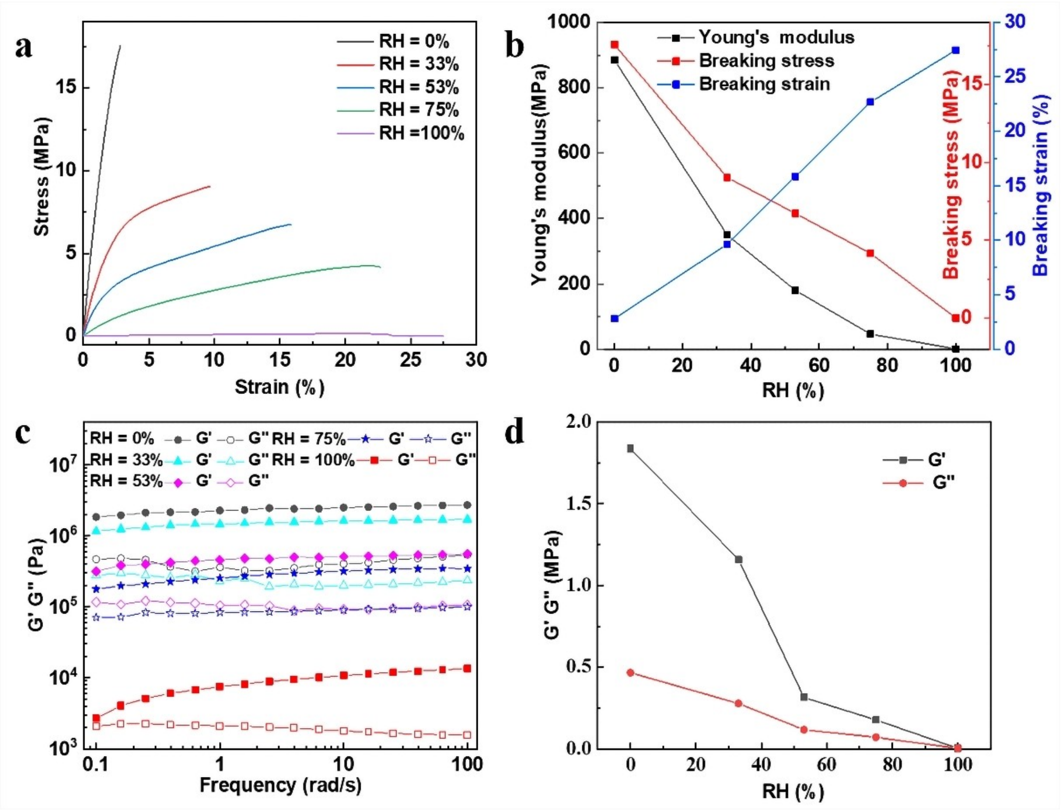


Figure 3. The superior hydroplasticity of QCS-SL film. (a) Stress–strain curves of the QCS-SL films under different RH. (b) Young's modulus, breaking stress and breaking strain change with RH. (c) Frequency sweeps showing the storage moduli (G′, filled data points) and loss moduli (G″, open data point) of the QCS-SL films under different RH. (d) The G′ and G″ change with RH at a frequency of 0.1 rad/s.

demonstrate the self-healability, two star-shaped QCS-SL films, which were respectively dyed with methylene blue and rhodamine B, were cut and placed in contact. The cut pieces completely adhered together with the aid of a drop of water at room temperature (Figure 4a). Optical microscope images show the rapid self-healing of the damaged section (Figure 4b). Strain-stress curves display the mechanical property of the healed film almost completely recovers after drying (Figure 4c). This efficient self-healability is highly expected to prolong the service life of materials. Furthermore, fragments of the QCS-SL films can be reprocessed into new ones by mechanically pressing at room temperature with the assistant of water (Figure S5). Owing to the sufficient molecular rearrangement and ionic bond reconstruction, the mechanical properties show no fatigue even after 5 times recycle (Figure 4d–f).

