

Tunable dynamics of a chemically- and physically-crosslinked hydrogel

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Inspired by the mussel byssus, an organ which allows mussels to attach to surfaces thanks to metal ligand coordination complexes^{1,2}, we developed a chemically crosslinked hydrogel of poly(acrylamide-co-vinylimidazole), physically crosslinked by metallic cation (Ni^{2+} or Zn^{2+}) – Imidazole coordination bonds. Those coordination bonds introduce a dissipation mechanism in the material, due to the reversible breaking and formation of the coordination bonds, thus increasing the toughness of the otherwise fragile gels. The characteristic exchange time can be modified by simply changing the metallic cation used: this changes the kinetics of the complex, thus changing the lifetime of the physical bond.

We found the extensibility of the dual-crosslinked gels to be much higher than that of the bare chemical gel (strain at break increases from 200% to 700%). The elastic modulus was found to increase with strain-rate, and, at fixed strain rate, to change with the metallic cation introduced: gels with Ni^{2+} ions had a higher modulus than gels with Zn^{2+} ions, which have a modulus close to the modulus of the chemical gel. This would imply that gels with Zn^{2+} ions have a much shorter characteristic relaxation time, the Imidazole- Zn^{2+} bonds being then less mechanically active than the Imidazole- Ni^{2+} bonds at the same strain-rate.

We performed rheological experiments, studying the evolution of the storage and loss moduli over a large frequency range. Those experiments confirm what we see in tensile tests, but show also the existence of two characteristic relaxation modes in the gels. The characteristic relaxation time of the two modes (one slow, one fast) are well separated from each other, and we were able to model the behavior of the gel by fitting the rheological data with a fractionary rheological model³.

To confirm the existence of those two relaxation times, we then performed dynamic light scattering (DLS) experiments. The results show again two relaxation modes (besides the gel mode), whose characteristic relaxation times (fast and slow) superpose very well with those found by rheological measurements and modelling. The same experiments (rheology and DLS) were performed by varying the temperature, and the resulting activation energy is the same for both experiments.

In summary we introduced a simple method to create dynamic, dual crosslinked hydrogels, with increased extensibility, where dynamics and mechanical behavior can easily be controlled by changing the metallic cation introduced. In those gels, we found two characteristic relaxation times. This implies the existence of more than one relaxation phenomenon in our dual-crosslink gel.

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