Development of time-controllable self-healing gel depending on temperature

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Abstract

In this study, we prepared tetraphenylethylene (TPE) gel by introducing benzophenone (BP) into the side chain of the polymer in the gel. We have developed a self-healing gel that can control the healing time by switching between two reactions, McMurry coupling and pinacol coupling, depending on temperature (Fig. 1).

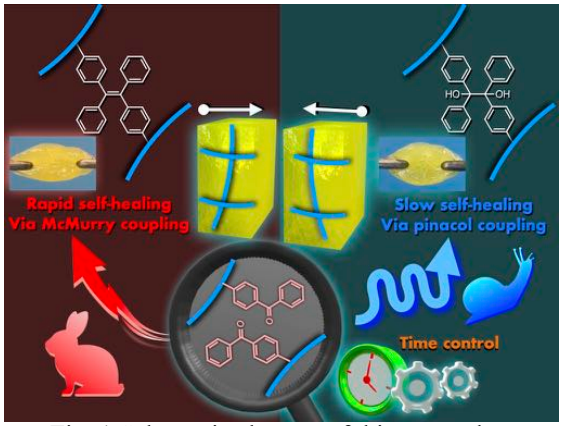

Fig. 1 Schematic abstract of this research.

1. Introduction

Gels, which are soft materials consisting of three-dimensional polymer networks and containing a large amount of solvent, are expected to be applied in the industrial and medical fields because they have a wide variety of functions by changing the properties of the network chains, cross-linking points, and solvents.[1] Furthermore, if gels have the ability to heal wounds on their own (self-healing), they can be effectively utilized as long-lived materials. For this reason, self-healing gels have been the subject of active research in recent years. In addition, the control of self-healing time according to the application is very important for the actual practical use of self-healing materials, such as for emergency treatment as soon as possible, if not precisely, or for slow repair to an exact shape. In this study, we developed self-healing gel materials which self-healing speed can be regulated by temperature as shown in (Fig. 1). To regulate the self-healing speed, we focused on the McMurry coupling proceeding rapidly under high temperature conditions, and the pinacol coupling proceeding slowly under low temperature conditions. As can be seen in the figure, the TPE gel has BP units as the side chains of the gel networks. BP

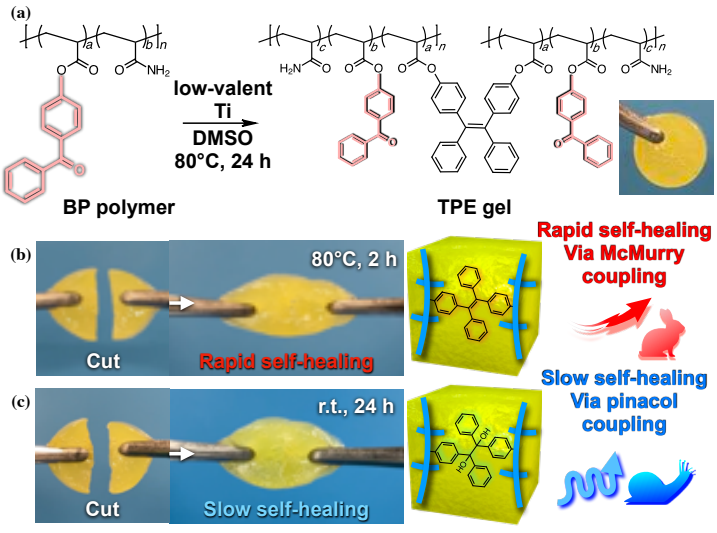

Fig. 2 (a) Chemical structure of TPE gel and photo of gel before self-healing. Photographs and illustrations of (b) the rapid self-healing at high temperatures via McMurry coupling, and (c) the self-healing at low temperatures via pinacol coupling.

substituents reacted with low-electron-valent Ti in the gel, and consequently, TPE gels self-healed rapidly at high temperatures via McMurry coupling and slowly at low temperatures via pinacol coupling.

2. Experiment

TPE gel with tetraphenylethylene (TPE) as a cross-link was prepared by reacting BP in benzophenone (BP) polymer with titanium tetrachloride and zinc powder as catalysts (Fig. 2a). In this TPE gel, low-electron-valent Ti remained as a catalyst, and unreacted BP remained in the gel. Therefore, the gel has reactivity even after fabrication. Using this residual reactivity, self-healing of TPE gel was performed under high and low temperature conditions (Fig. 2b, c). The self-healing of TPE gel by McMurry coupling and pinacol coupling was evaluated by shear tests and Young's modulus obtained from the shear tests (Fig. 3).

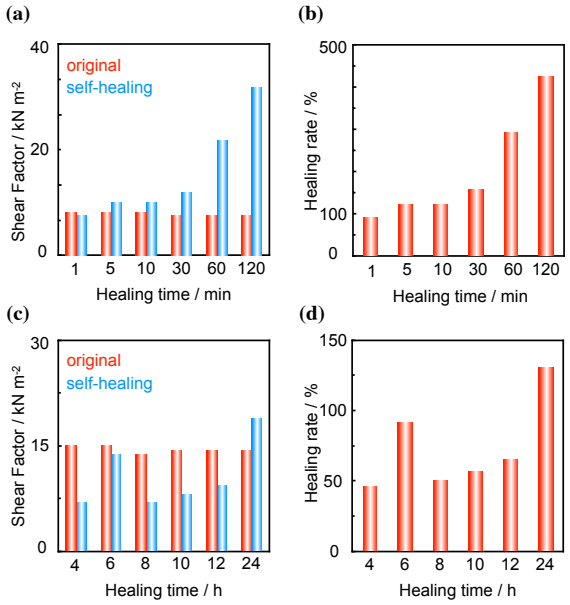

Fig. 3 Time-course changes of self-healing ratio of TPE gels on the self-healing time via the McMurry coupling and pinacol coupling: (a) and (b) Time-course change of (a) the Young's modulus and (b) the self-healing ratio of the self-healed interfaces via McMurry coupling. (c) and (d) Time-course change of (c) the Young's modulus and (d) the self-healing ratio of the self-healed interfaces via pinacol coupling.

3. Results and discussion

First, the self-healing property of TPE gel was checked. As shown in Fig. 2b, self-healing was observed in 2 hours after heating. In Fig. 3a, Young's modulus was calculated from the stress-strain curve to evaluate the dependence of the self-healing time on the self-healing rate. As a result, the self-healing rate reached 100% after about 5 minutes of heating (Fig. 3b). This indicates that McMurry coupling progressed quickly and the TPE was self-healed as a cross-linked part. On the other hand, in Fig. 2c, self-healing was performed at room temperature, and it was confirmed that self-healing occurred in 24 hours at room temperature (Fig. 3c). The self-healing rate reached 100% in 24 hours according to the results of the shear test shown in Fig. 3d. This may be due to the slow progress of pinacol coupling at room temperature, resulting in gradual self-healing with benzophenone pinacol (BPI) as the cross-linked part.

4. Conclusions (or Summary)

In this study, we obtained gels in which the healing time can be controlled by varying the temperature and by using both McMurry coupling and pinacol coupling. In addition, shear tests confirmed that the gels self-heal quickly at high temperatures and slowly at room temperature.

References

1) Tamesue, S.; Noguchi, S.; Kimura, Y.; Endo, T. *ACS Appl. Mater. Interfaces* **2018**, *10* (32), 27381–27390.