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博士の専攻分野の名称 博士 (生命科学) or (薬科学) or (ソフトマター科学) or (臨床薬学) 氏 名 鄭 庸

学 位 論 文 題 名

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)

Double-network (DN) concept has attracted great attention as an effective and general toughening strategy for both gels and elastomers. The DN concept is 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. The DN gels with optimized structure can achieve an extremely high toughness of 10^3 – 10^4 J/m², which far exceed the conventional single network polymer materials ($\sim 10^1$ – 10^2 J/m²). The extremely high toughness of typical DN gels 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 soft materials. Despite that the fracture mechanisms have been extensively studied for DN gels, 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, one of the aims of this dissertation is to elucidate the effect of polymer dynamics on fracture in DN systems. In a solvated gel, the dynamics of polymer network is governed by the hydrodynamic friction between the monomeric unit and the solvent, described by the Rouse-like motion. In this dissertation, we tune the polymer network dynamics of DN gels by varying solvent viscosity η_s .

On the other hand, because of the simple synthesis process and fascinating mechanical properties, the DN concept was then applied to elastomers (Creton et al, *Science*, 2014), where two hydrophobic networks are made interpenetrating with each other. Besides, the applicant's group has successfully invented a hybrid DN elastomer system made from two immiscible polymers: the first is polyelectrolyte while the second is hydrophobic and nonpolar. Compared with the 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. Such phase-separation structure in hybrid DN systems has not been revealed yet. Another aim of this dissertation is to confirm and elucidate the effect of phase-separation structure inside DN systems.

Taking together, the aims of this dissertation is to address the effect of polymer dynamics and the role of phase-separation inside DN systems. In the dissertation, the applicant mainly focuses on the following two important parts: 1) investigating the effect of polymer dynamics and 2) confirming and elucidating the effect of nanophase-separated structure.

In **Chapter 1**, general introduction and outline of the dissertation are discussed.

In **Chapter 2**, a brief review on the soft materials, toughening strategies and DN concept from gels to elastomers is introduced. Meanwhile, the deformation and toughening mechanisms for typical DN hydrogels will be overviewed. Some recent advances on the DN systems including DN gels and DN elastomers will be introduced. This chapter provides some basic understandings which will be helpful to initially understand the purpose of this dissertation.

In **Chapter 3**, I focus on the effect of polymer dynamics on the deformation and fracture behaviors of DN gels. To control the polymer dynamics, here I utilize 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. This is further confirmed by the unchanged swelling ratios and macroscopic mechanical properties of the gels. I observed that the tensile behaviors of unnotched DN gels remain unchanged while the fracture energy measured by pure shear test of notched specimens decreases significantly with increasing solvent viscosity. This reduction in fracture toughness is 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.

In **Chapter 4**, I systematically investigate the nanophase-separation structure in DN elastomers and MN elastomers. The nanophase-separation structure in the DN elastomers is clarified by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). I have found that the nanophase-separated structure of DN elastomers can be controlled by varying ionic monomer fraction f_{AMPS} and crosslinking density (C) in the first copolymer network. In addition to controlling the f_{AMPS} and C , increasing network multiplicity can also tune the nanophase separation structure accordingly.

In **Chapter 5**, I investigate the effect of the nanophase-separated structure in hybrid DN elastomers. To control the nanophase-separated structure, the copolymer made from ionic and non-polar monomers is used as the first network and homopolymer made from non-polar monomers is used as the second. I systematically tune the nanophase separation by changing the ionic-monomer fraction in the first network while maintaining almost the same primary double-network structure. I investigate the effects of the nanophase-separated structure on the internal fracture and energy dissipation during tensile deformation in DN elastomers. The effect of the nanophase-separated structure on the fracture and fatigue resistance of the DN elastomers is also studied. I elucidate 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.

As shown in **Chapter 5**, all the phase-separated DN elastomers exhibit remarkable yielding and necking behaviors as typical, non-phase-separated DN hydrogels. For potential widespread applications of phase-separated DN elastomers, it is of great practical importance to understand yielding criteria of phase-separated DN materials and control their yielding point by their compositions. In **Chapter 6**, I further investigate the yielding criteria of phase-separated DN materials. I choose $f_{\text{AMPS}} = 0.1, 0.5$ 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 increases the prestretch ratio of first network in the obtained MN samples. Then I conduct the tensile tests 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 with or without phase separation.

In **Chapter 7**, conclusions of the whole dissertation are summarized.