Bioinspired High Resilient Elastomers to Mimic Resilin
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Supporting Information

ABSTRACT: Natural resilin possesses outstanding mechanical properties, such as high strain, low stiffness, and high resilience, which are difficult to be reproduced in synthetic materials. We designed high resilient elastomers (HREs) with a network structure to mimic natural resilin on the basis of two natural abundant polymers, stiff cellulose and flexible polyisoprene. With plasticization via mineral oil and mechanical cyclic tensile deformation processing, HREs show ultrahigh resilience, high strain, and reasonable tensile strength that closely mimic natural resilin. Moreover, the mechanical properties of HREs can be finely tuned by adjusting the cellulose content, providing the opportunity to synthesize high resilient elastomers that mimic different elastic proteins, such as elastin.

The properties of elastic proteins, such as high resilience, play an important role in dictating the movement and sound production for animals.1−5 Among them, resilin exhibits the highest resilience,6,7 which was first discovered by Weisfogh in the early 1960s.8,9 During recent years, interest in emulating the unique mechanical properties of natural resilin has gained significantly in designing resilin-mimicking materials.10−12 Various resilin-like polypeptide-based biomaterials have been developed and found applications in biorubbers13 and biosensors,14 exhibiting high resilience comparable to natural resilin.6,15 Meanwhile, many efforts have been devoted to improving mechanical properties of synthetic materials, mimicking the performance of resilin. For example, high resilient hydrogels were recently synthesized by using efficient cross-linking chemistry.6,7 These hydrogels possess uniform networks, which could lead to high resilience (>97%) and high extensibility (up to 300%). However, there are also obvious shortcomings of these resilin-mimicking materials; e.g., their mechanical strength is much lower than that of natural resilin.18 Thus, the preparation of robust synthetic materials closely mimicking natural resilin still remains a great challenge.

In order to design natural resilin-mimicking materials, it is important to understand the relationship between structures and remarkable mechanical properties of natural resilin. All elastic materials, including resilin, exhibit three molecular characteristics: sufficient polymer chain length, high chain flexibility, and the presence of interchain cross linking.19,20 A microstructure model was proposed to explain the high resilience property of elastic proteins (Figure S1 in Supporting Information).21 Compared with rubber materials, the interchain cross-linking in natural resilin only takes place between specific amino acids, leading to a well-defined network structure.22 Moreover, they are in the hydrated state, thus lowering the friction between molecular chains and allowing them to recoil without appreciable energy loss.23,24 It is the network and low intermolecular friction responsible for the remarkable elastomeric properties of natural resilin.7

In order to obtain elastomers with high resilience, we envision that it would be crucial to generate a network composed of long and flexible polymer chains, possessing low intermolecular friction. Herein, we report bioinspired high resilient elastomers with a network structure by combining cellulose and natural rubber, two abundant plant-based biopolymers (Figure 1). Specifically, initiator-anchored cellulose allowed the preparation of grafted polymers with a stiff cellulose backbone and flexible polyisoprene side chains.25 The
end groups of side chains were subsequently cross linked via activator regenerated by electron transfer atom transfer radical coupling (ARGET ATRC). The use of high fidelity polymerization and cross-linking methods yields HREs with a desirable network structure, which could lead to ultrahigh resilience comparable to that of natural resilin. More importantly, the introduction of stiff cellulose increases the strength of HREs, which helps overcome the drawbacks of the existing resilin-mimicking materials.

At the first step, cellulose was modified with 2-bromoisobutyryl bromide to form macroinitiator (Cell-Br). Then grafted polymers with a stiff cellulose backbone and flexible polyisoprene brushes were synthesized by activator regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP). When isoprene monomers were mostly consumed, the viscosity of the polymerization system increased greatly because the radical–radical coupling (atom transfer radical coupling, ATRC) started to take place, and inter- and/or intramolecular carbon–carbon coupling formed at the periphery of the grafted polyisoprene side chains (Figures S2–S5).

