Eco-friendly Self-healing Materials Derived from Carboxymethyl Cellulose

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Abstract

In this report, we successfully fabricated the self-healing materials derived from carboxymethyl cellulose (CMC) by cross-linking with water-soluble diepoxy compounds. The self-healing was made possible through cross-linking via dynamic covalent bonds (DCBs), which could be dissociated or reassociated by heating above 140 ºC. The self-healing time was decreased by the increase in the number of DCBs. Our CMC-based self-healing materials can be potentially applied in many industrial fields due to their eco-friendly and biocompatible features and contribute to the realization of a sustainable society.

1. Introduction

Cross-linked polymers such as rubbers or resins are widely adopted in our daily lives. However, they have a serious defect as they cannot be reshaped or recycled because of their strong cross-linking formation through static bonds. To solve this crucial problem, we focused on dynamic covalent bonds (DCBs) that can be dissociated or reassociated by heating. Polymers cross-linked through DCBs can be self-healed and recycled because they behave as viscoelastic liquids when they are exposed to heat even though they act as elastic solids at room temperature. Vitrimer is a kind of polymer cross-linked via DCBs developed by L. Leibler[1)]. To date, various vitrimers were prepared by incorporating DCBs into synthetic polymers. Such a strategy to prepare vitrimers is not desired from the viewpoint of conserving the finite petroleum resources on the Earth. Recently, M. Hayashi prepared vitrimers by the reaction of polyesters with pendant carboxylic groups (COOH) and diepoxy cross-linkers[2)]. The free OH groups and esters in the polymer network induce intermolecular trans-esterification which acts as DCBs (Fig. 1A). In this study, we focused on CMC, which is a cellulose derivative possessing COOH side chains via methyl ether groups (Fig. 1B). CMC is well known for its safety and widely used in many industries. In this presentation, we report on a series of new vitrimers derived from CMC, which have the ability to control their self-healing time. We believe that this research established a promising strategy for preparing self-healing materials from biomass resources and contributed to the realization of a sustainable society.

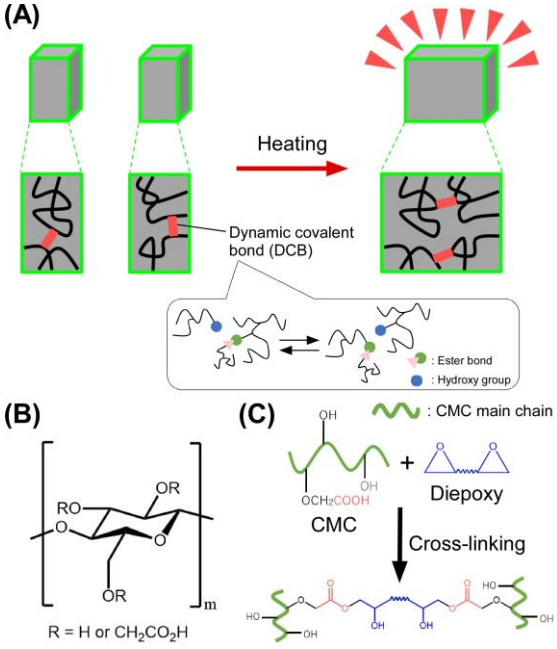

Fig. 1. (A) Schematic of self-healing materials cross-linked with DCBs, in which intermolecular trans-esterification acts as DCBs. (B) Chemical structure of carboxymethyl cellulose (CMC). (C) Cross-linking reaction between CMC and diepoxy compounds.

2. Experiment

The CMC-based vitrimers were prepared from mixtures of CMC, water-soluble diepoxy cross-linkers, and an ester exchange catalyst (Fig. 1C) [3,4]. Their vitrimeric properties were evaluated by stress relaxation measurements using a rheometer. Moreover, we demonstrated the unique properties of our CMC-based vitrimers such as self-healing and reshaping.

3. Results and discussion

CMC-based vitrimers were obtained as free-standing films with colorless and high transparency at room temperature. They exhibited stress relaxation above 140 ºC because of the reversibility of cross-linking through DCBs. The Arrhenius-type dependence of relaxation time was observed as a typical characteristic of vitrimers[1].

As expected, the CMC-based vitrimers were recyclable and reshapable owing to their self-healing property. The cut pieces of CMC-based vitrimer film could be merged into a disk-shape by hot-pressing at 150 °C for 3 hours (Fig. 2A). In addition, we succeeded in the transcription of a channel pattern on the CMC-based vitrimer film to exhibit iridescent reflection by imprinting the track pitches, i.e. microgrooves, on the surface of a blank compact disk (CD) (Fig. 2B, image *a*). Moreover, stable spiral-shaped sample could be obtained by rolling a CMC-based vitrimer film around a metal rod and heating at 160 ºC for 2 hours (Fig. 2B, image *b*). These unique properties of CMC-based vitrimers can be ascribed to their softening caused by the dissociation of DCBs triggered by heating.

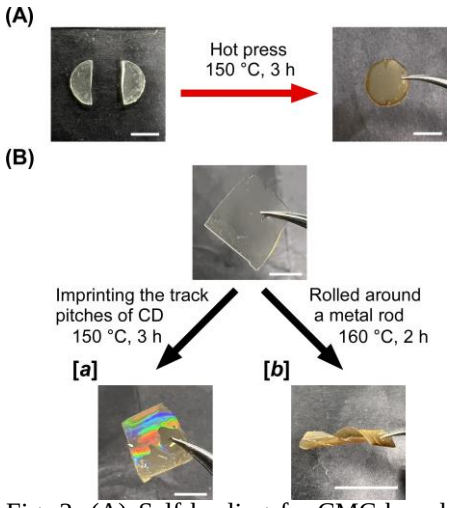

Fig. 2. (A) Self-healing for CMC-based vitrimer. (B) Reshaping for CMC-based vitrimer. [*a*] CMC-based vitrimer film with a channel pattern to exhibit iridescent reflection. [*b*] The transformation to a new spiral shape. White scale bars represent 5 mm. All samples thickness were adjusted to ~0.35 mm.

Another important property of our CMC-based vitrimers is the ability to control their relaxation time by utilizing CMC with different etherification degrees (i.e. the number of COOH groups in a monomer unit of CMC) or by changing the chain length of the diepoxy cross-linker. For instance, it was found that the relaxation time became shorter with the increase in the number of DCBs triggered by the increase of etherification degree of CMC (Fig. 3) The self-healing time was shortened accompanied with the reduction of relaxation time. Such a tunability of self-healing time is highly demanded for the practical applications of the vitrimers.

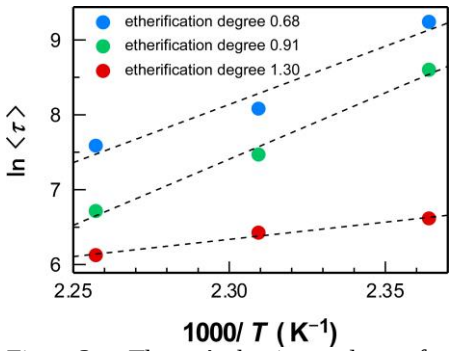

Fig. 3. The Arrhenius plots for CMC-based vitrimers derived from CMC with different degrees of etherification. $\langle\tau\rangle$ and T represent the relaxation time and the absolute temperature, respectively.

4. Conclusions

In this study, we successfully fabricated the CMC-based vitrimers by cross-linking between CMC and diepoxy compounds. We demonstrated the unique properties of our CMC-based vitrimers such as self-healing and reshaping, which would be potentially applied in many industrial fields for a sustainable society.

References

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