

THÈSE DE DOCTORAT

de l'Université de recherche Paris Sciences et Lettres
PSL Research University

Préparée à Ecole Supérieure de Physique et de Chimie
Industrielles de la Ville de Paris

Structure et propriétés des hydrogels à réticulation chimique et
physique

Ecole doctorale n°397

PHYSIQUE ET CHIMIE DES MATERIAUX

Spécialité CHIMIE PHYSIQUE

Soutenue par Jingwen ZHAO
le 14 Mars 2018

Dirigée par **Costantino CRETON**
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Acknowledgements

I would like to express my gratitude to those who have given me the chance to complete this dissertation.

I would first and foremost like to thank my supervisors, Costantino and Tetsu. Thank you for giving me the opportunity to study in the SIMM lab. I wouldn't have been able to accomplish this without your support, patience and encouragement. With your profound knowledge in the field, you always pointed me in the direction to go when I was confused; with your generosity of your time, you helped me to overcome the difficulties I have encountered; and with your kindness, you helped me to have the courage to live in a new country and became more confident.

I appreciate the support from Koichi Mayumi, who started this project. I am deeply impressed by your very nice work within only two years, and I have been reading your papers so many times and trying to follow your path. Thank you for your contribution to this project and for your help with the experimental details and the advice. I would also like to thank Hiroto Ozaki for his work and being helpful and supportive.

I am very grateful to Professor Chung Yuen Hui and his students Jingyi and Mincong, thank you for your help with the theoretical study, with which a more comprehensive study was able to be carried out.

I would like to thank all the members of my jury: Professor Sebastian Seiffert, Professor Taco Nicolai, Professor Michel Cloitre and Professor Qian Huang. Thank you for your interest in my work and your evaluations of my thesis.

I would like to express my appreciation to all the permanent members in SIMM, thank you for your warm help. Especially, I would like to thank Guylaine, thank you for your help with the rheometer, and for your kind message before my defense, which gave me courage and confidence for the last and most important day of my study.

I feel very lucky to have been able to work with all the students in the lab, thank you all for your kindness and help, it was a privilege to be able to work among friends, to be able to talk about problems in experiments and weekend plan. You have made my working time meaningful and joyful. Especially, I would like to thank Robert, Pierre, Francisco, Hui, Menghua, Thitima, Ekkachai, Jessica, Davide, Laure, Romain, Tom, Charles, Paul, Valentine, Cécile, Yinjun, Antoine, Gabriel, Artem, Helen ...

I would also like to thank all my friends outside of the lab, Leonie, Madda, Melissa, Connie, Pekka, Loïc, Tamara ... Thank you for your company, I appreciate all the time we spent together, you made my life in Paris sweet and wonderful. I am very lucky to have the best roommates in the world: Kunyun, Jun, Suyuan, Xiaohan, Congcong and Ran. With you being there, that tiny apartment is the real home to me, and it will be the place I miss the most in Paris.

I would like to thank my parents and my sister, thank you for your support and encouragement.

Thank you Robert, for your encouragement and for always being there for me. It hasn't always been easy with me writing my thesis and you trying to adapt Chinese life, but with your patience and support and help, we both overcame difficulties, both in work and in personal life. I wouldn't have been able to do this without you.

I would also like to thank the Chinese Scholarship Council (CSC) for the financial support.

Thank you all for participating in these three and a half most memorable years in Paris!

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General introduction

Hydrogels are very common in nature. One can find ‘living hydrogels’ in algae, jellyfish and sea cucumber. They are also be found in our everyday life, such as contact lenses, diapers, food, cosmetics... Their high water content and soft solid mechanical properties make also hydrogels promising candidates for biomedical applications like targeted drug delivery systems and tissue engineering. However, their fragility due to the heterogeneous network structure and the lack of dissipative mechanisms is the largest limitation of the potential applications of hydrogels.

In order to reach the objective of reinforcing the mechanical properties, different strategies have been studied, aiming at improving the homogeneity of the network by having homogenous chain length thus mesh size of network, or developing dissipative mechanisms in the bulk of the gel. The pioneering work of Gong¹ in 2003 gave a good answer by creating two interpenetrated networks having different properties: a low volume fraction of highly crosslinked and stretched network and a high volume fraction of loosely crosslinked second network. This hydrogel has a fracture toughness a hundred times better than either network on its own.

However, the limitation of this double network hydrogel is that the ‘sacrificial’ network breaks irreversibly, which brings permanent damage to the network. A successful strategy to avoid this is by introducing reversible physical crosslinks into the network, the irreversible rupture of chemical networks can be prevented by sacrificing the transient physical bonds which can break and heal.

Based on this principle, in our laboratory a new dual crosslink hydrogel was developed²⁻⁵, with chemical and physical crosslinks in the same network. Based on poly(vinyl alcohol), this new gel was shown to have good mechanical properties and its linear rheological and nonlinear properties have been studied. However, some open question remained:

- What is the effect of the relative density of chemical and physical crosslinks?

- What are the limitations of this dual crosslink gel?
- What could be done to overcome the limitation and to have a wider view of dual crosslink gels?

In order to answer these questions and perform more systematic experiments, this PhD was started on the subject. The present work is divided into 5 chapters.

The first chapter is devoted to an overview of the hydrogel science, the classification and applications will be presented, following which, a description of mechanical shortcomings of hydrogels, and the corresponding reinforcement strategies will be introduced.

After a brief recall of what has been done for the PVA-borax dual crosslink gels, the second chapter focuses on the effect of varying the chemical and physical crosslinking density on the mechanical properties of this dual crosslink gel.

Chapter 3 describes a constitutive model for the PVA-borax dual crosslink gel, after a short introduction of the continuum theory, the validity of the model for both tensile and torsion tests will be evaluated with dual crosslink gels at various crosslinking ratios.

In Chapter 4, designed to overcome the intrinsic design limitations of the PVA-borax gel, a new dual crosslink gel, the AAm-VIm- M^{2+} gel, will be introduced, the background of this bio-inspired system will be introduced, followed by the characterization of the mechanical properties of this gel, as well as the comparison of two systems.

Chapter 5 will be dedicated to the resistance to crack propagation of these two dual crosslink gels after a brief introduction of basic fracture mechanics. The fracture energy and crack propagation velocity of these two systems will be discussed and compared and we will discuss the relation between the molecular structure of the gels and their mechanical properties. Finally, the main contributions of this work will be summarized in a concluding part, along with the prospects.

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Chapter 1: Introduction

1.1 Hydrogels

1.1.1 Definition and general properties of hydrogels

A polymer gel is a three-dimensional macromolecular network swollen in a liquid, as schematically represented in **Figure 1**. Gels are classified in three groups according to the swelling liquid: hydrogels (for water), organogels (for organic solvents) and aerogels (for air)^{1,2}. Hydrogels are commonly seen in nature and daily life, such as in jellyfish, contact lenses, diapers, cosmetics and many types of food. Due to the hydrophilic functional groups attached to the polymeric backbones, they are capable of holding large amounts of water in their three-dimensional networks^{3,4}. At the same time, they can retain their solid form thanks to the crosslinks between network chains. These crosslinks can come from many types of interactions: covalent bonds, ionic bonds, hydrogen bonds, hydrophobic interactions and strong van de Waals interactions between chains.

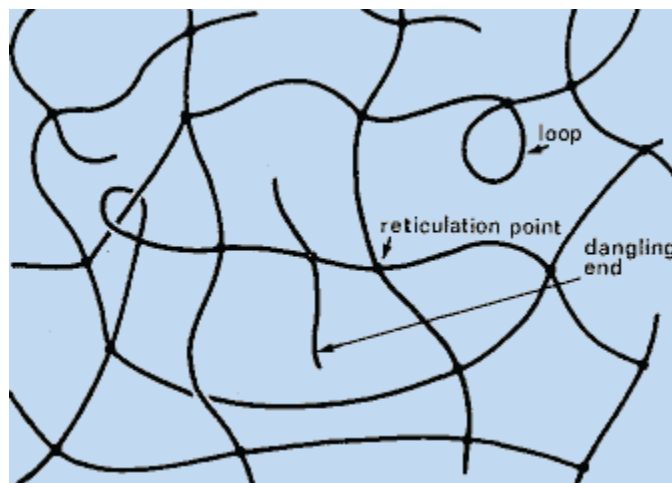


Figure 1. The schematic presentation of hydrogels. ⁵

1.1.2 Classification of hydrogels

1.1.2.1 Type of crosslinking

Hydrogels can be divided into chemically- or physically-linked networks based on the nature of the crosslink junctions: chemically crosslinked networks have permanent crosslinks where strong chemical bonds connect polymer chains in the network, while physical networks are linked by transient crosslinks due to polymer chain entanglements or attractive/associative physical interactions.

1.1.2.2 Polymeric composition

The polymeric composition of hydrogels differs according to the preparation method. Hydrogels can be classified into homo-polymeric, co-polymeric and interpenetrating polymeric hydrogels⁴.

Homo-polymeric hydrogels are prepared from a single species of monomer which forms the entire network, while co-polymeric hydrogels are comprised of two or more monomer species, in which at least one is hydrophilic⁶.

Interpenetrating polymeric hydrogels are a combination of two polymer networks, where at least one is synthesized in the presence of the other⁷. They can be synthesized by immersing a first network into a solution of monomers. Compared to homo-polymeric hydrogels, these gels could have a very different topology, which can lead to tougher mechanical properties.

1.1.2.3 Network electrical charge

Another way to classify hydrogels is on the basis of the electrical charges of the building blocks. Hydrogels can be classified as neutral (no charged groups), anionic (negatively charged groups), cationic (positively charged groups) or ampholytic (both positively and negatively charged

groups) hydrogels. Anionic, cationic and ampholytic hydrogels are also defined as ionic hydrogels⁸.

1.1.3 Applications of hydrogels

Due to their solid-like and liquid-like properties, high water content and biocompatibility, synthetic hydrogels attract academic and industrial interests for their use in a variety of applications, such as contact lenses, wound dressing, drug delivery, tissue engineering, and cosmetic and hygiene products.

1.1.3.1 Contact lenses

In 1960, Wicheterle and Lim first studied poly-2-hydroxy-ethylmethacrylate (PHEMA) as potential biocompatible material for contact lenses⁹. Hard contact lenses are based on glassy polymers such as poly (methyl methacrylate) (PMMA) or poly (hexa-fluoroisopropyl methacrylate) (HFIM), while hydrogels are the ideal candidate for soft contact lenses¹⁰. To produce contact lenses from hydrogels, several characteristics should be considered: light transmittance, refractive index, sufficient oxygen permeability, wettability and permeability to water, suitable mechanical properties and biocompatibility¹¹. For example, PHEMA contact lenses contain 38 – 40% of water in the fully hydrated state and show low variability with changes in external factors¹², certain hydrophobic monomers can act as strengthening agents when copolymerized with hydrophilic monomers such as HEMA, or N-vinyl-2-pyrrolidone (NVP)¹³.

1.1.3.2 Drug delivery

Hydrogels have attracted interest for their use in drug delivery due to their high permeability to hydrophilic molecules, oxygen and water and good biocompatibility. There are several mechanisms to control drug release: diffusion controlled, swelling controlled, chemically controlled and environmentally-responsive release¹¹. As shown in **Figure 2**, there are two different forms of hydrogel diffusion control systems: the reservoir delivery system and the matrix system, both allowing the diffusion of a drug through the hydrogel mesh or the pores inside hydrogels at a controlled rate, which results in desirable sustained drug release^{11,14} over relatively long times (days). A reservoir delivery system includes a drug-containing core coated with a hydrogel membrane, the drug concentration is higher in the center to allow a constant release rate. A swelling-controlled release device is a matrix system, with the drug dispersed within a solid polymer that starts to swell when the system is in contact with bio fluid. The hydrogel starts to expand becomes rubbery and wells in bio-fluid. The relaxation of polymer chains of the gel allows then the diffusion of the drug¹⁴.

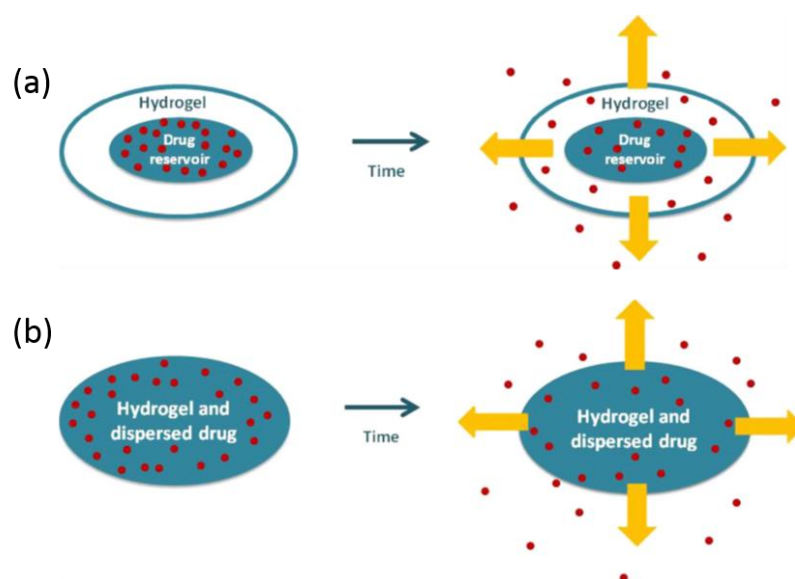


Figure 2. Scheme of drug release in reservoir system (a) and matrix system (b).¹¹

1.1.3.3 Tissue engineering

Hydrogels play an important role in tissue engineering, with applications such as space-filling agents, delivery vehicles, or three-dimensional structures to ensure the development of certain tissues such as cartilage and tendon. Good biocompatibility means hydrogels have the ability to be in contact with internal body organs without causing damage or triggering any undesirable responses¹⁵. Hydrogels based on poly (ethylene oxide) (PEO), PVA, PAA and polypeptides are suitable for tissue engineering. One of the most important future challenges is to synthesize hydrogels with excellent mechanical properties that can match strength and response of their biological counterparts, which will be required in order for hydrogels to be successful in tissues such as bone, muscle and blood vessels.

