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Abstract of Doctoral Dissertation

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Title of Doctoral Dissertation

Study on mechanoradical generation and application in azo-crosslinked double network hydrogels
(アゾ架橋ダブルネットワークゲルにおけるメカノラジカルの発生と応用に関する研究)

Double-network (DN) hydrogels are a class of promising soft and tough hydrogels which consist of two interpenetrating polymer networks with contrasting mechanical properties. As a typical example, one is highly crosslinked brittle poly(2-acrylamido-2-methyl-1-propanesulfonic acid) as the first network, the other is loosely crosslinked stretchable polyacrylamide as the second network. Under the influence of an external force, such a contrasting structure leads to a great number of bond ruptures of the first brittle network, whereas the second stretchable network maintains the integrity of the gel. Recent research has demonstrated that this massive cleavage of the first network strands accompanies the generation of chemically active (mechano)radicals. With the supply of monomers and crosslinkers, generated mechanoradicals can trigger the polymerization inside the DN gels, resulting in significant mechanical and functional improvements to the material. Thus, DN gels were designed to be mechanoresponsive self-strengthening materials. However, the low concentration of mechanoradicals in conventional DN gels leads to the long-time polymerization process and limits the further mechanoresponsive function development in DN gels utilizing mechanoradical polymerization.

In this study, to increase the mechanoradical concentration, we incorporated weak azoalkane crosslinker into the first network of DN gels. Compared with the traditional crosslinker *N,N'*-methylenebis(acrylamide), the azoalkane crosslinker caused a slight decrease in the yield stress but significantly increased the mechanoradical concentration in DN gels after stretching. In the azoalkane-crosslinked DN gels, the concentration of mechanoradicals can reach a maximum of $\sim 220 \mu\text{M}$, which is 5 times that of the traditional crosslinker. Interestingly, DN gels crosslinked by a mixture of azoalkane crosslinker and traditional crosslinker also exhibited excellent radical generation performance. Such high mechanoradical concentration attained in DN gels can significantly accelerate the mechanoradical polymerization process. More importantly, it enables us to easily introduce more unique properties to azo-crosslinked DN gels via mechanoradical polymerization.

First, we achieved the force-controlled morphogenesis on azo-crosslinked DN gels. In this part, we ensured the mechanoradical-induced network formed in the deformed gels. This new network conferred plasticity to the elastic DN gel, which maintained its force-induced shape deformation, along with an increase in volume and strength. With this plasticity, we successfully regulated the sheet-shaped double network hydrogels into various three-dimensional shapes at ambient temperature by applying existing shaping processes such as blowing and drawing.

Then, we achieved the crack resistance enhancement on azo-crosslinked DN gels. Crack remarkably reduces the stretchability of the materials due to the stress concentration and resultant early bond rupture in the crack tip. In this part, we utilized the mechanoradicals and resultant newly formed network in the crack tip to enhance the crack resistance. Due to the relatively time-consuming polymerization process, such crack resistance enhancement showed strong rate dependence. We demonstrated that, at the slow loading rate, the

crack tip enhancement improved the stretchability of notched DN gels under the single edge notched test, induced the fast crack propagation under the pure shear test and induced the stick-slip behavior under the tearing test.

In summary, this dissertation achieved a high concentration of mechanoradicals in DN gels by adopting azoalkane crosslinkers in the first network. Utilizing the increased mechanoradicals, we successfully achieved force-controlled hydrogel morphogenesis and rate-dependent crack resistance enhancement in DN gels via mechanoradical polymerization. This work should significantly broaden the application range of mechanoresponsive DN gels to biomedical fields and soft robots.