With higher water content, the superior hydroplasticity behaves as water-solubility due to the reversible electrostatic interactions and precipitation-dissolution equilibrium. 0.2 wt% (5 mM) QCS-SL film can be well dissolved in water within 12 hours (Figure 5a). TEM images show the dissolved QCS-SL complexes reform vesicles in water (Figure 5b–c), as an inverse process of vesicles to precipitates (Figure S1). Because both QCS and SL are highly biocompatible and biodegradable, the dissolved QCS-SL films are supposed to be environmentally friendly. In order to investigate the biotoxicity of the dissolved films, in vitro cell culture experiments were performed. Human kidney epithelial cells (293T) and mouse epithelial fibroblasts (L929) were respectively incubated in cell culture medium with different concentrations of dissolved QCS-SL for 24 h. Cytotoxicity measurements suggest that the cell viability is above 90% for both 293T and L929 in the presence of up to 50 μM QCS-SL (Figure 5d), indicating the good biocompatibility. The cell viability is even above 30% for both 293T and L929 when the concentration reaches 1 mM (Figure S6). Moreover, this bioplastic exhibits excellent biodegradability in the natural environment. For demonstration, we buried the QCS-SL and PBAT/PLA (a commercial biodegradable plastic) films in soil at a depth of 5 cm (Figure 5e). The QCS-SL film became fractured and completely biodegraded within 20 days (Figure 5f). In contrast, the PBAT/PLA film was just slightly biodegraded after the same burial time. Thus, this remarkable hydroplasticity and biodegradability make the QCS-SL bioplastic film an ideal substitute for nondegradable plastic to relive the plastic waste pollution.

3. Conclusions

In summary, we report a highly sustainable supramolecular bioplastic film involving the full life cycle from production to end-of-life options. (1) From the source, the raw materials of the QCS-SL film are derived from renewable and abundant biomasses in nature. (2) For the production, a room-temper-

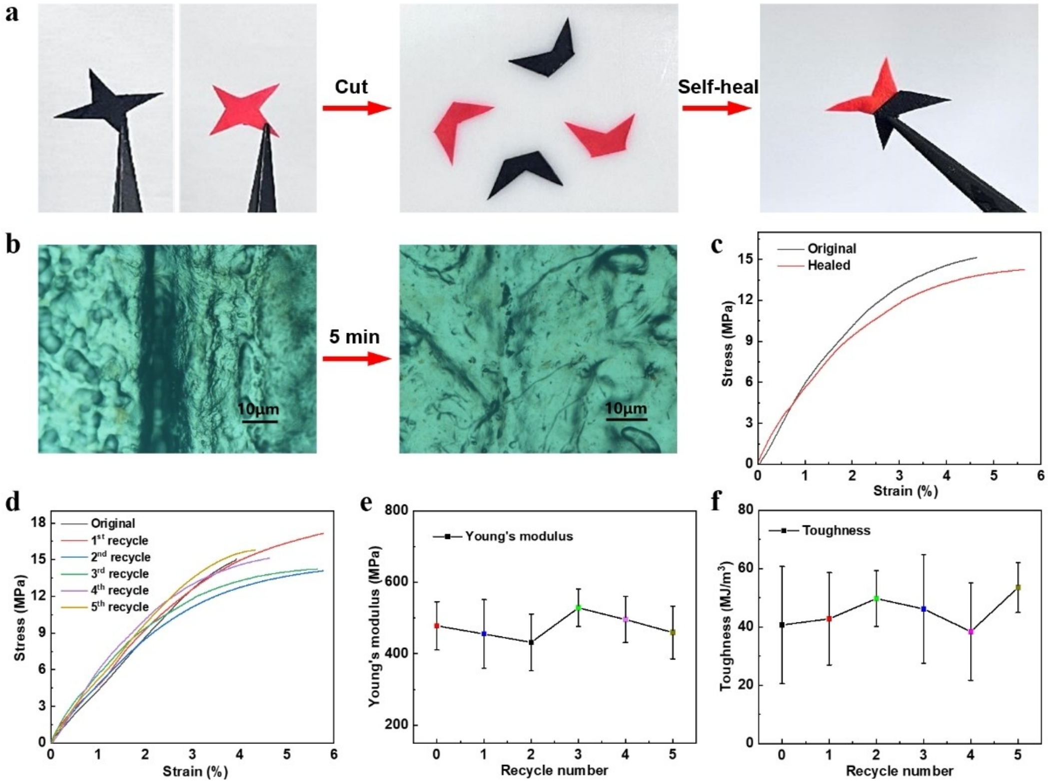


Figure 4. Self-healability and recyclability of QCS-SL film. (a) Digital images showing the self-healing behavior of the star-shaped QCS-SL films. (b) Optical microscopic images showing the fracture self-healing with the aid of a drop of water at room temperature. (c) Stress–strain curves of the original and healed QCS-SL films. (d) Stress–strain curves, (e) Young's modulus and (f) toughness of the QCS-SL films after multiple recycling.