1.1.4 Mechanical shortcomings of chemical gels

Simple chemically crosslinked hydrogels are typically brittle, in that they break under moderate stresses, making them unsuitable for industrial applications requiring a certain mechanical toughness. The mechanical brittleness of hydrogels drives from an inhomogeneous network structure and/or a lack of dissipative mechanism.

1.1.4.1 Inhomogeneous network structure

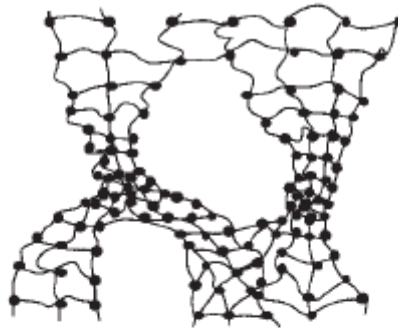
An inhomogeneous network gives rise to localized stress on certain chemical bonds at the molecular level, and favors the nucleation of larger defects that can propagate onto cracks, strongly reducing the stress and strain at break of hydrogels. According to Shibayama's study (**Figure 3**), there are three types of inhomogeneities¹⁶:

Chapter 1: Introduction

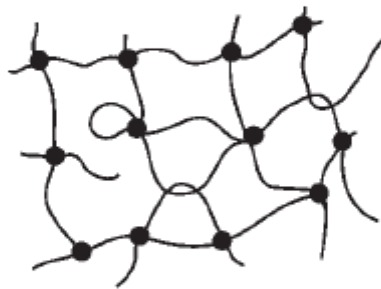
- 1) Spatial inhomogeneities, which comes from non-uniform spatial distribution of crosslinks, with densely crosslinked zones and loosely crosslinked zones.
- 2) Topological inhomogeneities, which depends on the topological state of the network, such as loops, trapped entanglements and dangling chains.
- 3) Connectivity inhomogeneities, which are related to the size and spatial distribution of branched polymer clusters.

Factors such as monomer or cross-linker concentration, or initiator system properties during the synthesis can impact the network homogeneity and give rise to the inhomogeneities categorized above. The consequences of inhomogeneities can affect the properties both at the microscopic scale^{17,18} (diffusion properties) and at the macroscopic scale (elastic and swelling properties, fracture toughness).

Types of Inhomogeneities



(a) spatial inhomogeneities



(b) topological inhomogeneities



(c) connectivity inhomogeneities

Figure 3. Inhomogeneities in gels. ¹⁶

1.1.4.2 Lack of dissipative mechanisms

There are two types of bulk dissipative mechanisms in conventional hydrogels: pendant polymer chain relaxation and fracture of stretched chains by bond breakage. These bulk dissipative mechanisms become important when the material is under stress and determine what

happens at the point of failure (crack propagation). A material lacking in one or both of these bulk dissipative mechanisms results in a concentration of stress at the crack tip when a crack is formed and a very localized energy dissipation mechanism (near the crack plane) during crack propagation. As shown in **Figure 4**, Lake and Thomas proposed a model to account for the energy dissipated by the breakage of a single polymer chain, located across the plane of crack propagation¹⁹. They proposed that the energy required to break a particular polymer strand is proportional to the number of covalent bonds in the strand and therefore is much greater than the dissociation energy of one single bond. Based on this idea a theoretical estimate of the threshold fracture energy Γ_0 to propagate a crack was proposed:

$$\Gamma_0 = N_x U_b \Sigma \quad (1)$$

where, N_x is the number of C-C bonds between crosslinks, U_b is the energy of a C-C bond, and Σ is the areal density of chains crossing the plane²⁰.

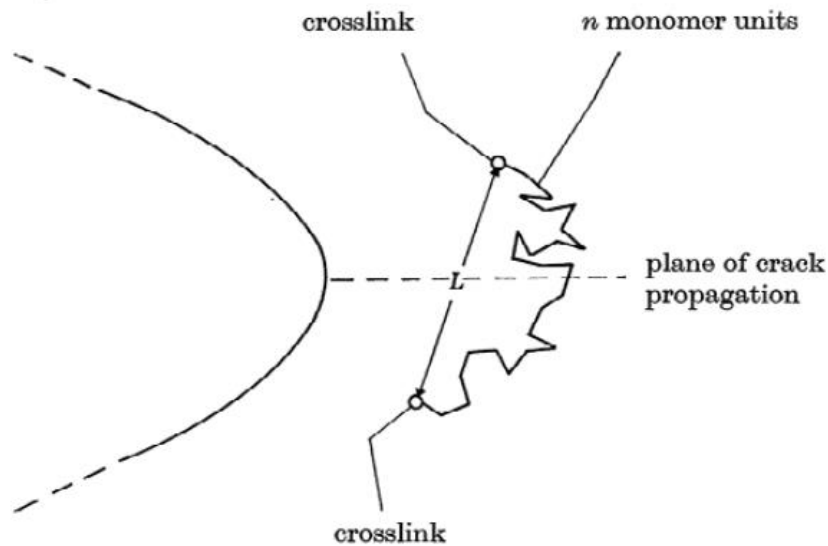


Figure 4. Schematic view showing a polymer chain lying across the plane of crack propagation. ¹⁹

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Experimentally, the value of fracture energy Γ measured at a given temperature and strain rate, can be much higher than the Γ_0 prediction. Gent^{21,22} proposed that the total fracture energy is composed of an interfacial term multiplied by the viscoelastic losses in the volume near the crack tip:

$$\Gamma = \Gamma_0 [1 + f(R, T)] \quad (2)$$

$[1 + f(R, T)]$ depends on the separation rate R and temperature T .

The low fracture resistance of chemical hydrogels can be explained by Eq. (1), since the highly swollen networks contain elongation much lower areal density of chains Σ than elastomers. In addition the presence of water decreases dramatically the internal friction mechanisms responsible of viscoelastic losses in elastomers. Without effective dissipative mechanism, the failure by crack propagation will occur at a low deformation.

1.2 Reinforcement of hydrogels

As described in the previous section, hydrogels have various potential applications as biomaterials, but conventional hydrogel materials are limited, particularly at higher loads due to their poor mechanical properties because of structural defects. Consequently, their mechanical properties and reinforcement mechanisms have been intensively studied in the last two decades. Several strategies have been developed aiming at either increasing homogeneity of the network or introducing bulk energy dissipative mechanisms in order to reinforce the hydrogel.

1.2.1 Hydrogels with improved homogeneity

1.2.1.1 Tetra-PEG hydrogels

One strategy to minimize the inhomogeneities is by achieving a well-defined mesh size with fixed crosslinks. Sakai *et al.*²³ developed Tetra-PEG hydrogels by combining two symmetrical four arm star-shaped macro monomers with the same chain length: tetra-NHS-glutarate-terminated PEG (TNPEG) and tetra-amine-terminated PEG (TAPEG). These two materials are schematically represented in **Figure 5**, with the functional groups at the end of their arms. They must be connected to each other while avoiding self-reaction between the two TNPEG (and between the two TAPEG) macro monomers.

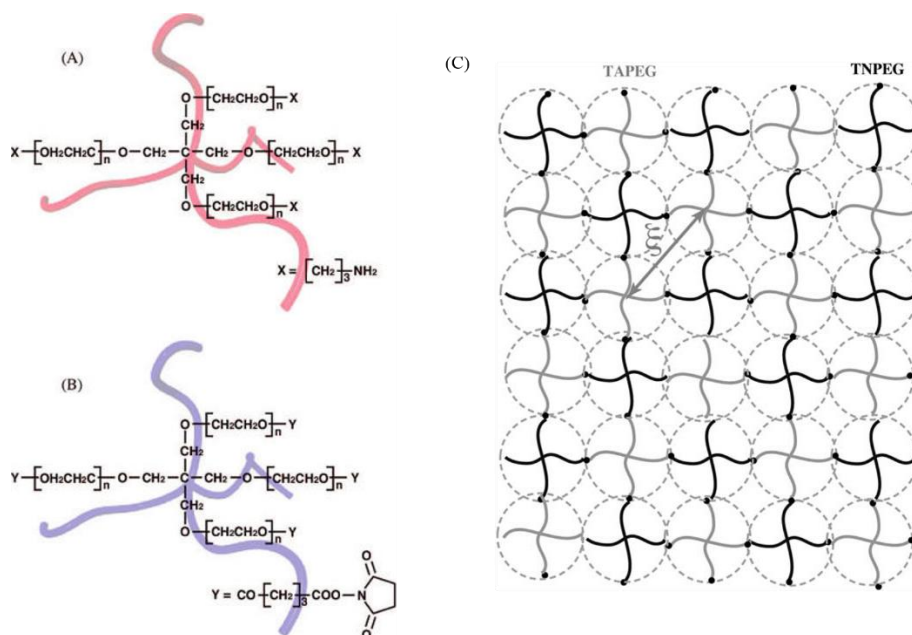


Figure 5. Molecular structure of TAPEG (A) and TNPEG (B)²³, and the schematic illustration of the constitutive tetra-PEG hydrogel network.²⁴

The mechanical behavior of the star-shaped macro system showed an extremely high maximum compression strength of 27 MPa, and high deformability was obtained^{25,26} (**Figure 6**). Analysis by SANS showed the absence of inhomogeneities while under deformation. Noted that the strain ϵ in **Figure 6a** equals to the ratio of total deformation to the initial length, while the stretch ratio λ represents the ratio between the final length and the initial length.

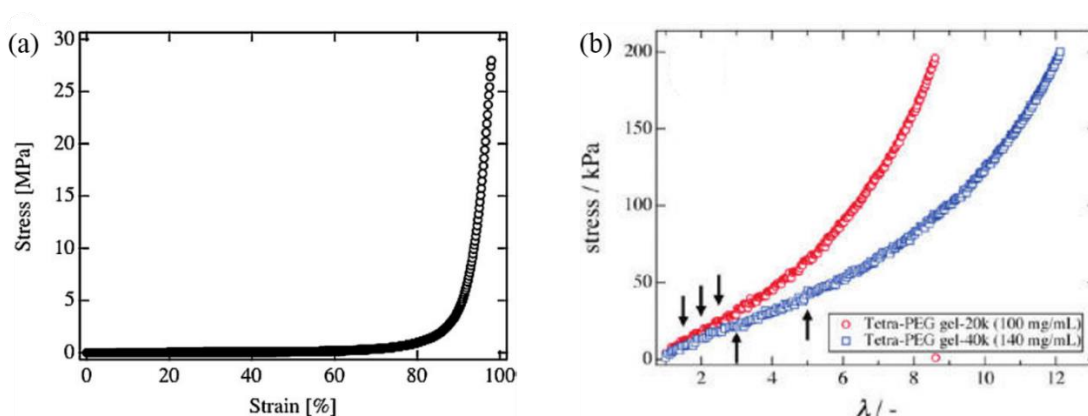


Figure 6. Nominal Stress-Nominal strain curves of Tetra PEG network in (a)²⁵ compression and (b)²⁶ traction.

Fracture studies confirmed that this system is free from trapped entanglements²⁷. That is to say: the fracture behavior showed good agreement with the Lake & Thomas model, an efficient dissipation process was not involved²⁸. It should be noted however that these highly elastic gels are not intrinsically tough: once a notch is introduced the fracture energy is quite low in agreement with the Lake and Thomas theory. Yet the very regular structure of the gels prevents the nucleation of cracks efficiently and increases the stress and strain at break for unnotched samples.

1.2.1.2 Topological hydrogels

Ito *et al.* developed topological, or slide-ring hydrogels, which were made from necklace-like macromolecules²⁹. This structure, schematically represented in **Figure 7c**, is based on the concept of movable crosslinks. The crosslinking points are able to move along the polymer chains, with the aim of tension equalization among the chains. These slide ring hydrogels were synthesized by the chemical crosslinking of polyrotaxane, comprising α -cyclodextrin and poly(ethylene glycol) (**Figure 7a**). The coupling of the α -cyclodextrin rings results in the figure-of-eight crosslinks (**Figure 7b**), leading to the formation of topological polymer chains.

These self-homogenizing hydrogels can de-swell then re-swell in the water up to 400 times their dry weight in water. These changes are reversible, without damage such as pattern formation on the surface²⁹.