A series of HREs with the cellulose contents ranging from 0.5 to 2.3 wt% were synthesized (samples HRE1–4 in Table S1). The cross-linking densities for HREs were determined by swelling tests (see the Supporting Information). The result in Table S1 indicates that the cross-linking density increases with the increase of cellulose weight content. The mechanical characteristics of HREs, as demonstrated by the monotonic nominal stress–nominal strain curves at a strain rate of 0.17 s⁻¹ (Figure 2a), are very close to those of natural resilin as reported in the literature. The stress increases almost linearly with the strain, implying that HREs may exhibit high elasticity and resilience. The ultimate tensile strength for HREs ranges from 2.1 ± 0.3 to 4.3 ± 0.4 MPa, the strain at break from 104 ± 8% to 233 ± 17%, and the elastic modulus from 2.3 ± 0.1 to 5.7 ± 0.5 MPa. Figure 2b shows the representative stress relaxation curves at the constant strain of 80% for HREs. When the deformation was held at a constant strain of 80%, the initial stress was 3.5, 2.4, 1.4, and 1.0 MPa, respectively, for HRE1, HRE2, HRE3, and HRE4. The stress of HRE1 reduces rapidly to about 2.6 MPa and then stabilizes within 10 h, with a total stress relaxation of 23.5%. The degree of stress relaxation decreases with the decrease of cellulose content; for example, HRE4 only exhibits a total stress relaxation of 11% within 10 h. The stress–relaxation tests suggest that all HREs show high elasticity. The increased elasticity for HREs with the decrease of cellulose content is probably due to the increased molecular mass of polyisoprene chains, which are responsible for the entropic elasticity.

Resilience is the ability of a material to recover energy during cyclic deformation. The HREs possess long and flexible nonpolar polyisoprene chains as the elastic recoil component and polar cellulose domains as cross-linking points. The combination of these two unique components associated with a network structure may endow the HREs with high resilience. However, there is energy loss during the first cyclic tensile test. The resilience values for HRE1–4 are calculated to be 63.2 ± 1.4, 74.6 ± 1.9, 79.4 ± 1.6, and 87.1 ± 1.2%, respectively. These resilience values are relatively lower than that of natural resilin, indicating that some degrees of entanglement of polyisoprene chains may exist in the network. Our early work has demonstrated that the entanglements of polymer chains can be significantly reduced through mechanical processing of polymer materials. Thus, we hypothesized that the resilience of HREs might be improved if the cyclic tensile deformation processing is applied to the HREs. Figures 2c,d and Figure S6 show the nominal stress–nominal strain curves at a repetitive cyclic tensile deformation with a maximum strain of 100% for HREs. A small residual strain of about 10% as well as a decrease of the peak stress was observed, which was largely caused by the deformation-induced chain disentanglements. After 10 cycle tensile deformations, the elastic recovery increased greatly (from 90.5 ± 0.7 to 98.7 ± 0.2% for HRE1, Figure 2e). These results demonstrate that the mechanically processed HREs exhibit excellent elasticity that is close to 100%. The resilience increments during the 10 cycle tensile deformations are shown in Figure 2f, increasing to 81.2 ± 0.9%.
for HRE1 and 93.4 ± 1.1% for HRE4. The resilience increases rapidly during the first three cyclic tensile deformations. After that, the resilience becomes almost stable. This is possibly due to the deformation-induced entanglement reduction, leading to a perfection of the network structure in the HREs. Both the elastic recovery and resilience of the HREs increase with the decrease of cellulose content. We can conclude that with the assistance of mechanical processing, the HREs show sufficiently high resilience, closely mimicking natural resilin.

It is well-known that elastic proteins are typically in the hydrated state, and the water content plays a critical role in the resilience of elastic proteins like elastin and resilin. Water serves as a plasticizer to reduce the interchain friction. Inspired by the plasticizing effect, we added mineral oil to plasticize HREs. Note that HREs are mostly composed of hydrophobic polyisoprene, which cannot be plasticized by water. HREs containing 10 wt % mineral oil were prepared and defined as HRE1M, HRE2M, HRE3M, and HRE4M. The monotonic nominal stress–nominal strain curves for mineral oil plasticized HREs are shown in Figure S7. The ultimate tensile strength for mineral oil-plasticized HREs ranges from 1.1 ± 0.1 to 3.0 ± 0.2 MPa, the strain at break from 102 ± 6% to 180 ± 13%, and the elastic modulus from 0.9 ± 0.1 to 3.9 ± 0.3 MPa. As compared with HREs, the ultimate tensile strength and elastic modulus decrease, due to the free volume increase of HREs after being plasticized by mineral oil. Meanwhile, the strain at break is still determined by the formed chemical networks. Although the introduction of plasticizers makes HREs softer, the ultimate strain at break only shows a light decrease.

