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Doctoral Dissertation Evaluation Review

Degree requested: Doctor of Life Science Applicant's name ZHEN TAO

Examiner :

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| Chief examiner | (Professor) Jian Ping Gong |
| Associate examiner | (Professor) Kenji Monde |
| Associate examiner | (Associate Professor) Tasuku Nakajima |

Title of Doctoral Dissertation

Fabrication of Tough Hydrogels Composites from Photo-Responsive Polymers
to Show Double Network Effect
(光応答性ポリマーを用いた新規高靱性ハイドロゲル複合材料の合成と
そのダブルネットワーク効果に関する研究)

Results of Evaluation of the Doctoral Dissertation (Report)

Since the first report of double-network hydrogel (DN gel) in 2003, great achievements on developing soft materials with high strength and toughness have been achieved. Recently, tough macro-scale composites from two different materials, soft elastomers or gels and rigid plastics or metals, were also developed, applying similar toughening mechanism of DN gels. However, there are several challenges to develop macro-scale hydrogel composites showing the double network effect. First, the soft matrix hydrogel must be highly stretchable and possess a higher strength than the rigid skeleton hydrogel. Otherwise, the fracture of the rigid skeleton causes catastrophic failure of the material without showing multi-step fracture of the rigid skeleton. The interface bonding between the soft and rigid gels present another challenge for the hydrogel composites. A good interface between two components in composite materials plays an essential role in force transmission and dissipation of energy, ensuring effective reinforcement on the mechanical properties.

In this work, the author provided a strategy to develop macro-scale hydrogel composite to show double network effect. First, the author integrated the mechanical strength and photo-responsiveness in one hydrogel by copolymerizing hydrophobic photo-responsive monomers (2-nitrobenzyloxycarbonylaminoethyl methacrylate, NBOC) into polymer chains from hydrophilic 2-ureidoethyl methacrylate (UM). The P(UM-*co*-NBOC) forms very soft and stretchable physical gels due to formation of the hydrogen bonds between UM and hydrophobic association between NBOC. These dynamic bonds dissipate energy to impart the gels with high toughness.

Using the P(UM-*co*-NBOC), the author developed rigid and less stretchable gel based on the photo-responsiveness of NBOC. Specifically, 2-nitrobenzyl functionalities exhibit photo-labile characteristics under UV irradiation, and the resultant amino groups of 2-aminoethyl methacrylate (AMA), which is transformed from NBOC by self-immolative reaction, will further attack the close-by ester bonds. Accordingly, the original hydrophobic association, which acts as physical crosslinking, is replaced by forming new chemical crosslinks. As a result, after UV irradiation, the physical P(UM-*co*-NBOC) gels transform to chemical P(UM-*co*-AMA) gels without significant change in swelling ratio. Such photo-switching of physical gels to chemical gels brings about a dramatic change in the mechanical behavior

of the hydrogels from soft and highly stretchable to rigid and less stretchable. By controlling the UV irradiation, the NBOC-based hydrogels can be easily reconstructed into various composites.

Based on these results, the author fabricated by UV radiation sandwich-type hydrogels composition, consisted of rigid chemical hydrogel in the outer layers and soft physical hydrogel in the middle layer. The macro-scale composite hydrogels, having a strong interface and negligible swelling mismatching, are mechanically tough showing feature similar with the DN hydrogel, where the hard layers, P(UM-*co*-AMA), play a role of the first network, imparting high modulus and rupturing to dissipate energy, and the soft layer, P(UM-*co*-NBOC), plays a role of the second network, maintaining the global integrity. The author successfully changed the mechanical balance of the two components by varying the molar fraction of NBOC, the UV irradiation time, and the thickness ratio of hard to soft layers. Characteristic hard layer fracture morphologies were observed in accompany with the variation in the mechanical balance of the two components. The macro-scale fracture process of this composite gives important insight to understand the micro-scale fracture process of DN gels.

In conclusion, the author provides a facile method to prepare hydrogel composites using photo-triggered local crosslinking transformation strategy. The gel consists of two modulus regions with molecular-level continuous interfaces and matched swelling ratio, it and can be used as ideal macroscopic model for studying the fracture process of DN gels.

Therefore, we acknowledge that the author is qualified to be granted a Doctorate of Life Science from Hokkaido University.