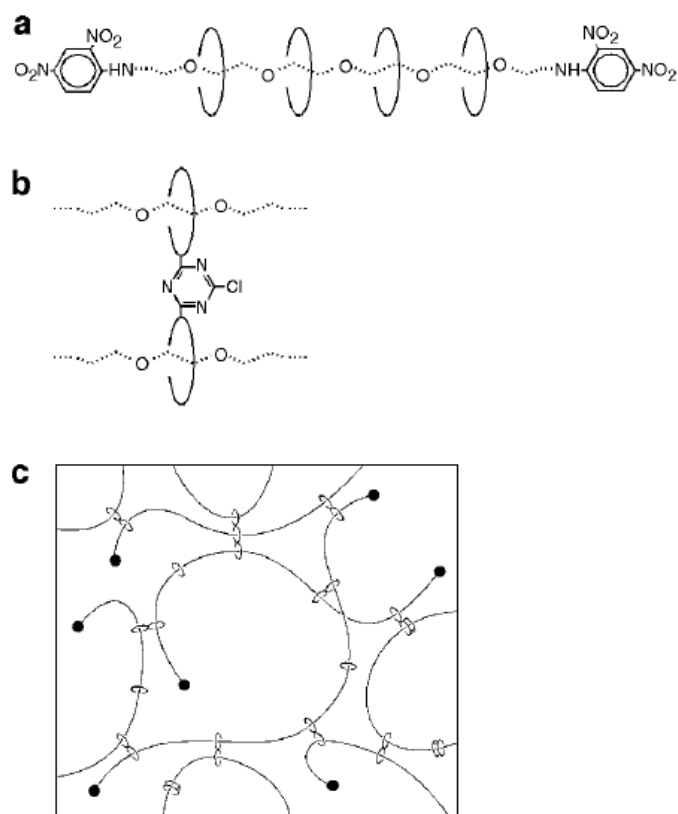


Figure 7. (a) The polyrotaxane consisting of α -cyclodextrin and poly (ethylene glycol). (b) The figure-of-eight crosslink: covalently crosslinked cyclodextrins. (c) Schematic diagram of the polyrotaxane gel prepared from the sparse polyrotaxane by covalently crosslinking cyclodextrins. ²⁹

For classical chemical hydrogels, small angle neutron scattering (SANS) can be used to track the increase in crosslinking density. The frozen inhomogeneities introduced by crosslinking give rise to an increase in the scattering intensity. Conversely, in the slide-ring hydrogels, the opposite phenomenon was observed³⁰: with the existence of crosslinking, the scattering intensity was lower, indicating less inhomogeneities. This decrease is due to the ‘pulley’ effect (**Figure 8b**), which can minimize the local strain and reduce the spatial inhomogeneities upon swelling.

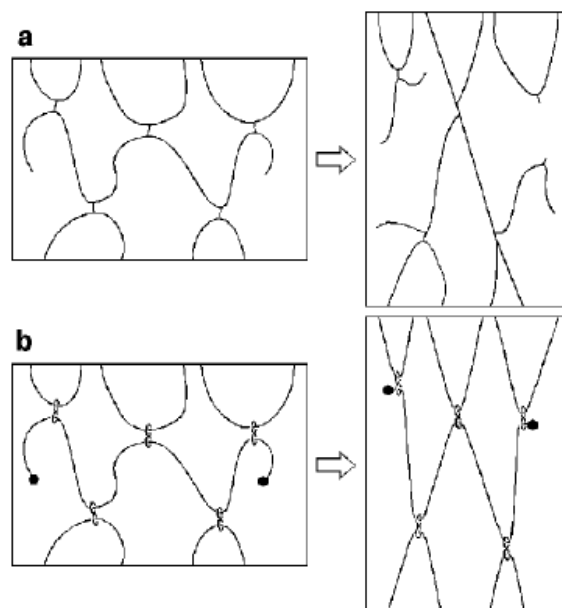


Figure 8. Comparison of deformation between a chemical gel (a) and slide ring gel (b). ²⁹

The mechanical properties of the slide-ring hydrogels were studied by uniaxial deformation measurements, and they displayed abnormal behavior compared to that expected according to conventional rubber elasticity theory³¹. With materials of increasing crosslink density, the elastic modulus E initially increases then decreases (**Figure 9**). A theory³¹ has been proposed to explain this behavior: in addition to the conformational entropy, the positional entropy of cyclic molecules along the chain must also be considered. This suggests that the decreasing elasticity at high crosslink density is mainly derived from the positional entropy change of uncrosslinked cyclic molecules.

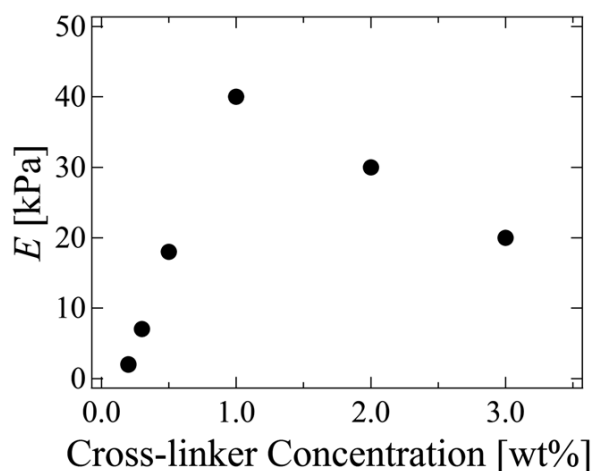


Figure 9. Plot of elastic modulus E as a function of cross-linker concentration. ³¹

The viscoelastic properties were also investigated and two relaxation modes were observed³². This behavior is based on the change of the mean mass distribution between the crosslinking points, due to the sliding of the α -cyclodextrin along the backbone of the chains.

1.2.2 Toughening hydrogels with dissipative mechanisms

1.2.2.1 Ionically crosslinked hydrogels

Tough and self-healing hydrogels have been developed by introducing ionic cross-linkers into covalently crosslinked network. Polymers such as Alginate, Chitosan and poly (methacrylic acid) (PMAA) can be good candidates, while cations such as Zn^{2+} , Ca^{2+} , Ni^{2+} , and Fe^{3+} can be used.

A good example of ionically crosslinked hydrogels is demonstrated in **Figure 10**, where an ionically crosslinked alginate- Ca^{2+} frame serves as a special second network to reinforce a covalently crosslinked PAAm network³³. The polymer chains and ionic crosslinks can form a special ‘zip’ structure, which is the key point of the reinforcing mechanism: the hysteresis caused by unzipping the crosslinks and the healing process by re-zipping. Mechanical tests

(Figure 11) show that the stretch ratio at break of unnotched samples can reach 21 and still up to 17 for notched samples, with a fracture energy over 3000 J/m².

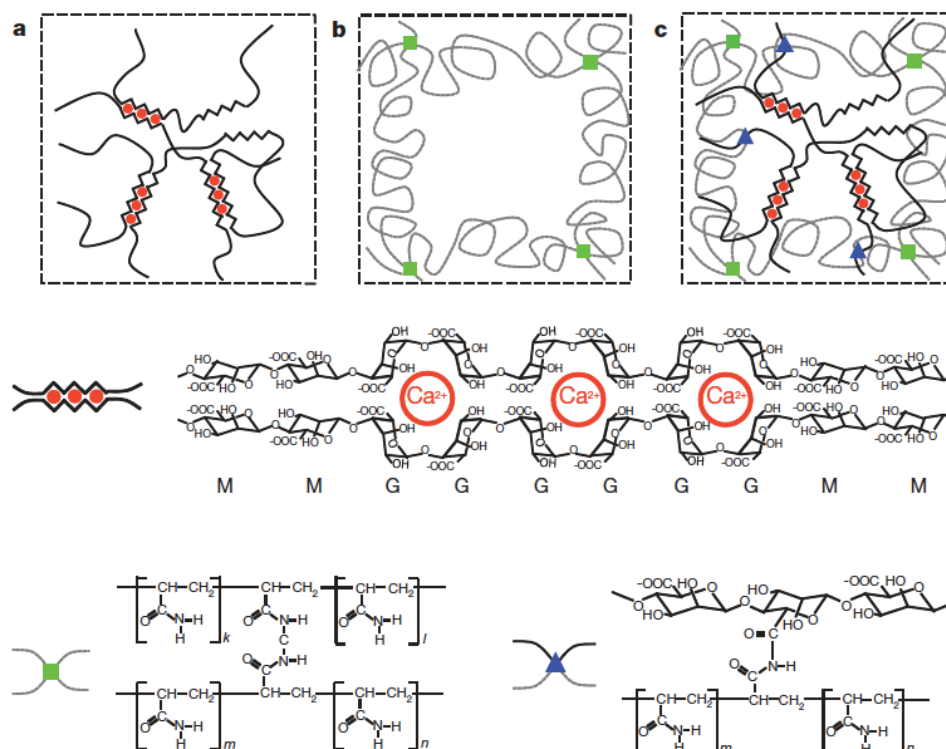


Figure 10. Schematics of three types of hydrogels: (a) in an alginate gel, the G blocks on different polymer chains form ionic crosslinks through Ca^{2+} ; (b) in a polyacrylamide gel, the polymer chains form covalent crosslinks through MBAA; (c) in an alginate-polyacrylamide hybrid gel, the two types of polymer networks are intertwined. ³³

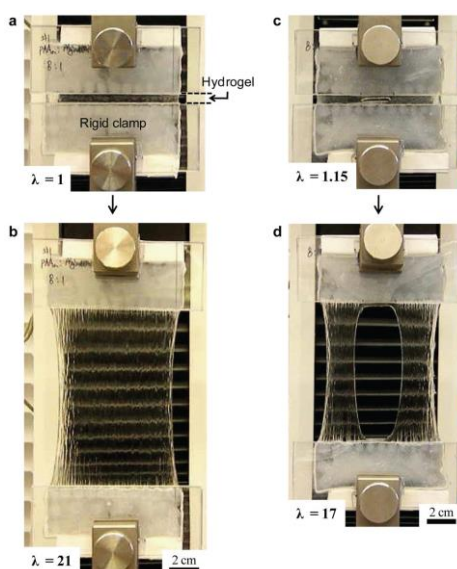


Figure 11. This type of hydrogels is highly stretchable and notch-insensitive. ³³

1.2.2.2 Double network hydrogels

In 2003, Gong *et al.* first reported double network hydrogels with high mechanical toughness³⁴. A double network hydrogel consists of a second polymer network implanted within a first network. As shown in Figure 14a, the first network is made of highly crosslinked polymer while the second one is loosely crosslinked. Those networks were synthesized via a two-step free radical polymerization. In the classical system studied by Gong and coworkers, the first network is made of poly (2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) by UV-initiated polymerization. This charged first network is then swollen in a solution containing a very small concentration of cross-linker and a high concentration of the second network polymer, acrylamide (AAm). This swollen gel is UV polymerized and swollen to equilibrium to obtain a double network hydrogel.

Compression tests of each of the single network hydrogels and of the double network hydrogels were performed and results are shown in **Figure 12**. The highly crosslinked PAMPS gel is very brittle while the loosely crosslinked PAAm gel can be highly deformed but with a low breaking stress. The double network on the other hand has a good performance on both deformation and stiffness. As seen in **Figure 12c**, the double network shows no visible damage after 90 % compression.

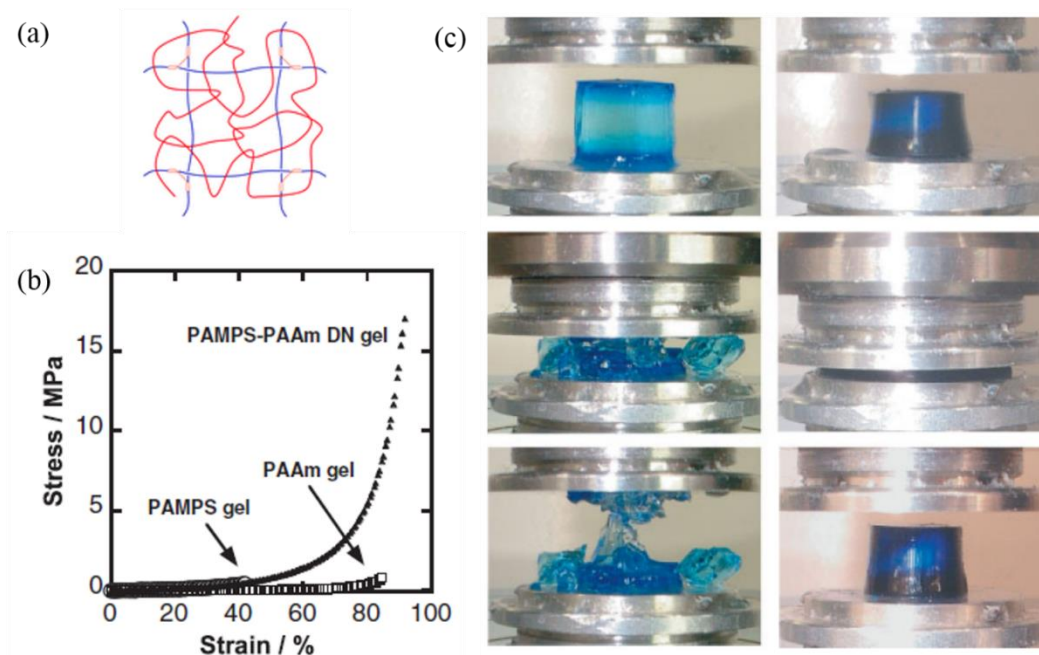


Figure 12. (a) Schematic representation of the structure of double network hydrogel;³⁵ (b) Uniaxial compression stress-strain curves for the single networks (PAMPS and PAAm) and the corresponding double network (PAMPS-PAAm); (c) the compression of PAMPS single network (left) and PAMPS-PAAm double network.³⁴

These double network hydrogels show excellent mechanical properties in terms of stiffness, extensibility and strength. The internal fracturing of the brittle network dissipates energy and prevents crack propagation. Extensive experimental and theoretical studies have been carried out to understand the mechanism behind the toughening.