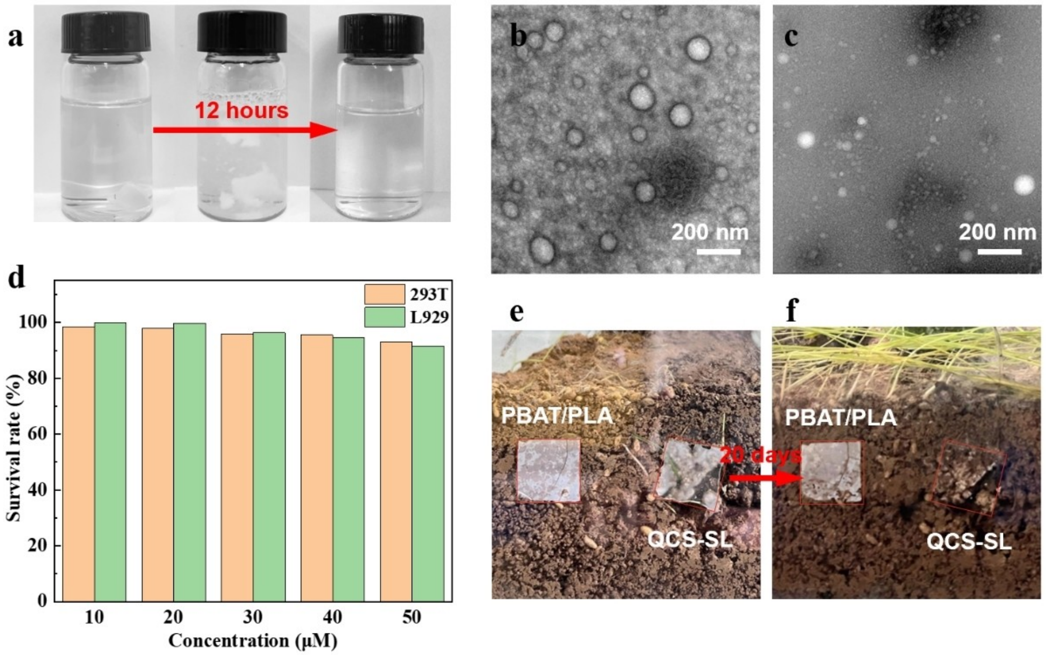


Figure 5. The water-solubility, biodegradability and cytotoxicity of QCS-SL film. (a) Digital images showing the water-solubility. TEM images of the aqueous solutions with dissolved QCS-SL at (b) 5 mM and (c) 1 mM. (d) Cell viability of 293T and L929 cells cultured with different concentrations of dissolved QCS-SL for 24 h. (e–f) The biodegradability tests of the QCS-SL film and the PBAT-PLA film under moist soil for 20 days.

ature pressing strategy with low-energy consumption is achieved through the solid-phase molecular self-assembly (SPMSA). (3) During use, damaged film can be facilely healed with the aid of water, significantly extending the service lifetime. (4) After the end-of-use, QCS-SL film can be reprocessed at room temperature without any fatigue in mechanical properties even after multiple recycling. (5) For the disposal film waste, it can be effectively biodegraded in natural environment. Notably, this room-temperature manufacturing, self-healing and recycling are essentially derived from the superior hydroplasticity, which behaves as considerable water-solubility at higher water content. Thus, this water-soluble bioplastic film is prospective to mitigate the plastic accumulation in aquatic environment including freshwater and marine systems, which are considered to be the final receptors of plastic debris. Thus, this full-life-cycle sustainable QCS-SL bioplastic film will be a promising supplement for traditional plastic to relive the plastic waste pollution.

4. Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NSFC 22202044) and the Natural Science Foundation of Fujian Province, China (2023J05036).

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: supramolecular materials · sustainable bioplastic · biodegradation · self-heal · recycle

[1] C. Jehanno, J. W. Alty, M. Roosen, S. D. Meester, A. P. Dove, E. Y.-X. Chen, F. A. Leibfarth, H. Sardon, *Nature* **2022**, *603*, 803–814.
[2] G. Roland, R. J. Jenna, L. L. Kara, *Sci. Adv.* **2017**, *3*, e1700782.
[3] J. Brahney, M. Hallerud, E. Heim, M. Hahnenberger, S. Sukumaran, *Science.* **2020**, *368*, 1257–1260.
[4] R. J. Jenna, et al., *Science* **2015**, *347*, 768–771.
[5] M. Matthew, P. H. A. Hans, B. T. Mine, J. Annika, *Science* **2021**, *373*, 61–65.
[6] V. Nava, et al., *Nature* **2023**, *619*, 317–322.
[7] S. Pahl, K. J. Wyles, R. C. Thompson, *Nat. Hum. Behav.* **2017**, *1*, 697–699.
[8] K. M. V. G. Geem, *Science* **2023**, *381*, 607–608.
[9] J.-G. Rosenboom, R. Langer, G. Traverso, *Nat. Rev. Mater.* **2022**, *7*, 117–137.
[10] K. Ragaert, L. Delva, K. V. Geem, *Waste Manage.* **2017**, *69*, 24–58.
[11] A. Rahimi, J. M. García, *Nat. Chem. Rev.* **2017**, *1*, 1–11.
[12] H. Q. Li, et al., *Science* **2023**, *381*, 660–666.
[13] Z. Xu, et al., *Science* **2023**, *381*, 666–671.
[14] M. Kusenberg, et al., *Waste Manage.* **2022**, *138*, 83–115.
[15] A. R. Bagheri, C. Laforsch, A. Greiner, S. Agarwal, *Global Challenges* **2017**, *1*, 1700048.
[16] B. Khan, M. B. K. Niazi, G. Samin, Z. Jahan, *J. Food Process Eng.* **2016**, *40*, e12447.
[17] H. Cheng, et al., *Trends Food Sci. Technol.* **2021**, *114*, 70–82.
[18] H. Tu, M. X. Zhu, B. Duan, L. N. Zhang, *Adv. Mater.* **2020**, *33*, 2000682.
[19] M. Brodin, M. Vallejos, M. T. Opedal, M. C. Area, G. Chinga-Carrasco, *J. Cleaner Prod.* **2017**, *162*, 646–664.
[20] H. Haghighi, F. Licciardello, P. Fava, H. W. Siesler, A. Pulvirenti, *Food Packag. Shelf Life* **2020**, *26*, 100551.
[21] R. Priyadarshi, J.-W. Rhim, *Innovative Food Sci. Emerging Technol.* **2020**, *62*, 102346.
[22] J. P. Han, Y. F. Guo, H. Wang, K. Y. Zhang, D. Y. Yang, *J. Am. Chem. Soc.* **2021**, *143*, 19486–19497.
[23] A. M. Duraj-Thatte, et al., *Nat. Chem. Biol.* **2021**, *17*, 732–738.
[24] W. W. Niu, et al., *ACS Appl. Mater. Interfaces* **2020**, *12*, 30805–30814.
[25] Y. X. Li, S. H. Li, J. Q. Sun, *Adv. Mater.* **2021**, *3*, 2007371.
[26] Q. Zhang, et al., *Matter* **2021**, *4*, 1352–1364.
[27] Q. F. Guan, H. B. Yang, Z. M. Han, Z. C. Ling, S. H. Yu, *Nat. Commun.* **2020**, *11*, 1–7.
[28] Q. F. Guan, Z. C. Ling, Z. M. Han, H. B. Yang, S. H. Yu, *Matter* **2020**, *3*, 1308–1317.
[29] Y. Cui, H. X. Gong, Y. J. Wang, D. W. Li, H. A. Bai, *Adv. Mater.* **2018**, *30*, 1706807.
[30] Q. Q. Xia, et al., *Nat. Sustain.* **2021**, *4*, 627–635.
[31] H. J. Jin, et al., *CCS Chemistry* **2020**, *2*, 98–106.
[32] W. K. Wang, et al., *Mater. Chem. Front.* **2020**, *4*, 1530–1539.
[33] H. J. Jin, et al., *ACS Materials Lett.* **2021**, *4*, 145–152.
[34] P. L. Liao, et al., *Nat. Commun.* **2021**, *12*, 1–9.
[35] H. J. Jin, et al., *Adv. Mater.* **2022**, *35*, 2207688.
[36] P. S. Bakshi, D. Selvakumar, K. Kadirvelu, N. S. Kumar, *J. Biol. Macromol.* **2020**, *150*, 1072–1083.
[37] M. M. Chakrabarty, K. Talapatra, *J. Am. Oil Chem. Soc.* **1966**, *68*, 310–313.
[38] F. M. Dayrit, *J. Am. Oil Chem. Soc.* **2014**, *92*, 1–15.
[39] D. K. Beaman, E. J. Robertson, G. L. Richmond, *J. Phys. Chem. C* **2011**, *115*, 12508–12516.
[40] J. Yu, et al., *Angew. Chem. Int. Ed.* **2022**, *61*, e202204611.

