Doctoral Dissertation Evaluation Review

Degree requested Doctor of Soft Matter Science Applicant's name Yong Zheng

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Title of Doctoral Dissertation

Study on the Effect of Polymer Dynamics and
Phase Separation on the Mechanical Performance of Double Network Materials
（ダブルネットワーク材料の力学性能に及ぼす
ポリマーダイナミクスと相分離の影響に関する研究）

Results of Evaluation of the Doctoral Dissertation (Report)

Double-network (DN) concept has attracted great attention as an effective and general toughening strategy for both gels and elastomers. The DN concept was firstly applied to hydrogels (Gong et al, Adv. Mater., 2003), where two interpenetrating hydrophilic networks with contrasting network structures are made: the first network is rigid and brittle while the second is soft and ductile. In 2014, the DN concept was further extended to elastomers (Creton et al, Science, 2014). The extremely high toughness of DN materials lies in the ability of the material to dissipate a large amount of the mechanical energy through breakage of sacrificial bonds in the first (rigid and brittle) network, while the second (soft and ductile) network maintains the integrity of the whole material without failure. Understanding the fracture mechanisms has been one of the major subjects for double network materials. Despite that the fracture mechanisms have been extensively studied for DN materials, there is still lacking the understanding at polymer network scale, and few have focused on the effect of polymer dynamics at network scale on the fracture of DN gels. To supplement the full understanding of fracture mechanisms for DN gels, in this dissertation, the author first elucidated the effect of polymer dynamics on fracture in DN systems.

Recently, a hybrid DN elastomer system made from two immiscible polymers, the first is polyelectrolyte while the second is hydrophobic polymer, was reported (Matsuda et al., 2019). Compared with the conventional DN systems from two hydrophilic or hydrophobic networks, the hybrid DN systems from two immiscible polymer networks are expected to induce phase-separation considering the substantial immiscibility between the two networks. However, such phase-separation structure in hybrid DN systems has not been revealed yet. In this dissertation, the author systematically studied the phase separation structure and further elucidated the effect of such phase-separation structure on the mechanical performance of DN systems.

In chapter 3, the author first focused on the effect of polymer dynamics on the deformation and fracture behaviors of DN gels. To control the polymer dynamics, the author utilized the ethylene glycol (EG)/water mixtures and glycerol/water mixtures as solvents to systematically tune the solvent viscosity while keeping comparable solvent quality as like water to the constitutive polymers of DN gels. The good solvent quality of EG/water mixtures and glycerol/water mixtures to DN gels was further confirmed by the unchanged swelling ratios and tensile properties of the gels. The author observed that the tensile behaviors of unnotched DN gels remained unchanged while the fracture energy measured by pure shear test of notched specimens decreased significantly with increasing solvent viscosity. This reduction in fracture toughness was found directly related to the decrease of the yielding zone size around the crack tip at increased solvent viscosity. These results suggest that viscous solvents control the dynamics of the stretchable network, which play an important role in the load-transfer process ahead of crack tips.

Then, in chapter 4 and 5, the author systematically investigated the nanophase-separation structure in the hybrid DN elastomers. To control the nanophase-separated structure, the copolymer made from ionic and non-polar monomers was used as the first network and homopolymer made from non-polar monomers was used as the second. The author systematically tuned the nanophase separation by changing the ionic-monomer fraction f_{AMPS} in the first network while maintaining almost the same primary double-network structure. The author had found that the nanophase-separated structure of DN elastomers occurs at f_{AMPS} >0.4. The author also clarified that the size of phase separation is independent of f_{AMPS} but decreases with the increase of the crosslinking density (C) in the first copolymer network. The author further investigated the effects of the nanophase-separated structure on the internal fracture and energy dissipation during tensile deformation in DN elastomers. The author elucidated that the interplay mechanism between the double network structure and the nanophase separation structure enhances the elastic modulus, strength, fracture toughness, and fatigue resistance all together.

In chapter 6, the author also investigated the correlation between the yielding criteria and the pre-stretching of the first network in the double network and multiple network (MN) elastomers with or without phase-separated structure. The author chose f_{AMPS} = 0.1, 0.5 and 1.0 as typical examples, and control the prestretch ratio and the phase separation of the first network while keeping other conditions constant by performing multiple swelling/polymerization steps to create samples with multiple networks from double to quintuple or sextuple. Such increase of network multiplicity effectively increased the prestretch ratio of first network in the obtained MN samples. Then the tensile tests were conducted to determine and discuss the relationships of the yielding conditions (i.e., yielding stretch ratio and yielding stress) and the prestretch ratios for these samples. The author found a systematic correlation between the yielding criteria and the pre-stretching of the phase-separated elastomers, which correlates the molecular structure to the macroscopic properties. For samples without phase-separated structure, the yielding criteria were found to be only determined by the prestretch ratio of first network; while for samples with strongly phase-separated structure, the yielding criterial were deviated from the prediction based on the prestretch ratio, suggesting that the strongly phase-separated structure restricts the strands conformation of the first network.

In conclusion, the author has new findings of the effect of polymer dynamics and phase separation on the mechanical performance of double network materials, and these will contribute to the understanding of fracture mechanisms of double network materials.

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