Using material from Gong's group, Webber *et al.* found a large hysteresis between loading and unloading cycles, which was attributed to the irreversible breakage of covalent bonds in the first network. This was the first time this phenomenon was observed in hydrogels³⁶. This phenomenon can be compared to the Mullins effect in elastomers³⁷, where the large hysteresis can be explained by different dissipation mechanisms.

A necking phenomenon was observed while uniaxial tensile tests were carried out^{35,38}: as shown in **Figure 13a**, yielding occurs at point C, followed by a plateau region during the

necking propagation, until the un-necked region disappears at point E, then the uniform elongation continues. This phenomenon results in a much softer material, corresponding to the irreversible structure changes: the first network break into small clusters, which act as physical crosslinking points for the flexible second network³⁴ (**Figure 13b**).

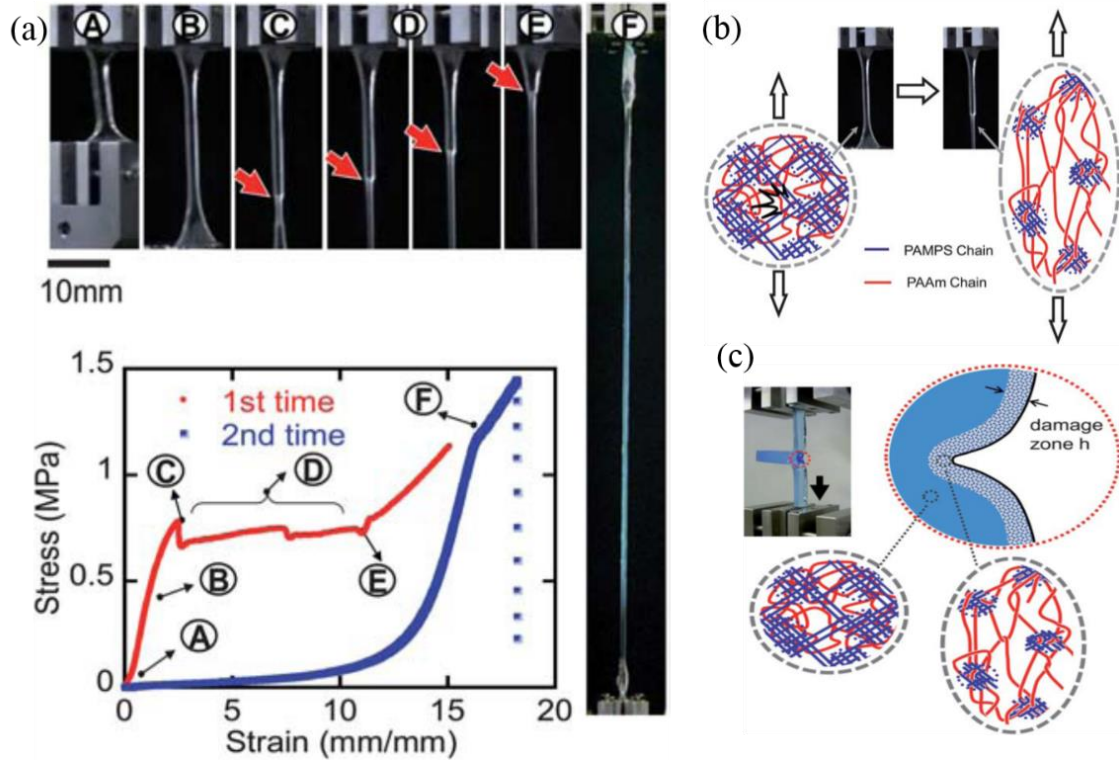


Figure 13. (a) Uniaxial stress-strain curve of gel, and pictures demonstrating the necking process; (b) Illustration of the network structure of the double crosslink gel before and after necking. (c) Illustration of local damage zone at the crack front.³⁴

Tearing tests were carried out to determine the fracture energy Γ .³⁹ The double crosslink hydrogels display a fracture energy from 10^2 to 10^3 J/m², which is up to 1000 times larger than the corresponding values for single network hydrogels. A sharp modulus decrease around the crack tip was observed, indicating that there is local yielding in the damage zone. As illustrated in **Figure 13c**, the presence of a local yielding, caused by the breakage of first network and the forming of a highly damaged and softer structure, followed by a hardening at the crack tip, is responsible for the high fracture energy of these double crosslink hydrogels³⁴.

1.2.2.3 Physical hydrogels composed of polyampholytes

The double network concept offers a new strategy to design tough hydrogels: intentionally introducing a mechanically fragile structure to create sacrificial bonds and dissipate energy³⁴. In this case, the breaking of the brittle network is irreversible, which may be undesirable in terms of recovery of the initial properties. A solution is to replace the covalent bonds with reversible non-covalent bonds^{33,40,41}.

Gong *et al.* developed physical hydrogels from polyampholytes, which have randomly dispersed cationic and anionic repeat groups with strong and weak bonds respectively⁴² (**Figure 14**). The strong bonds serve as permanent crosslinks while the weak bonds serve as reversible sacrificial bonds which enhance the fracture resistance and toughen the materials. These hydrogels have a relatively low water content (50 – 70 wt. %), and show very good mechanical properties: tensile fracture stress 0.1 – 2 MPa, fracture strain 150 – 1,500%, and tearing energy up to 4,000 J m⁻². This is a good example of mechanical reinforcement by a supramolecular structure.

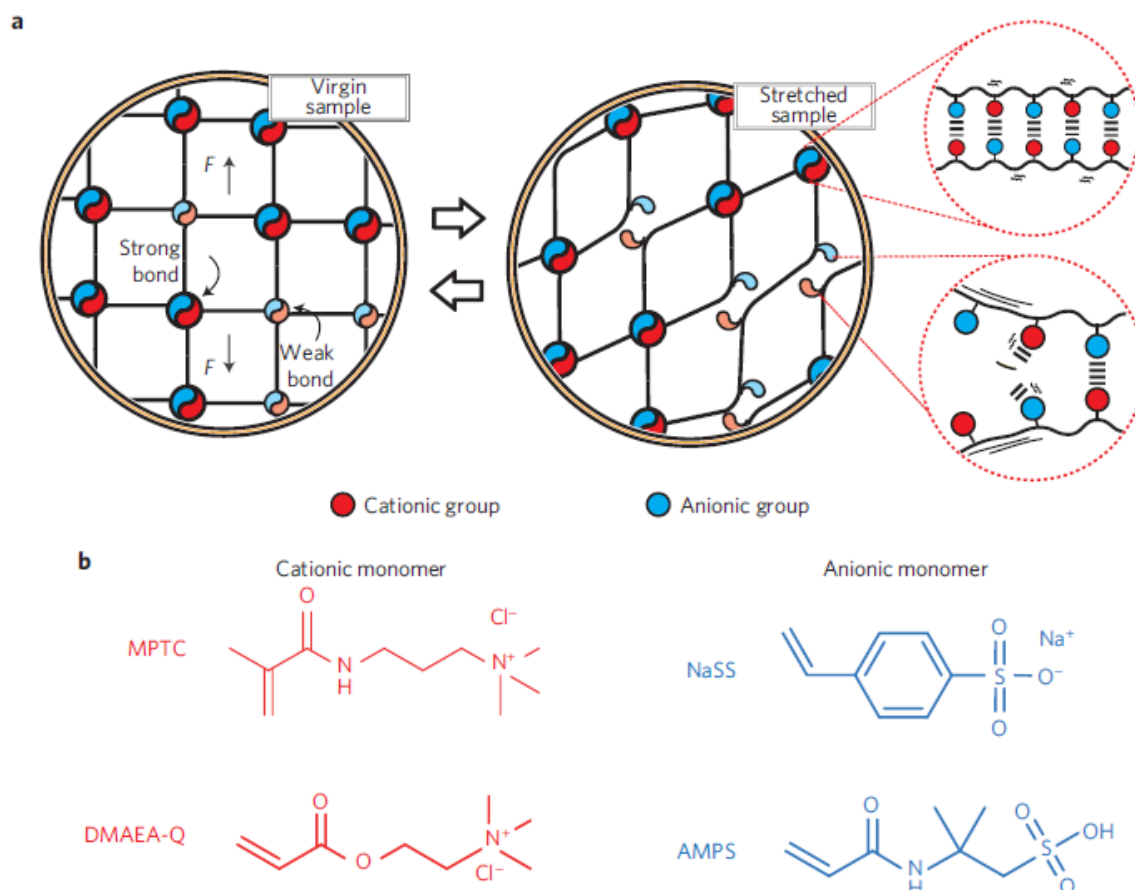


Figure 14. Schematics of physical hydrogels composed of polyampholytes. (a) An illustration of polyampholyte networks with ionic bonds of different strengths. (b) The chemical structures of monomers used in this work. Cationic monomers: MPTC, DMAEA-Q; anionic monomers: NaSS, AMPS.⁴²

1.2.2.4 Organic-inorganic hybrid hydrogels

Introducing inorganic components into organic networks is an efficient way to reinforce the mechanical properties of hydrogels. These inorganic components are often nanocomposites, so hybrid hydrogels can be considered as organic networks swollen in water with the presence of nanoparticles.

1.2.2.4.1 Hybrid hydrogels with clay platelets

Haraguchi *et al.* designed organic-inorganic hybrid hydrogels by introducing exfoliated clay platelets into a poly (N-isopropylacrylamide) (PNIPAm) network⁴³. As illustrated in **Figure**

15a, these dispersed platelets act as multi-functional cross-linkers, which results in enhanced mechanical properties: extremely high deformability (up to 1000 %, while only 30 % for the corresponding organic hydrogels) and a strong dependence of these properties on the concentration of clays, as shown in **Figure 15b**. A significant increase in fracture energy and instantaneous residual strain is also observed. (For NC gels, the clay content for the solution of 0.66 g clay / 100 g water is expressed as 1, the corresponding gel NC1)

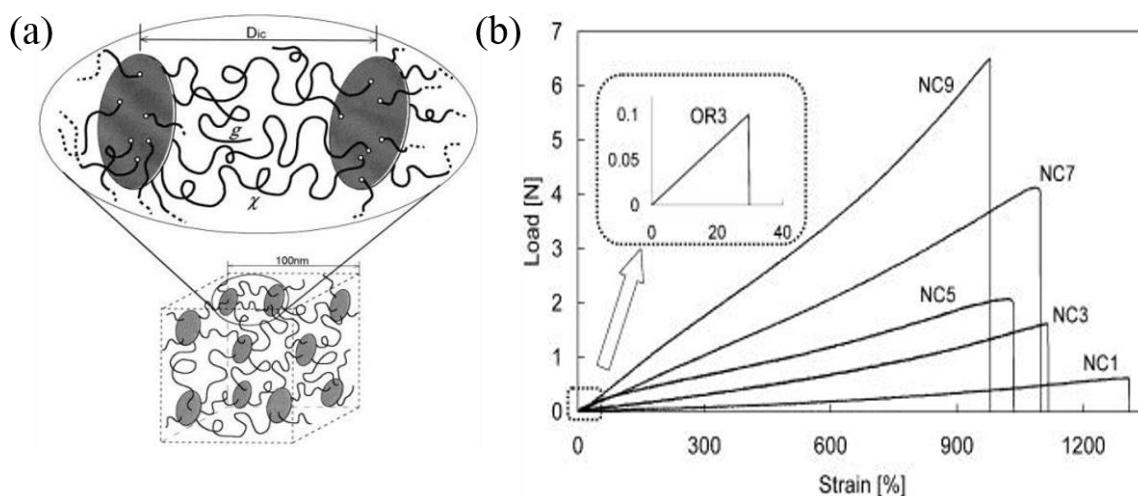


Figure 15. (a) Schematic representation of the structure of PNIPAm/clay hydrogels; (b) Stress-strain curves of PNIPAm/clay hydrogels and the corresponding organic hydrogels. ⁴³

The gelation mechanism was also studied by the same researchers. As illustrated in **Figure 16**, the formation of the hybrid hydrogels starts from the clay surface, where the initiator is concentrated, followed by the progressive formation of microgel clusters; the percolation of these clusters forms the gel⁴⁴.