The cyclic tensile deformation processing was also applied to the mineral oil plasticized HREs (Figure S8). After 10 cycles, the resilience is 89.0 ± 1.5%, 92.3 ± 0.6%, 97.3 ± 0.5%, and 98.1 ± 0.4% for HRE1M, HRE2M, HRE3M, and HRE4M, respectively (Figure S9). It can be seen that the resilience of cyclic tensile-processed HREs can be improved greatly if HREs are plasticized with mineral oil. The reason is that the introduction of mineral oil may reduce the intermolecular friction of polyisoprene chains, which lowers the energy loss and increases the resilience of HREs.

To further investigate the resilience of mineral oil plasticized HREs after cyclic tensile deformation at different strains, step-cycle tensile tests were performed (Figure 3a–d). For clarity, the curves of each cycle are shifted on the strain axis, and the final strain values are given in the plots. These samples, especially HRE3M and HRE4M, show negligible hysteresis for the entire strain range applied. The changes of resilience as a function of time for the corresponding strain profiles is shown in Figure 3e. The resilience of natural resilin was reported to be 92%, which is indicated by the dashed line in Figure 3e, HRE1M, HRE2M, HRE3M, and HRE4M respectively. For these samples, the resilience increases with the decrease of cellulose content. For example, HRE1M shows resilience values lower than that of natural resilin; HRE2M possesses resilience values close to that of natural resilin; while HRE3M and HRE4M possess higher resilience values than natural resilin. It can be concluded that the mineral oil-plasticized HREs show excellent mechanical properties, which closely mimic natural resilin, at the aspects of the ultrahigh resilience, high elasticity, high strain, and reasonable tensile strength (Table S1).

Dynamic mechanical analysis (DMA) was performed to understand the origin of high resilience. A representative DMA curve for HRE1 (Figure 3f) shows two distinct glass transition temperatures (Tgs), which indicate a two-phase morphology. We attempted to characterize morphology of HREs by microscopy and X-ray scattering (as shown in Figure S10). However, due to the extremely low contents of cellulose (0.5–2.3 wt %) in HREs, aggregates of cellulose are probably too small to be visible or weakly scattered. On the basis of DMA results and our previous studies on the phase separation behavior of cellulose-g-polyisoprene copolymers, we propose the following scenario to understand the high resilience and high elasticity of HREs. As shown in Figure 4, highly polar cellulose chains could phase separate from the polyisoprene matrix, which act as cross-linking junctions embedded in the grafted nonpolar polyisoprene matrix. The ATRC process introduces cross-linking between polyisoprene chains. Reduction of chain entanglements can occur through plasticization by adding mineral oil or through the mechanical cyclic tensile deformation processing, which leads to the formation of desirable networks in the HREs. The increased entropy of the relaxed state relative to the stretched state is
driving force for elastic recovery of the HREs. Upon stretching under an external force, the entropy of HREs decreases, and the system stores energy. After removal of the external force, the stretched HREs recoil to their relaxed state, and the energy can be released. The network structure, long and flexible polyisoprene chains, and low intermolecular friction (through mineral oil plasticization) lead to low energy loss for the HREs during the stretching and elastic recovery processes, thus behaving as high resilience.

In summary, we report a simple and effective strategy to prepare high resilient elastomers (HREs) with mechanical properties closely mimicking those of natural resilin. By combining ARGET ATRP and ATRC, we prepared cross-linked cellulose-graft-polyisoprene elastomers, which show high resilience with the formation of a chemical network. Mechanical cyclic tensile deformation processing and mineral oil plasticization were further applied to improve the resilience of HREs. The well-controlled synthetic method allows for finely tuning the mechanical properties of high resilient elastomers to mimic natural resilin. Given the simplicity, efficiency, and tunability, this approach may provide a promising approach to generating elastic protein-mimicking materials for a variety of applications.

■ ASSOCIATED CONTENT
* Supporting Information
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Materials, details of synthesis, polymer characterization, mechanical property tests, and cyclic tensile deformation processing (PDF)

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■ REFERENCES
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