An Ionoically Crosslinked PDMS Elastomer that Quickly Self-Heals Damage with the Aid of CO2 Gas

We have developed an ionically crosslinked poly(dimethyl siloxane) elastomer that quickly self-heals in a CO2 gas atmosphere. In this elastomer, carboxy groups attached to the main chain were partially neutralized with sodium. Both neutralized and neutralized carboxy groups aggregate with each other in the hydrophobic polymer matrix and form spherical-shaped ionic aggregates that act as physical crosslinks. This ionic network is dynamic because the ionic moieties continually hop between ionic aggregates at room temperature. We found that CO2 gas effectively plasticizes the ionic aggregates and accelerates the network rearrangement. As a result, self-healing of this elastomer was dramatically accelerated by CO2 gas.

Synthetic materials that spontaneously self-heal damage have long been dreamed of and many scientists have designed various self-healing materials [1]. Many self-healing elastomers have been designed on the concept of a dynamic network in which flexible polymers are crosslinked via dynamic bonds, such as metal–ligand coordination, hydrogen bonding, π–π, host–guest interactions, ionic interactions, etc. In this work, we report a poly(dimethyl siloxane) (PDMS) elastomer in which the polymer chains are crosslinked via aggregations of neutralized and unneutralized COOH groups attached to the polymer chain [Fig. 1(A)] [2]. In this PDMS elastomer, the neutralized and unneutralized COOH groups are continually hopping between neighboring ionic aggregates at room temperature [Fig. 1(B)]. That is, the ionic network in this elastomer is dynamic and spontaneously rearranged. As a result of interdiffusion of polymer chains between the damaged faces, this elastomer exhibits autonomous self-healing capability at room temperature [Fig. 1(C)]. We have shown that the elastomer quickly self-heals damage with the aid of CO2 gas.

In this work, we attached COOH groups at the chain ends and at the midchain positions randomly placed along the PDMS backbone. The number average molecular weight and the molecular weight distribution of the PDMS are determined to be 7,300 and 1.56, respectively, by size exclusion chromatography with polystyrene standards. The total COOH concentration of this PDMS determined by titration is 3.8 mol%. The COOH groups were partially neutralized with sodium hydrate. The neutralized PDMS is denoted as PDMS-xNa where x indicates the percentage of neutralization. The obtained PDMS-xNa is perfectly colorless and transparent. Figure 2(A) shows a small-angle X-ray scattering (SAXS) pattern of the PDMS-xNa at room temperature. A broad scattering peak attributable to the interference between ionic aggregates is observed. The size of the ionic aggregates in PDMS-xNa was determined by simulating the SAXS pattern on the basis of the Yarasoo-Cooper model [3]. This model assumes that spherical-shaped ionic aggregates with a radius of $R_i$ are randomly dispersed with the closest approach limitation, $2R_i$. From the simulation, $R_i$ and the number density of the ionic aggregates in PDMS-xNa were 1.2 nm, 2.0 nm, and 24 (10 nm)$^{-3}$, respectively. These values are almost independent of the neutralization level. This suggests that almost all neutralized and unneutralized COOH groups are involved in ionic aggregates because of the high hydrophobicity of PDMS matrix.

We found that the PDMS-xNa demonstrates “gas-plastic” properties. As shown in Fig. 2(B), the storage modulus ($E'$) of PDMS-80Na dropped steeply when it was in CO2 gas atmosphere, which indicates that the CO2 gas softens the elastomer. However, $E'$ quickly recovered by the exchange of CO2 with air. That is, the gas-plastic behavior is reversible. Such gas-plastic behavior was not observed for commercially available chemically-crosslinked PDMS elastomer, whereas ionically crosslinked polysiloxane elastomer exhibited the gas-plastic behavior [2]. Therefore, our results clearly suggest that CO2 gas affects ionic component regions. Furthermore, our electron spin resonance and Fourier-transform infrared spectroscopy results demonstrated that CO2 gas plasticizes the ionic aggregates that act as physical crosslinks in this elastomer [2]. As a result of the plasticization of the ionic aggregates, the network rearrangement is accelerated in this elastomer. Figure 2(C) compares the rheological results for PDMS-80Na measured at 5°C in air and in CO2. Relaxation corresponding to the network rearrangement is observed and the replacement of the relaxation peak with CO2 gas shows that the network rearrangement in PDMS-80Na is dramatically accelerated by CO2 gas because of the plasticization of the ionic aggregates.

The acceleration of the network rearrangement effectively enhances the self-healing of the elastomer. A PDMS-80Na sheet was cut using a razor and the cut faces were then gently contacted. The PDMS-80Na sheets were stored at room temperature (26°C) in either dry air or CO2 for different periods. In the CO2 atmosphere, self-healing proceeded more quickly than in air. In Fig. 2(D), time evolutions of the self-healing efficiencies of PDMS-80Na obtained in CO2 and in air are compared. The self-healing efficiency was calculated from the ratio between the tension energies required to break the original and self-healed PDMS-80Na. The self-healing behavior of PDMS-80Na was dramatically accelerated in CO2 compared with that in air. The rapid self-healing is due to the accelerated network rearrangement in CO2 atmosphere.

REFERENCES

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