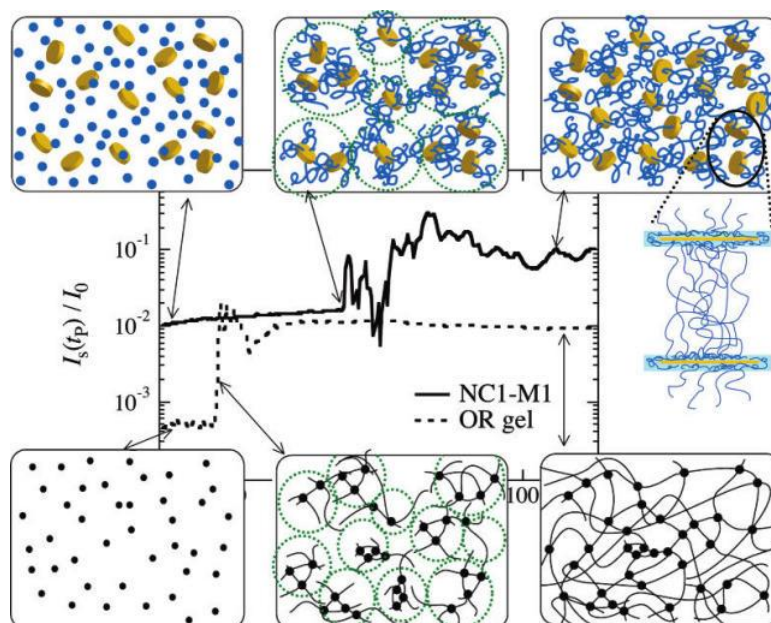


Figure 16. Schematic representation of the gelation mechanisms of PNIPAm/clay hydrogels (up) compared to that of organic hydrogels; Middle: normalized scattering intensity as a function of the polymerization time. ⁴⁴

This polymer/clay system has been intensely studied and the concept extended to other structures, such as the combination of the clay platelets with tetra-PEG hydrogels which resulted in a significant enhancement of the mechanical properties compared to the organic tetra-PEG system.

1.2.2.4.2 Hybrid hydrogels with silica nanoparticles

Following the concept of organic/inorganic hybrid hydrogels, silica nanoparticles were studied as the inorganic component due to their commercial availability, stability, isotropy and functionality. By adding an increasing amount of silica nanoparticles into the hybrid network, mechanical properties such as stiffness, strength and toughness can be dramatically enhanced⁴⁵. Marcellan *et al.* developed hybrid hydrogels by combining poly (N,N-dimethylacrylamide) covalent network and silica nanoparticles^{45,46}. As illustrated in **Figure 17a**, loosely crosslinked polymer chains are physically adsorbed onto the surface of nanoparticles with a certain sorption/desorption dynamics. The resulting hydrogels show strain rate dependent dissipative

and recovery processes (**Figure 17b**)⁴⁶, due to the reversible bonding between polymer chains and nanoparticle surface. As shown in Figure 18c, the tensile behavior was also studied, which demonstrates that the increase in silica particle content results in not only an increase in stiffness, but also in extensibility. These improved properties are attributed to the sacrificial silica/polymer interaction which avoid irreversible damage of the covalent bonds by dissipating energy.

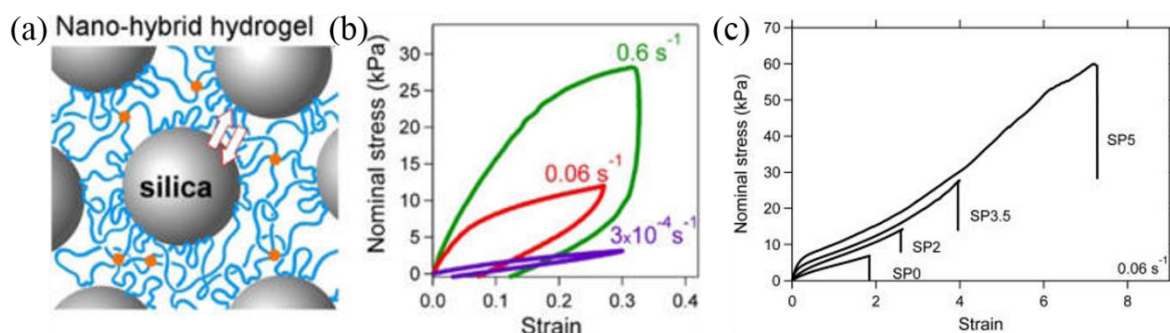


Figure 17. (a) Schematic representation of hybrid hydrogels combining covalent crosslinks (orange) and physical interactions sketched by polymer chains absorbed onto the surface of silica nanoparticles; (b) Strain rate effect on hysteresis of hybrid hydrogels; (c) Tensile stress-strain curves with for hydrogels with different silica contents. ⁴⁶

1.3 Objectives of this thesis

As described in this chapter, different approaches have been developed to reinforce the mechanical properties of hydrogels. One promising strategy relies on the introduction of two types of crosslink points in unison: (1) permanent (covalent) and (2) transient and reversible (non-covalent). During the deformation of the gel, transient bonds can break, dissipating a lot of elastic energy, preventing the irreversible rupture of the permanent bonds. Furthermore, the permanent bonds prevent the network from plastic flow.

For a more complete comprehension of the reinforcement mechanism, which can then be used as a feedback into the chemistry for achieving properties required for more demanding applications, it is necessary to realize a systematic study at multiple length scales. This study will range from the physicochemical molecular design to macroscopic mechanical characterization, bridged by structural and dynamical characterizations at the mesoscopic scales.

This manuscript will focus on two different systems: a PVA-borax system (following the work of K. Mayumi^{47–51}) and an AAm-imidazole-metal ion system. The similarities and differences between these two systems, on rheological, large strain deformation, and fracture behavior will be detailed in this manuscript.

The experimental part of this thesis is organized according to the following plan:

1. **Chapter 2** is dedicated to describing the rheological and mechanical properties of PVA-borax dual crosslink hydrogels, at various crosslinking density.
2. **Chapter 3** details the theory behind the breaking and re-forming kinetics of the transient bonds that occurs during large deformation behavior.

3. **Chapter 4** reports the synthesis and the mechanical properties of AAm-imidazole-metal ion dual crosslink hydrogels. The effect of different ions on rheological and large strain deformation behavior will be reported.
4. **Chapter 5** focuses on the fracture properties of these two systems. The fracture energy and crack velocities of these materials as a function of different strains rate will be reported.
5. **Chapter 6** will summarize these findings and address this research within the current state of the field, and give guidance for future systems wishing exploit permanent/transient bonds to form hydrogels with good mechanical properties.

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Chapter 2: PVA-borax dual crosslink gels

2.1 Introduction

2.1.1 General introduction of PVA-borax dual crosslink gels

PVA based dual crosslink gels have gained a lot of attention due to the well-defined characteristic time and well-defined simple chemical structure with only one type of physical crosslink between PVA chains. As schematically illustrated in **Figure 1**¹, PVA dual crosslink gels are chemically (permanently) crosslinked by glutaraldehyde (red) and physically (transiently) crosslinked by borate ions (green).

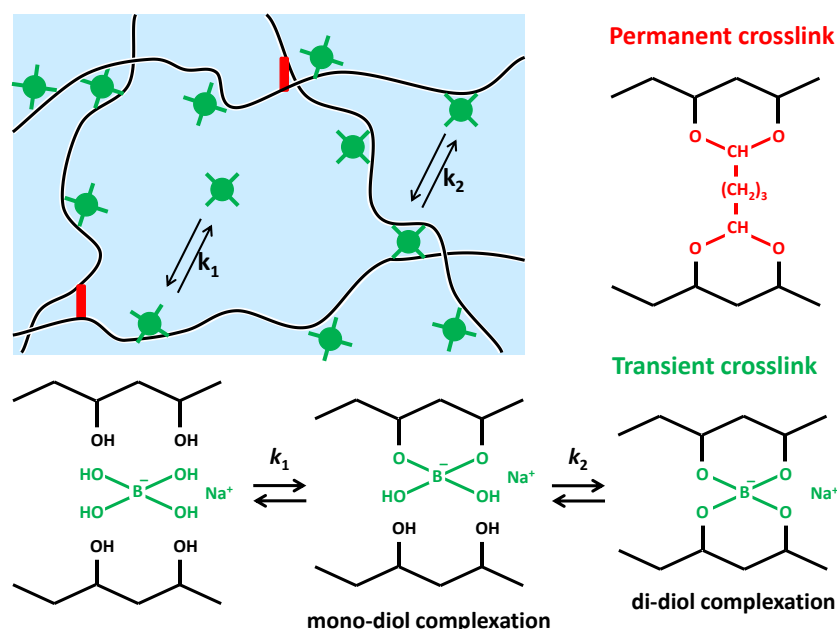


Figure 1. Schematic illustration of dual crosslink gels having permanent crosslinks by glutaraldehyde (red) and transient crosslinks by borate ion (green).¹

2.1.1 Properties of the corresponding chemical and physical PVA gels

2.1.1.1 PVA chemical gels

The swelling, structural, dynamic, and rheological properties of the corresponding chemical²⁻⁴ and physical⁵⁻⁹ PVA gels have been intensively studied. Glutaraldehyde is a common

crosslinking agent for PVA due to the high activity of the aldehyde groups. **Figure 2** shows the expected chemical crosslinking reaction between the PVA chains and GA¹⁰. This reaction results in polymer with different content of ‘acetal bridges’, which affects the chemical properties, solubility and crystallizability¹¹.

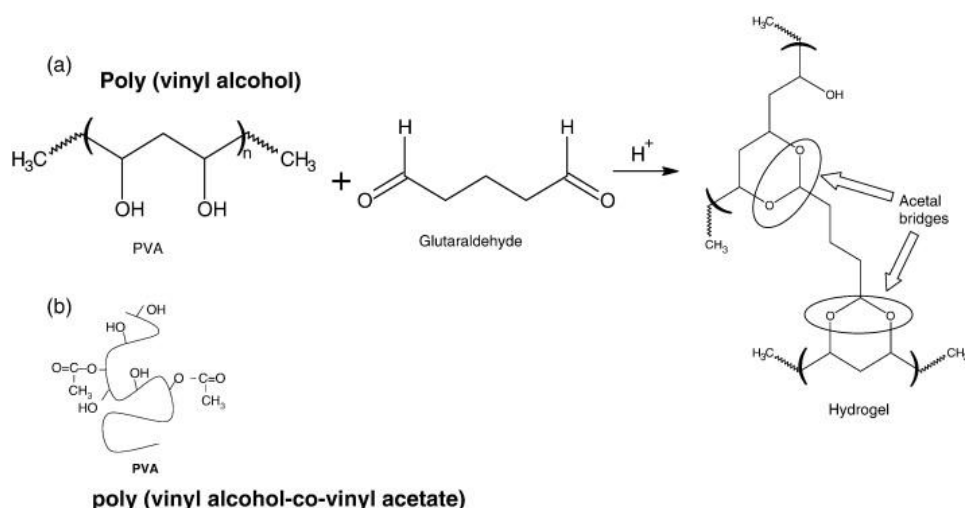


Figure 2. Scheme of the chemical reaction of PVA polymer with glutaraldehyde catalyzed by acid.¹⁰

2.1.1.2 PVA physical gels

In water, sodium borate (borax) dissociates completely into boric $B(OH)_3$ and monoborate $B(OH)_4^-$ molecules¹³. These two species exist in an acid/base equilibrium, $B(OH)_4^-$ molecules can be used to crosslink PVA chains. As shown in the ‘transient network’ part of **Figure 1**, The PVA – borate crosslinking mechanism is divided into so-called mono-diol complexation (only one borate ion is attached to a polymer chain) and di-diol complexation^{14,15}. The study of Lin et al. shows that the equilibrium constant K_1 decreases with the increasing borax concentration, it also depends on the electrostatic charge repulsion and the shielding of excess free ions¹⁶.

2.1.2 Swelling properties of PVA –borax dual crosslink gels

By incorporating physical crosslinks by the diffusion of borate ions into a previously prepared chemical gel, physical crosslinks can be introduced and their density can be controlled, up to a high value, by varying the concentration of the borate solution in which the chemical gel is immersed. Back in 1994, Shibayama et al. first studied the swelling/shrinking behaviors of the dual crosslink gels and compared with the viscosity of the physical gels^{17,18}. As demonstrated in **Figure 3**, with the increasing of the borate ion concentration, the equilibrium swelling ratio first decreased from 1.0 to 0.724, then increased to 1.122. This phenomenon was explained by the formation of heterogeneity and microsineresis: in the swelling mode, borate ions accelerate the cooperative diffusion of the polymer network; while in the shrinking mode, the presence of borate ions reduce the miscibility of PVA in water.

