

Reusable Elastomer Films from Polymer-grafted Particles and their Application to Strain Sensors

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Abstract

In this study, we successfully fabricated reusable elastomer films by hot-pressing silica particles (SiPs) surface-modified with block copolymers consisting of amorphous poly(*n*-octyl acrylate) (P8A) and crystalline poly(*n*-octadecyl acrylate) (P18A) by surface-initiated atom transfer radical polymerization (SI-ATRP). The strain at break of elastomer films increased with the decrease in the diameter of SiPs. Surprisingly, these elastomer films could be reused multiple times only by hot-pressing even though they were fractured. Furthermore, the elastomer films from SiPs of 120 nm in diameter showed Bragg reflection color by applying oscillatory shear strain at 100 °C. The reflection color changed reversibly upon stretching and release. Such elastomer films can be used as the flexible materials and sensors in diverse industries to contribute to the realization of the SDGs.

1. Introduction

Although elastomer films are indispensable in our daily lives, they cannot be recycled because of their permanent and robust cross-link formation via covalent bonds. Therefore, it is essential to fabricate reusable elastomer films to contribute to the conservation of finite petroleum resources. Previously, Benciewicz and colleagues prepared elastomer films by utilizing silica particles surface modified with a block copolymer of amorphous polymers with different glass transition temperatures.¹⁾ In this case, grafted polymer chains act as a steric barrier to prevent the aggregation of silica particles as well as an elastomeric matrix. However, these types of elastomer films were not sufficiently strong and tough.

To solve this problem, we focused on the physical cross-linking by the incorporation of crystalline moieties into the grafted polymer chains on silica particle surfaces to offer reusable and highly stretchable elastomer films. Moreover, we found that silica particles can form a colloidal crystal (CC) structure—three-dimensional array of monodisperse colloidal particles—in the elastomeric matrix by applying oscillatory shear strain. These elastomers showed vivid Bragg reflection color because they reflected the visible light of a specific wavelength corresponding to the lattice spacing of CCs. Such elastomer films can be also used for strain sensors because the Bragg reflection color changes reversibly upon stretching and release.²⁾

2. Experiment

Four kinds of SiP with different diameters of 36, 60, 83, and 120 nm were surface-modified with block copolymers consisting of P8A and P18A (SiP-P8A-*b*-P18A) by SI-ATRP. The elastomer films with a thickness of 500 μm were obtained by hot-pressing SiP-P8A-*b*-P18A at 100 °C. The elastomers with CCs were prepared from a film of SiP-P8A-*b*-P18A with SiPs

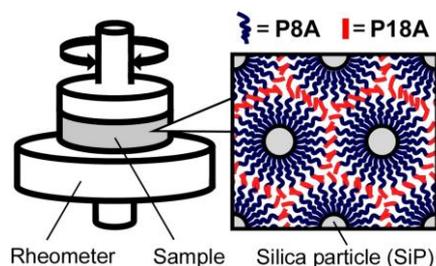


Fig.1. Illustration of the CC elastomer film of SiP-P8A-*b*-P18A fabricated by applying shear strain.

of 120 nm. The hot-pressed film was oscillatory sheared for 10 min at 100 °C using a rheometer with a parallel plate geometry with a disk with a diameter of 20 mm.³⁾

3. Results and discussion

Stretchable elastomer films could be obtained regardless of the particle size of SiPs (**Fig.2**). Wide-angle X-ray scattering measurements and dynamic viscoelastic measurements revealed that crystalline P18A chains at the outermost surface of the SiP-P8A-*b*-P18A act as physical cross-linking points below 50 °C. The strain at break of elastomer films could be controlled by changing the diameter of SiPs (**Fig.3**). In particular, the elastomer film could be stretched over 300% when the diameter of SiPs was 36 or 60 nm. This can be attributed to the increase in volume fraction of flexible P8A chains in the elastomer films with respect to the decrease of the diameter of SiPs.

Interestingly, the elastomer film of SiPs with 120 nm diameter showed Bragg reflection color by applying oscillatory shear strain at 100 °C (**Fig.4A**). It is considered that SiP-P8A-*b*-P18A was arrayed uniformly by shear force to form well-ordered CC structures. As expected, we successfully confirmed that SiP-P8A-*b*-P18A formed non-close-packed face-centered cubic lattice structures of SiPs by small-angle X-ray scattering measurements and scanning electron microscope observations. The reflection color reversibly changed from red to blue upon stretching and release due to the change in the lattice spacing of SiPs (**Fig.4B**). Although this elastomer film broke when stretched to 150% (**Fig.4C**), the fractured films could be merged into a single film by hot-pressing at 100 °C (**Fig.4D**). This is because the crystalline moieties of P18A chains on the outermost surface of SiPs melt upon heating to enable the flowing of P8A chains. Then this film showed red reflection color again by applying oscillatory shear strain at 100 °C (**Fig.4A**).⁴⁾ Notably, the mechanical and optical properties are not changed even after these processes, thereby implying that our elastomer films can be used as the recyclable strain sensors.

4. Conclusions

In this presentation, we successfully fabricated reusable elastomer films by hot-pressing SiP-P8A-*b*-P18A. The strain at break of elastomer films could be controlled by changing the diameter of SiPs. Moreover, elastomer films from 120 nm-diameter SiPs showed Bragg reflection color by applying oscillatory shear strain at 100 °C and their reflection color changed reversibly upon stretching and release. Our elastomer films can be used as flexible materials and sensors to contribute to realization of the SDGs.

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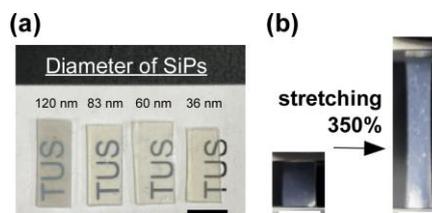


Fig.2. (a) Photographs of elastomer films of SiP-P8A-*b*-P18A that the diameter of SiPs is different, (b) Highly stretchable elastomer film (diameter of SiPs is 60 nm) (Scale bars: 5 mm).

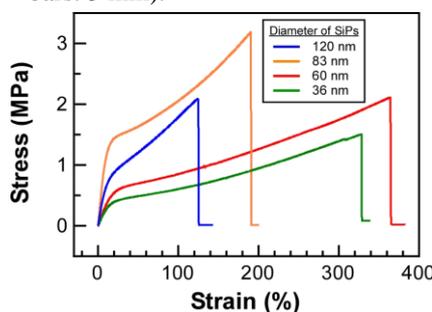


Fig.3. The stress-strain curves during the stretching process of elastomer films consisting of SiP-P8A-*b*-P18A.

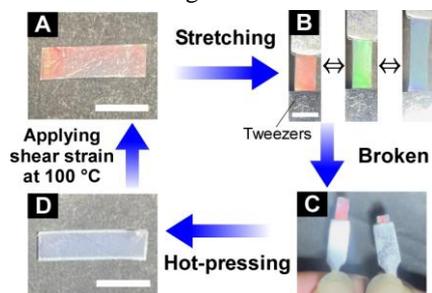


Fig.4. Recyclable CC elastomer film of SiP-P8A-*b*-P18A that diameter of SiPs is 120 nm (Scale bars: 5 mm).