

AUTONOMOUS SELF-HEALING OF POLYMERIC GELS CROSS-LINKED BY DIARYLBIBENZOFURANONE-BASED DYNAMIC COVALENT BONDS

K. Imato¹, T. Kanehara¹, T. Ohishi², A. Takahara^{1,2} and H. Otsuka^{1,2}

¹ Graduate School of Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan – e-mail: otsuka@ms.ifoc.kyushu-u.ac.jp

² Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan – e-mail: otsuka@ms.ifoc.kyushu-u.ac.jp

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ABSTRACT

Self-healing materials attract a lot of attention because of their ability to repair the internal and external damage, thereby extending the lifetime of the material in numerous applications that we cannot repair easily. Diarylbibenzofuranone (DABBF), which is a novel dynamic covalent bond unit, can reach a state of radically thermodynamic equilibrium under air at room temperature without any stimuli. Furthermore, DABBF and radical species formed from cleaved DABBF are tolerant of oxygen. Here we report that gels cross-linked by DABBF show autonomous self-healing under air at room temperature.

Cross-linked polymers with DABBF as a cross-linker were prepared by polyaddition of tetrahydric DABBF and tolylene-2,4-diisocyanate-terminated poly(propylene glycol) (PPG). To confirm whether or not DABBF units in the cross-linked polymers were a state of equilibrium and could exchange their bonds, de-cross-linking reaction was performed in DMF under air at room temperature by adding excess DABBF. After de-cross-linking for 24 h, a THF-soluble high-molecular-weight component was detected by GPC measurement. It was expected to be linear polymers and/or cross-linked oligomers. ¹H-NMR spectrum of the solution without fractionation after de-cross-linking clearly indicated the presence of soluble PPG, which had constituted a three-dimensional network. In contrast, these results were not observed in the case of the usual cross-linked polymers (control experiment). Consequently, we confirmed that the reorganization of the cross-linked polymers was due to the autonomously exchangeable DABBF units.

The self-healing property of the polymeric gels swollen with DMF was also investigated under air at room temperature. The gels were cut with a razor blade and the cut pieces were brought together immediately without pressing them strongly. After 24 h, self-healing of the contacted samples could be observed and the scars had almost disappeared. This self-healing behavior was also verified from the almost complete recovery of mechanical properties.

1. INTRODUCTION

Polymers with the ability to repair themselves after sustaining damage without external human intervention can extend the lifetimes and improve the inherent safety of the materials. One way to endow polymeric materials with self-healing ability is introducing dynamic bonds into the polymer networks such as hydrogen bonds, ionic bonds, host-guest interaction, and dynamic covalent bonds. Diarylbibenzofuranone (DABBF) can exist as a state of thermodynamic equilibrium of bond breaking and reformation under air at room temperature. In the present research, we employed DABBF as a dynamic covalent bond and demonstrated bond-exchanging property of DABBF in polymer networks. Furthermore, we attempted to prepare autonomously self-healable cross-linked polymer gels by introducing DABBF as a cross-linker [1].

2. MATERIALS

Tetrahydric DABBF (**DABBF-tetraol**) was prepared from 4-hydroxymandelic acid and 2,4-di-*tert*-butylphenol in three steps. Cross-linked polymers with DABBF were synthesized by polyaddition of **DABBF-tetraol** and toluene-2,4-diisocyanate-terminated poly(propylene glycol) (PPG, $M_n = 2400$), in the presence of di-*n*-butyltin dilaurate (catalyst) in 1,4-dioxane. The fluidity of the reaction mixture slowly decreased during the course of the reaction. The reaction mixture finally lost fluidity after 48 h, indicating that polymerization was successful. The samples for self-healing tests were prepared by similar method in DMF and used without purification. A typical cross-linked polymer was also prepared and used as a control sample. It was prepared from tetrahydric bisphenol A and diisocyanate-terminated PPG in a manner outlined for the polymers cross-linked by DABBF.

3. METHODS

To confirm whether or not DABBF units in the cross-linked polymers were a state of equilibrium and could exchange their bonds, de-cross-linking reaction of the polymers was performed in DMF under air at room temperature by adding excess **DABBF-tetraol**.

Self-healing properties of the cross-linked polymer gels were investigated under air at room temperature. DMF was selected as a solvent for the gels, because it prevents the urethane units from hydrogen bonding and it has low volatility. The gel samples were cut with a razor blade to expose fresh surfaces. The fresh surfaces were wetted with a small amount of DMF to contact tightly and then were brought together immediately without pressing them strongly. The in-contact samples were kept at room temperature under air for 24 h.

Tensile tests were performed to quantitatively evaluate the self-healing properties. The healing process of the samples was performed in the dark under saturated vapor pressure of DMF for 3–24 h (healing times). The gels for tensile tests were fabricated into ISO 37-4 specimens (dumbbell shape, 12 mm × 2 mm × 0.6–1 mm) and were fixed at both ends on thin Al plates with glue and adhesion tape. The plates were pulled under air at room temperature at a crosshead speed of 5 mm min⁻¹. The measurements were performed using more than six test pieces for each healing time and three of them were chosen. Average values were determined from these three samples.

4. RESULTS AND DISCUSSION

After de-cross-linking of the polymers cross-linked by DABBF for 24 h, a THF-soluble high-molecular-weight component ($M_n = 28300$) was detected by GPC measurement. It was expected to be linear polymers and/or cross-linked oligomers. Although we tried to perform a detailed analysis by fractionating this component, the cross-linking reaction occurred again after fractionation. However, the $^1\text{H-NMR}$ spectrum of the solution without fractionation after de-cross-linking clearly indicated the presence of soluble PPG, which had constituted a three-dimensional network. In contrast, these results were not observed in the case of the control experiment. Consequently, we confirmed that the above-mentioned reorganization of the cross-linked polymers was due to the autonomously exchangeable DABBF units.