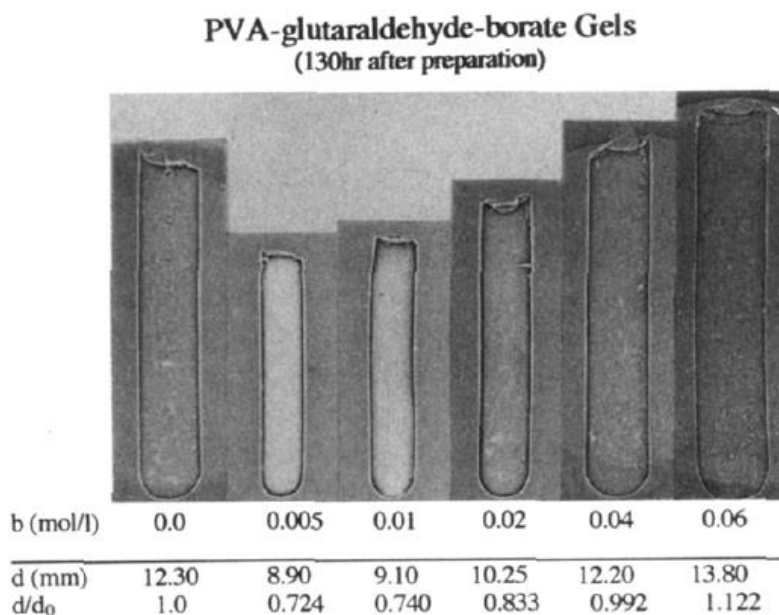


Figure 3. Borate concentration (b in mol/L) dependence of the diameter (d in mm) and the volume change of the gels. ¹⁷

2.1.3 Viscoelastic properties of PVA –borax dual crosslink gels

Contrary to certain associating polymers having a small numbers of functional groups covalently fixed to the backbone chains and capable of association, PVA can accept borate ions practically by any hydroxyl groups, thus the density of associations can be large. Some unique rheological features of the PVA dual crosslink gel as model system have been experimentally demonstrated¹. In **Figure 4(a, b)**, two (fast and intermediate) different relaxation modes were found for dual crosslink gels, while there were three (fast, intermediate and slow) for physical gels and PVA solution, only one (fast) for corresponding chemical gels.

Figure 4c shows G' and G'' , of the chemical, physical and dual crosslinked PVA gels as a function of the angular frequency measured by classical macrorheology and DWS-based microrheology. The dual crosslink gel has a maximum G'' , its relaxation mode can be characterized by associative Rouse mode: $G' = G'' \sim \omega^{0.5}$, while $G'' \sim \omega^1$ (Maxwellian behavior) for physical gel. The contribution of physical crosslinks was examined by subtracting the values of moduli of the chemical gels G_C from those of the dual crosslink gels G_D (**Figure 4d**): the chemical and physical crosslinks contribute to the viscoelasticity independently and additively, and the moduli of the dual crosslink gels can be decomposed into those stemming from the physical bonds and those due to the chemical bonds, identical to the corresponding chemical network.

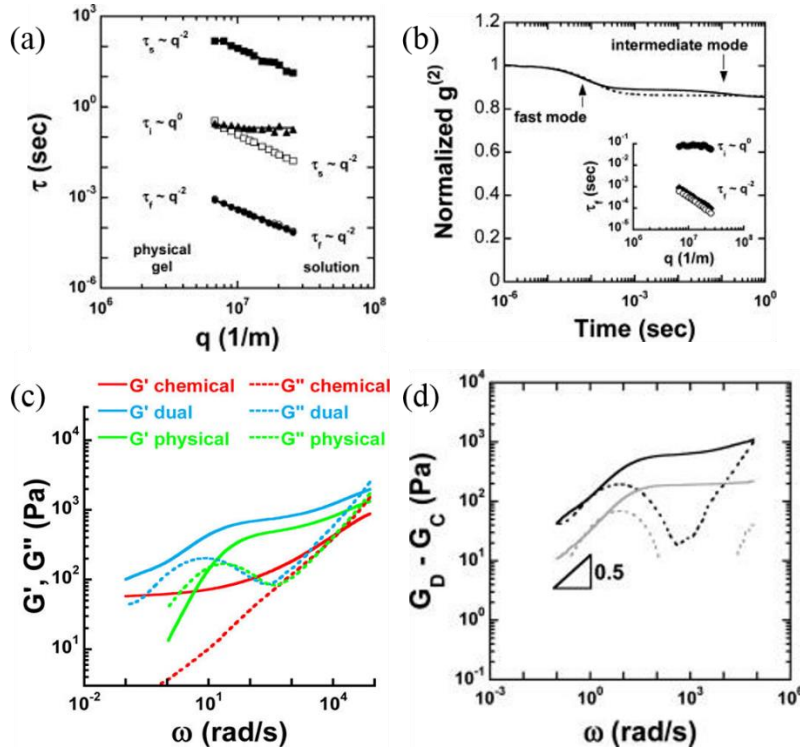
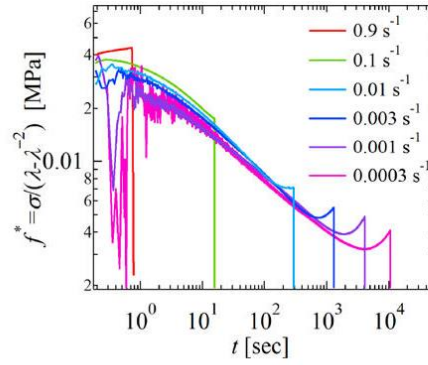


Figure 4. (a) Three characteristic times of the PVA solution and physical PVA gel as a function of diffusion vector q . (b) Autocorrelation function $g^{(2)}$ of the PVA chemical gel and dual crosslink gel measured by DLS. Inset: s dependence of the characteristic times. (c) G' and G'' of chemical, physical and dual crosslink gels as a function of angular frequency. (d) $G'_D - G'_C$ and $G''_D - G''_C$ as a function of angular frequency for the dual crosslink gel measured by DWS microrheology.¹

2.1.4 Large strain mechanical properties of PVA –borax dual crosslink gels

Following this study, the large strain mechanical properties were reported¹⁹. The PVA dual crosslink gels are considered as tough hydrogels having time-dependent elasticity and high extensibility. A strain rate-dependent stress under uniaxial elongation can be then separated into a time-dependent term and a strain-dependent term expressed as a neo-Hookean model (separability) (**Figure 5**). A constitutive model combining large strain elasticity and time-dependent sticker dynamics was developed to describe these hydrogels^{20–22}. A simplified description of the dynamics of the transient physical crosslinks with breaking and healing times determined by fitting continuous loading and relaxation tests, was able to predict very well loading/unloading cycles carried out at different stretch rates.



$$\sigma = \left(\lambda - \lambda^{-2} \right) \cdot f^* (t)$$

strain dependent
time dependent
(rubber elasticity)
(shear modulus)

Figure 5. Time dependence of the shear modulus f^* under uniaxial deformation at various strain rates.¹⁹

In this chapter, we rheologically studied a series of PVA dual crosslink hydrogels at various crosslinking densities, in comparison with the corresponding chemical gels. The effects of the chemical and physical crosslinking densities on the dynamics of the network and on the additivity of the moduli were extensively investigated in the linear domain. We also highlighted the other characteristics of the dual crosslink gels, extensibility and separability.

2.2 Experimental section

2.2.1 Sample Preparation

Poly(vinyl alcohol), PVA (molecular weight: 89,000–98,000, degree of hydrolyzation: 99 %, purchased from Aldrich) was dissolved in deionized water at 95 °C. PVA chemical gels were prepared by cross-linking PVA in aqueous solutions with glutaraldehyde, GA, (purchased from Aldrich) at pH =1.9. The PVA concentration was kept constant at 12 wt% for all the gels tested. The GA concentration in the feed varied from 5.5 to 16.5 mM, corresponding to 0.2 – 0.6 mol% of the monomer units of PVA. After the overnight crosslinking reaction, the obtained PVA chemical gels were used for measurements as prepared. PVA dual crosslink gels were prepared by incorporating borate ions, physical crosslinkers, to the chemical gels. For this process first the chemical gels were washed with a large amount of water to a neutral pH. The swollen chemical gels were then immersed in aqueous solutions of sodium tetraborate decahydrate (borax, Aldrich) and NaCl (Fluka) for 3 days. The NaCl concentrations used to prepare the different chemical and physical crosslinking ratios are listed in Table I. The volume of the borax/NaCl solution was 20 times that of the swollen chemical gels. The borax concentration in the solution varied from 1 to 50 mM. If we assume that all the borate ions in the solution were incorporated into the PVA gels, these concentrations correspond to a molar ratio of borate ions to PVA monomer units of 1.5 – 73 mol%. For comparison, physical gels were also prepared by mixing PVA, borax and water ($C_{\text{PVA}} = 4, 6$ and 12 wt%, $C_{\text{borax}} = 5 - 100$ mM).

Table I. NaCl concentrations (in mol/L) used to prepare the gels with different chemical and physical crosslinking ratios.

C_{borax} (mM)	1	3	5	10	20	50
C_{NaCl} (M)						
for GA 0.2 mol%	90	100	120	170	260	460
C_{NaCl} (M)						
for GA 0.6 mol%	60	80	110	160	260	450

2.2.2 Linear viscoelastic properties

In order to characterize the linear viscoelastic properties of the dual crosslink gels, small strain oscillatory shear measurements were performed on a parallel plates geometry having roughened surfaces (25mm in diameter) with the ARES LS1 rheometer (TA instruments). The sample thickness was 1.5 mm. Frequency sweep tests with a dynamic range varying from 0.1 to 100 rad/s were carried out at 25 °C within the linear viscoelasticity regime (0.8 – 1% strain). For comparison the same tests were performed for physical gels with a cone-plate geometry (diameter of 35 mm, angle of 2°).

2.2.3 Uniaxial tensile tests

The large deformation behavior of the gels was studied by uniaxial tensile and loading – unloading tests on an Instron 5565 tensile tester with a 10 N load cell. Samples were rectangular in shape with 5 mm width, 1.5 mm thickness, and 20 mm length (length between clamps). We kept the samples in paraffin oil during all the tests to prevent them from drying.

2.3 Results and Discussion

2.3.1 Gel swelling during preparation

First of all, let us comment on the swelling of the dual crosslink gels and the borax and NaCl concentration dependences. As described in the experimental section, and as schematically shown in **Figure 6a**, the dual crosslink gels were prepared in three steps: (1) preparation of chemical gels, (2) washing of the chemical gels and (3) incorporation of the physical crosslinks. The simple chemical gels (with no physical crosslinks) were on the other hand tested as prepared. Therefore in order to compare the dual crosslink gels and corresponding chemical gels, the polymer concentration in the gel was kept constant at the concentration of the preparation of the chemical gels ($C_{\text{PVA}} = 12\%$). The chemical crosslinking reaction is induced in acidic conditions, while at this acidic condition the physical crosslinking by borate ion is hindered since the borate ion is converted into non-crosslinking boric acid. Therefore the acid is washed out by immersing the chemical gel in a large quantity of water. Note that the chemical gels swell to equilibrium during washing process. The change in swelling is checked by weighing the gel samples. The weight ratio of the chemical gel at equilibrium swelling to the same gel as prepared is $w_1/w_0 = 2.5$ for $C_{\text{GA}} = 0.2\text{ mol\%}$ and 1.2 for $0.6\text{ mol\%}$.

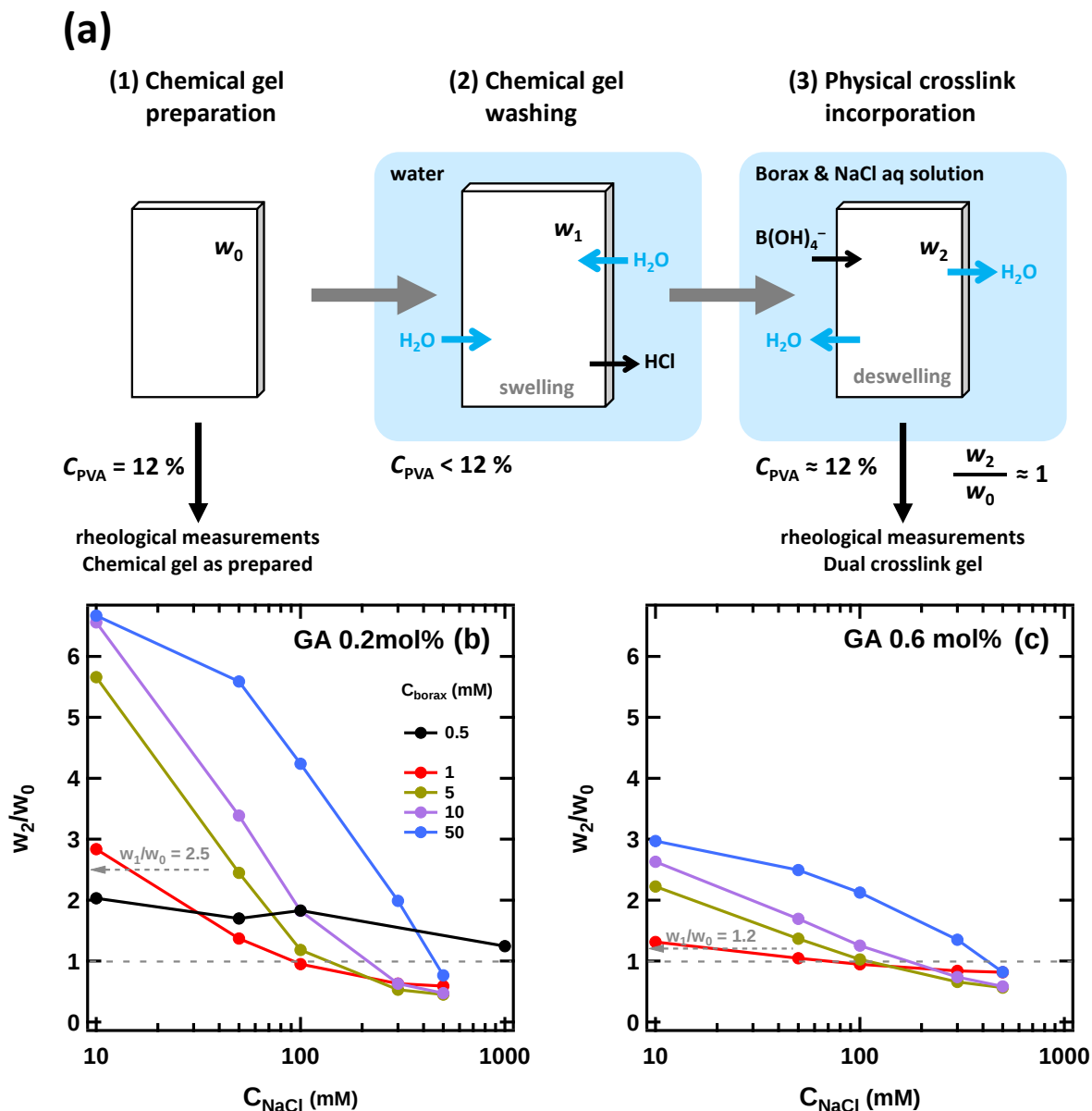


Figure 6. (a): Schematic illustrations of chemical and dual crosslink gels preparation. (b) and (c): Swelling ratio of the dual crosslink gels at different borax concentrations as a function of NaCl concentration. w_0 : weight of the chemical gel at preparation; w_1 : weight of the chemical gel after washing; w_2 : weight of the dual crosslink gel after complexation with borax in the presence of NaCl. Chemical crosslinking ratio: (b) $C_{GA} = 0.2$ mol%, (c) $C_{GA} = 0.6$ mol%.

