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Study on Force-Induced Polymerization and Growth in Double-Network Hydrogels with Vascular-Like Monomer Supply

(血管様モノマー供給を有するダブルネットワークゲルにおける力誘発重合と成長に関する研究)

Recently, force-triggered mechanical enhancement has been discovered in double-network (DN) hydrogels. The cause of such enhancement is the polymerization of a new network initiated by mechanoradicals generated from the brittle first network chain fracture upon mechanical actions. As indicated by the pioneer work, after a force trigger, the chain-end radicals are produced from internal fractures and initiate the mechanoradical polymerization in the hydrogel matrix, while the ductile second network that is highly stretchable insures its integrity and softness.

The mechanoradical polymerization is able to impart DN hydrogels or elastomers with functional improvements, for example, the self-growth that mimics muscle training, inducing DN gel to exhibit a metabolic-like behavior due to the transduction between chemical energy and mechanical work, which shares similar properties to muscle tissues. Besides the self-growth that mimics muscle training, the mechanochemical reactions also enables other functional properties of DN gel such as force stamp-induced surface patterning for cell culture, or using fluorescent mechanophores to map the real-time internal fracturing. Although the above-mentioned studies have promoted the branching of double network concepts into investigations of mechanochemistry, which starts a strategic junction of these two areas, one of the problems for a better usages of DN gels as the next generation of muscle-mimicking materials is that: a constant supply to complement the monomer consumption during the force-triggered mechanoradical polymerization, thus an opening system filled with monomer solution is required during stretching in order to sustain the mechanoradical polymerization, such an under-solution system largely confines their observations and usages.

Here, in order to attain continuous remodelling or growth in response to repetitive mechanical stimuli with a constant supply, a sustainable supply of chemical reagents to such dynamic materials is constructed taking inspiration from the vascular system. We incorporated a vascular channel inside the DN hydrogel as a delivering pathway, whereby attaining a continuous polymer growth in response to repetitive mechanical stimuli with an independent and constant monomer complementation. Due to the continuous supply of chemicals to the channel-containing DN hydrogel (c-DN gel), the material is able to sustain itself by the internal circulatory flow, which functions as the self-sustainable system of mechanoradical initiated polymer

growth. Besides, through programable supply from the channel, the perfusion of monomer solutions not only replenishes the monomers consumed by the polymerisation but also replenishes the water loss caused by the surface evaporation of hydrogel, therefore freeing the mechanochemical process of DN gels from the constraints of the under-solution environment.

As a result of the above mentioned design and mechanism, the c-DN gel can obtain monomers from the independently controllable solution supplied via internal circulatory flow. Through the diffusion of monomers into the permeable c-DN gels, our samples are mechanically trainable, sensitive to chemical supply, and renewable in constitutions. Utilizing such a facile chemical supply method, mechanochemical growth can be readily tuned by changing the monomer concentration flowing through the channel, allowing us to directly control the mechanical growth and trace the corresponding variations in the chemical components.

The tunable duration time of the monomer supply in the channel also helped to disperse the interplay between mechanoradical initiated polymer growth and self-strengthening. We observed a pronounced difference between the increasing trend of the polymer content and the mechanical parameters. Using Raman spectroscopy, we detected discrepancies in the kinetics of polymer growth and mechanical strengthening, deciphered unique features of mechanochemical reaction in DN gels including the extremely long-living radicals and delayed mechanical strengthening through a desirable feedback loop. Besides, by quantifying both monomer diffusion and in-situ polymerization area, the lifetime of the network-trapped mechanoradical is observed to be about 10 minutes. Benefiting from these long-existing macroradicals and the self-sustainable channel structure, the mechanochemical reactions in c-DN hydrogel may promote their use in applications such as soft robotics, real-time spectrum monitoring, and mechano-chemical reactors.