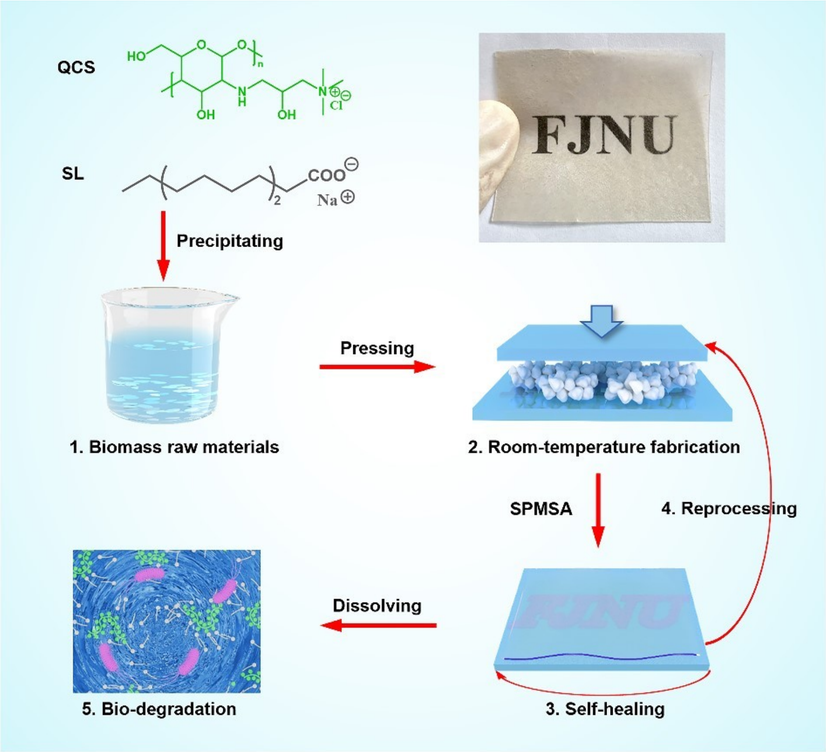
Manuscript received: March 8, 2024
Revised manuscript received: May 2, 2024
Accepted manuscript online: June 15, 2024
Version of record online: ■■, ■■

RESEARCH ARTICLE

Dr. H. Jin, Z. Wu, W. Lin, Y. Cai, L. He, C. Cao, Dr. X. Wang, Prof. Q. Qian*, Q. Chen, Prof. Y. Yan*

1 – 7

A Highly Sustainable Supramolecular Bioplastic Film with Superior Hydroplasticity and Biodegradability



Herein we offer a highly sustainable supramolecular bioplastic film involving the full life cycle from production to end-of-life options. This supramolecular bioplastic film is derived from renewable and abundant biomasses, which can be biocompatibly degraded in nature. Importantly, owing to the superior hydroplasticity, the film can be facilely fabricated, self-healed and reprocessed at room temperature.