The physical crosslinker borate ions are incorporated into the washed chemical gel by diffusion.

The borate ions complexed with PVA chemical gel have two effects on the gel swelling¹⁷. (a)

The borate ions crosslink the PVA chains thus the swelling ratio decreases. (b) They also

introduce negative charges to the PVA chains and due to the osmotic pressure of the counterions

(Na^+), the swelling ratio increases. At the chemical and physical crosslinking ratios studied in this work, the swelling by the osmotic pressure is always dominant. Therefore, in order to keep the polymer concentration at $C_{\text{PVA}} = 12\%$, the osmotic pressure is varied by the addition of NaCl. **Figure 6b** and **6c** shows the variation of the weight ratio w_2/w_0 of the dual crosslink gel swollen in borax/NaCl solution to the chemical gel as prepared as a function of the NaCl concentration. The value of C_{NaCl} at which w_2/w_0 reaches 1 is used for the following rheological tests. It should be noted that at $C_{\text{borax}} < 1\text{ mM}$ w_2/w_0 does not reach 1. As example the result for 0.5 mM was shown in **Figure 6b**. One can observe that (1) even at a low NaCl concentration, the value of w_2/w_0 is lower than w_1/w_0 , contrary to the higher borax concentration, and (2) the NaCl concentration dependence is weak. This result indicates that at $C_{\text{borax}} = 0.5\text{ mM}$, the effect of charges is weak and the physical crosslinking effect is dominating. Shibayama et al. previously discussed the swelling properties of the PVA dual crosslink gels¹⁷. They show that with the increase in the physical crosslinker concentration, first the swelling ratio decreases then it increases. We do not see a particular effect of salt on the neutral PVA chemical gels. The swelling ratio varies $\pm 8\%$ in a NaCl concentration range of 0.01 – 1 M (data not shown). At NaCl concentrations higher than 1 M the solubility of PVA can be influenced by the salt and the chemical gel can be turbid. We confirmed experimentally that the chemical gels containing NaCl show the same linear rheological properties (data not shown).

2.3.2 Additivity

In order to study the effects of the chemical cross-linking density at a fixed concentration of physical crosslinks, we studied the linear (small strain) viscoelastic properties of the hydrogels with different concentrations of glutaraldehyde C_{GA} (0.2, 0.3, 0.4 and 0.6 mol%) by oscillatory shear measurements. **Figure 7** shows the frequency dependence of the elastic and viscous moduli, G' and G'' , of the chemical and dual crosslink gels ($C_{\text{borax}} = 1\text{ mM}$), with $C_{\text{GA}} = 0.2$ and 0.6 mol%. For the chemical gels (as prepared, $C_{\text{PVA}} = 12\text{ wt\%}$), we found that G' was

independent of frequency, and G'' was too low to be accurately measured (< 0.1 kPa, data not shown in the figure). The chemical gels exhibit a typical elastic solid behavior. The value of the modulus at the elastic plateau of $C_{GA} = 0.2$ mol% was measured as 2 kPa, and that of 0.6 mol% was 8 kPa. The elastic moduli of dual crosslink gels were higher than those of chemical gels for all the frequencies tested. We found an elastic plateau at high frequency (10 – 100 rad/s) and G' decreased at low frequency, approaching the value of G' of the corresponding chemical gels. G'' showed a large peak around 1 rad/s, correlated with the decrease in G' . This result indicates that the physical crosslinks by PVA-borate ion interactions induce a large dissipation at this frequency. The chemical crosslinking density does not seem to strongly influence the moduli of the dual crosslink gels except in the low frequency range.

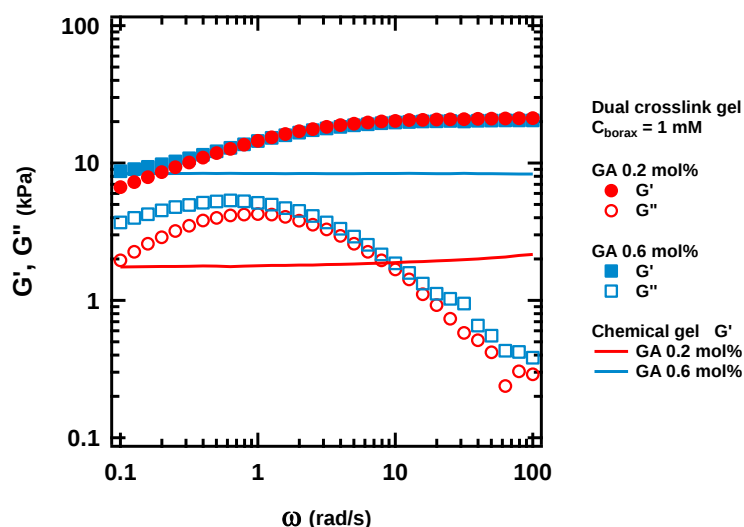


Figure 7. $G'(\omega)$ and $G''(\omega)$ of the PVA dual crosslink gels and chemical gels with different concentrations of GA.

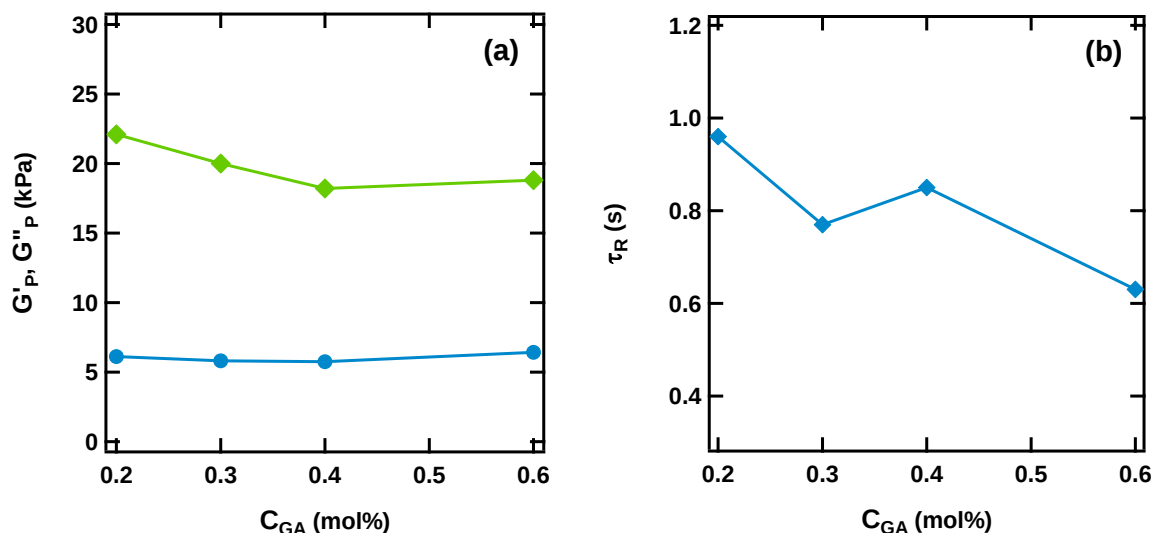


Figure 8. (a) G'_P (green), G''_P (blue) and (b) relaxation time τ_R of dual crosslink gels as a function of GA concentration C_{GA} for $C_{borax} = 1$ mM. G'_P were evaluated at $\omega = 100$ rad/s, while G''_P were evaluated at the peak frequency of G''_D .

In the previous papers^{1,19}, we showed that the chemical and physical crosslinks contribute independently to the moduli of the dual crosslink gels, thus the following additivity holds: $G'_D = G'_C + G'_P$ and $G''_D = G''_C + G''_P$, where the respective subscripts D, C and P refer to dual crosslink gels, chemical gels and contribution of the physical crosslinks to the dual gels^{1,19}. The contribution of the physical crosslinks to the modulus of dual crosslink gels cannot be directly measured but can be estimated by subtracting the modulus of the pure chemical gels from those of dual crosslink gel. This is reasonable since the two gels have the same polymer concentration. In **Figure 8a**, G'_P and G''_P are plotted as a function of the concentration of the chemical crosslinker. The values of both G'_P and G''_P at $C_{borax} = 1$ mM, changed very little with varying C_{GA} . These results indicate that the chemical crosslinking density does not influence G'_P , and the additivity holds at the studied conditions. The characteristic relaxation time τ_R deduced from the peak of G''_D is shown in **Figure 8b**. It decreases from 1 s to 0.6 s with increasing concentration of chemical crosslinker and this difference will be discussed later in the paper.

In order to study the effect of the density of physical cross-links on the additivity, we investigated the linear viscoelastic properties of dual crosslink gels with different borax concentrations ($C_{\text{borax}} = 1, 3, 5, 10, 20$ and 50 mM) at a fixed C_{GA} . **Figure 9** shows the frequency dependence of G' and G'' for dual crosslink gels and for the corresponding chemical gel, for $C_{\text{GA}} = 0.2$ (**Figure 9a**) and $C_{\text{GA}} = 0.6$ mol% (**Figure 9b**). For both concentrations of GA, the curves show the same trend. For all the borax concentrations tested, G'_D has a high-frequency plateau and a decrease toward the chemical gel elastic plateau at low frequency. We noticed that the high frequency elastic plateau as well as the value of G''_D at the peak increased with borax concentration, due to the increase in the physical cross-linking density. The frequency at the G''_D peak increased also with borax concentration.

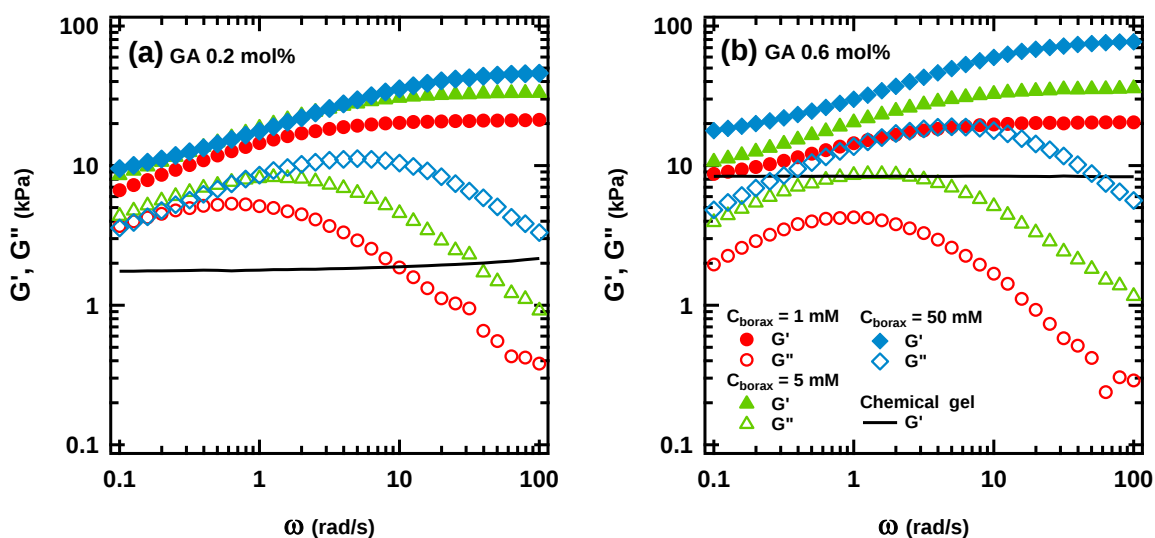


Figure 9. Angular frequency dependence of $G'(\omega)$ and $G''(\omega)$ of the PVA dual crosslink gels prepared at different borax concentrations and compared with the chemical gels. (a) $C_{\text{GA}} = 0.2$ mol%, (b) $C_{\text{GA}} = 0.6$ mol%.