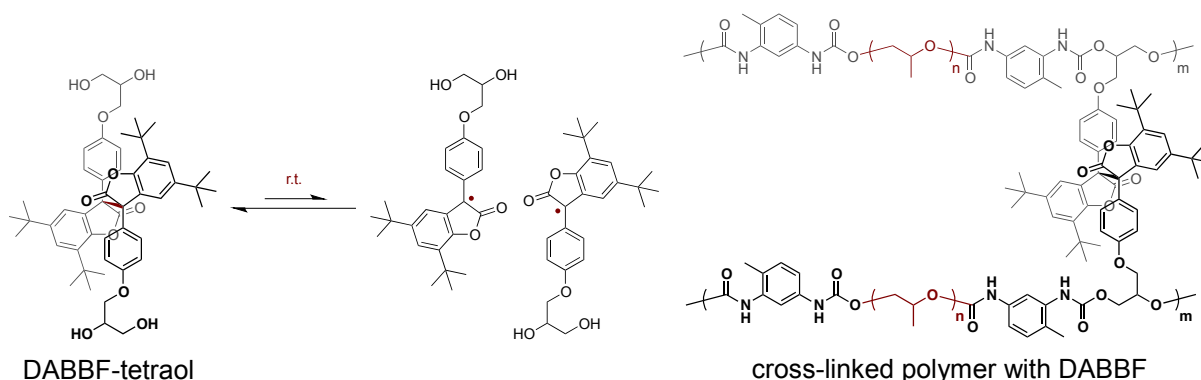


Figure 1: Chemical structures of DABBF-tetraol and of polymers cross-linked by DABBF-tetraol.

Self-healing of the contacted gel samples could be observed and the scars had almost disappeared after healed for 24 h (Figure 2, the gels with and without indigo for better visibility) at room temperature. Even after manually stretching the sample, no failure occurred. A similar self-healing test was performed on the usual chemical gels. These control chemical gels do not possess dynamic covalent bonds. The cut pieces of the control gels could not be coalesced and easily separated into two pieces by manual stretching of the sample. Furthermore, the self-healing behavior of the gels cross-linked by DABBF under air at 0 °C was not observed, indicating that the self-healing behavior depends on the temperature. In the present system, at room temperature, an autonomously self-healing system was successfully achieved.

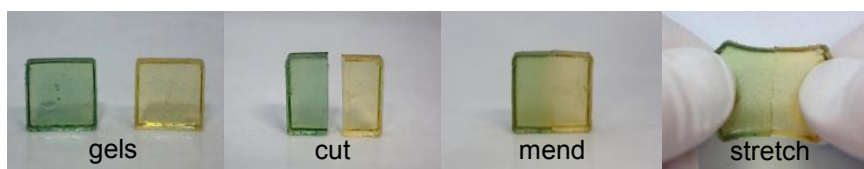


Figure 2: Photographs of self-healing behavior of gels cross-linked by DABBF under air at room temperature; original, cut, mended, and stretched state, respectively, after 24 h.

Figure 3a shows typical stress–strain curves of mended gels cross-linked by DABBF after different healing times. As shown in Figure 3b, longer healing times led to better healing. A recovery of 98% of the original elongation at breaking was possible over

periods of 24 h. An important result is that most of the healed samples did not break at the contacted surface under the tensile testing. This observation indicates that the mechanical strength of the cut samples recovered after being healed for 24 h and a state of equilibrium had been reached. In contrast, the control samples cross-linked by bisphenol A units showed a recovery of less than 5% of the original elongation at breaking even after healing for 120 h.

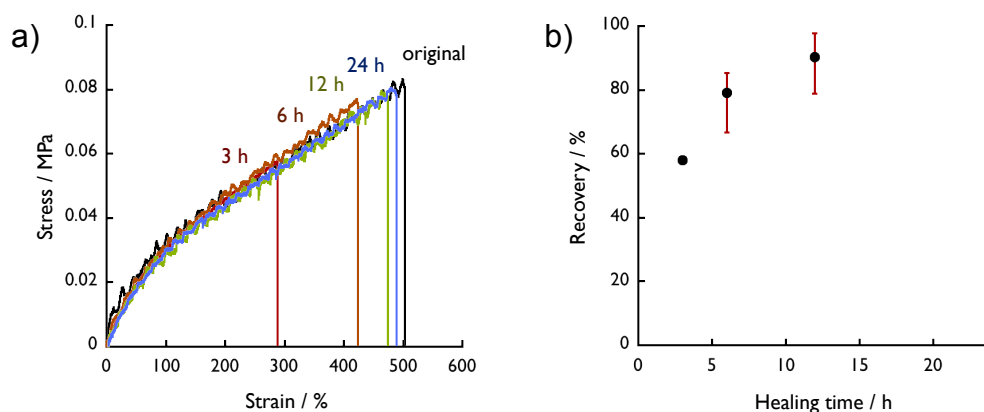


Figure 3: a) Typical stress–strain curves of gels cross-linked by DABBF before and after self-healing measured under air at room temperature. Colored vertical lines correspond to elongation at breaking for given healing times. b) Degree of recovery of healed gels in elongation at breaking depends on healing times. Error bars show maximum and minimum values of three samples.

5. CONCLUSIONS

Cross-linked polymers that contain a DABBF unit, which is a novel dynamic covalent bond unit, were successfully prepared by polyaddition of diisocyanate compounds and a DABBF cross-linker. The autonomous structural transformation and the macroscopic mending of separated gel pieces under mild conditions without any stimuli were accomplished by a dynamic covalent approach.

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