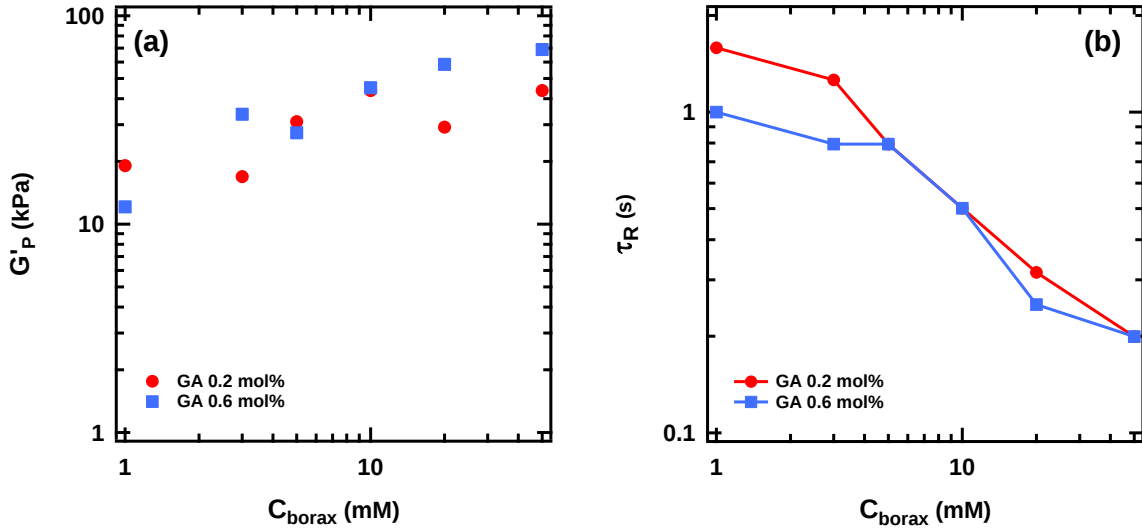


Figure 10. (a) Elastic modulus due to physical crosslinks G'_P and (b) relaxation time τ_R of dual crosslink gels as a function of the borax concentration.

In **Figure 10a**, the borax concentration dependence of the contribution G'_P of the physical crosslinking to the elastic modulus, and of the relaxation time τ_R are shown. The value of G'_P increases with borax concentration showing a weaker C_{borax} dependence than linear relation. G'_P on the other hand does not show a dependence on chemical crosslinker concentration since the results for $C_{GA} = 0.2$ and 0.6 mol% were found practically the same. If we assume that all the borate ions in the swelling solution are incorporated in the PVA gel, the molar ratio of Borax to $-OH$ would be 15 mol% for a concentration of 10 mM in the preparation solution. Since one borate ion molecule can interact with four hydroxyl groups, this assumption would lead to a near saturation of $-OH$ groups and amounts of borax in excess of 10 mM in the solution would not lead to additional crosslinking in the gel. We did not however measure the binding constant of this system due to the experimental difficulties.

We made another rough estimate of the effective crosslinking density from the value of elastic moduli. The plateau elastic modulus is proportional to the molar density of the effective crosslinks, v_{eff} (mol/m³), with $G' = 0.5v_{eff} RT = kT \cdot \xi^{-3}$ (the prefactor 0.5 is for tetrafunctional

crosslinks), where ξ (m) is the average distance between neighboring crosslinks. From the value of the elastic modulus G'_c of the chemical gels, we found $\xi = 13$ nm ($v_{\text{eff}} = 1.4 \text{ mol/m}^3 = 0.05 \text{ mol\%}$ of the OH group concentration $2.7 \times 10^3 \text{ mol/m}^3$) for $C_{GA} = 0.2 \text{ mol\%}$, and $\xi = 7.9$ nm and $v_{\text{eff}} = 6.8 \text{ mol/m}^3 = 0.25 \text{ mol\%}$) for $C_{GA} = 0.6 \text{ mol\%}$. From the values of G'_{DE} , $v_{\text{eff}} = 0.6 - 1.4 \text{ mol\%}$ for $C_{GA} = 0.2 \text{ mol\%}$, and $v_{\text{eff}} = 0.6 - 2.3 \text{ mol\%}$ for $C_{GA} = 0.6 \text{ mol\%}$. For $0.2 \text{ mol\%}$, we can vary the density of physical crosslinks from 11 to 26 times the density of chemical crosslinks, while for $0.6 \text{ mol\%}$, we can introduce between 2.4 and 9.2 times as many physical crosslinks than chemical crosslinks. This means that for $0.2 \text{ mol\%}$ the physical crosslinking density is much higher than that of the chemical crosslinking for all the borax concentrations tested, while for $0.6 \text{ mol\%}$ the physical crosslinking density can be nearly comparable to the chemical crosslinking density at low borax concentrations.

It should be noted that the estimated values of v_{eff} were much lower than those estimated from the total amounts of borate ions in the system. In this system the borate ion can thermodynamically take four different states: (1) unbound and diffusing freely in the gel (or in the outer solution of preparation), (2) bound but not crosslinking by monodiol complex, (3) crosslinking inefficiently by didiol intrachain complex (loop formation etc) and (4) crosslinking effectively (didiol interchain complex). Our result suggests that the proportion of intrachain complex is much higher than interchain complex. Huang et al. measured the amount of didiol complex in a PVA – borax physical gel at low borax concentration by ^{11}B NMR, and found that 35 % of boron formed didiol complex²³. Though the concentration ranges are different, we can expect a high proportion of ineffective association in our systems.

As shown in **Figure 10b**, the relaxation time τ_R decreases with borax concentration except in the low borax concentration range where the relaxation time showed a very weak borax concentration dependence, especially for $C_{GA} = 0.6 \text{ mol\%}$. In this concentration range, the

number of chemical and physical crosslinkers per chain are comparable, thus presumably the effect of the physical crosslinker concentration is weak. This may explain the fact that only in this low Borax concentration range a dependence on the chemical crosslinking ratio was observed. As shown in **Figure 8b**, an increase in physical crosslinking density results in a decrease of the relaxation time. The value of τ_R varied by about 1 decade in the investigated borax concentration range, and changing the crosslinking density is not an efficient way to control the dynamics of the dual crosslink gels. This result may appear surprising since in physical gels an increase in sticker groups always leads to an increase in the terminal relaxation time. However for dual crosslinks gels the terminal relaxation time does not exist (it is solid) and the relation between macroscopic relaxation time and molecular structure may be more complex.

The relaxation process in the dual crosslink gels was further characterized by comparing it with the same relaxation in the corresponding physical gels. In **Figure 11** we plotted the relaxation time determined from the peak of G'' for physical gels ($C_{PVA} = 12, 6, 4\%$). The values for the dual crosslink gels in **Figure 10b** are also plotted for comparison. The borax concentration is converted into the molar ratio of the borate ion to the OH group of PVA in the system, R_c . The value of the relaxation time τ_R for the physical gels increased with R_c (R_c less than about 0.03), reaching the maximum about $\tau_R = 0.7$ then decreased to level off about $\tau_R = 0.2$. These values are qualitatively close to those of the dual crosslink gels.

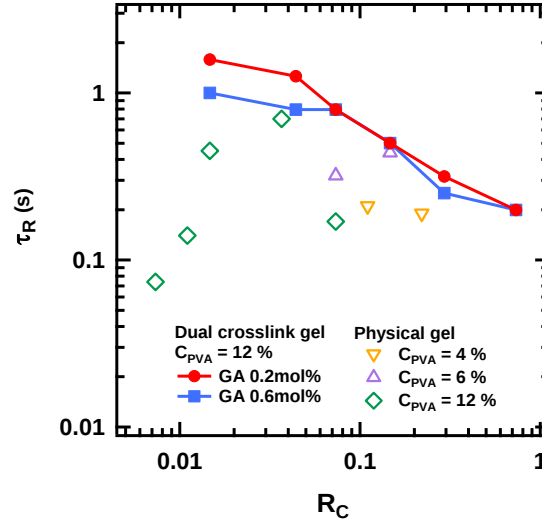


Figure 11. Characteristic time τ_R plotted against the physical crosslinking ratio R_C for physical gels and dual crosslink gels.

The increasing values of τ_R at low R_C are interpreted as follows. First we consider the dynamics of an elastic chain between two physical crosslinks (one of the two can be a chemical crosslink for the case of the dual crosslink gels). When a physical bond breaks with a breaking time (characteristic time for *one* closed physical crosslink to break) t_{break} , the elastic chain starts to relax to its equilibrium state. The characteristic time of this process is the Rouse relaxation time of the chain, τ_{Rouse} . Since $\tau_{\text{Rouse}} < t_{\text{break}}$, we rheologically observe the relaxation time $\tau_R \sim t_{\text{break}}$. This picture is true when the healing time (characteristic time for *one* open physical crosslink to close), t_{heal} , is also longer than τ_{Rouse} : reassociation does not occur during the relaxation thus the chain fully relaxes. When $\tau_{\text{Rouse}} > t_{\text{heal}}$, the open physical bonds can reassociate before full relaxation of the chain, thus the rheological relaxation rate slows down ($\tau_R > t_{\text{break}}$). To summarize, the following two cases are possible:

(1) $\tau_R \sim t_{\text{break}}$ (if $\tau_{\text{Rouse}} < t_{\text{heal}}$),

(2) $\tau_R > t_{\text{break}}$ (if $\tau_{\text{Rouse}} > t_{\text{heal}}$).

The increase in the density of physical crosslinks influences both the Rouse relaxation time τ_{Rouse} and the healing time t_{heal} . With increasing R_c , the chain length between two crosslinks and its Rouse relaxation time decreases, favoring the case (1). It should be noted that contrary to t_{break} , t_{heal} depends on the polymer concentration since an available binding site is necessary for association. With increase in R_c , there are less available binding sites on the chain and t_{heal} increases. Therefore, at high R_c , we also expect the case (1), $\tau_{\text{Rouse}} < t_{\text{heal}}$ and $\tau_R \sim t_{\text{break}}$. On the other hand, with decreasing R_c , τ_{Rouse} increases and t_{heal} decreases so that the case (2) can be favored. From the results shown in **Figure 11**, we suppose that t_{break} is about 0.2 s, corresponding to the lowest value of τ_R at high R_c . With decrease in R_c , τ_{Rouse} can be larger than t_{heal} , and τ_R increases.

How does τ_R vary with R_c when $\tau_{\text{Rouse}} > t_{\text{heal}}$? Indei and Takimoto derived with their model²⁴ $\tau_R \sim t_{\text{break}}(\tau_{\text{Rouse}}/t_{\text{heal}})^{0.5}$. If we take the Kuhn length as a characteristic length, τ_{Rouse} scales as $\tau_{\text{Rouse}} = \tau_0 \cdot N_K^2$, where τ_0 is the monomer relaxation time $\tau_0 = \eta_s \cdot a^3/kT$, (η_s is the solvent viscosity, a is the monomer characteristic length, here the Kuhn length $b_K = 0.62 \text{ nm}$ ²⁵ is chosen). The dependence of t_{heal} on R_c or N_K is complex: t_{heal} depends not only on the available binding site concentration which is supposed to be proportional to $1 - R_c$, but also on the concentration of physical bonds (mono-diol complex in **Figure 1**) which are not crosslinking but ready to reassociate. Indei and Takimoto did not discuss the concentration dependence in their single chain model²⁴. For our dual crosslink gels of various crosslinking densities, N_K was estimated from the average distance between the two crosslinks ξ , as $\xi = b_K \cdot N_K^{1/2}$, with a reference value of Kuhn length (ξ was estimated from the values of G'_D as discussed above). In **Figure 12** τ_R was plotted against N_K . Since the data are dispersed mainly due to the low reproducibility of the physical crosslinker concentration, quantitative discussion is difficult, still, one can qualitatively observe an increase in the relaxation time with increase in N_K . No clear

dependence on the chemical crosslinking density was found. From the relation $\tau_{\text{Rouse}}^{0.5} \sim N_K$, we expect $\tau_R \sim N_K$, while we found a stronger N_K dependence ($\tau_R \sim N_K^{1.7}$), suggesting the presence of N_K dependence of t_{heal} . Previously we reported a constitutive model which can describe the uniaxial stress at different types of deformation with several parameters including healing time. Detailed analysis of the crosslinking ratio dependences with the model is in progress.

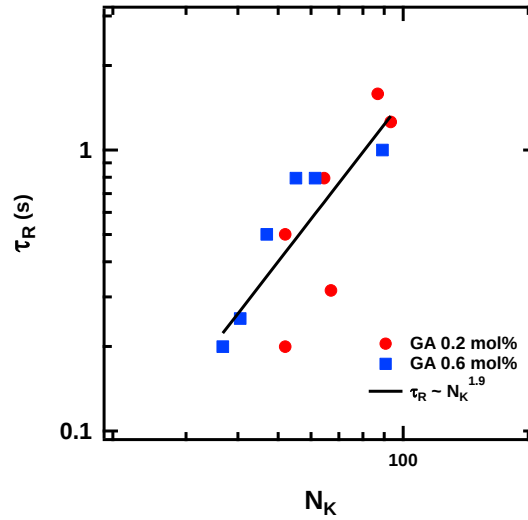


Figure 12. Characteristic time τ_R plotted against the average number of Kuhn segments in the chain between crosslinks, N_K . The power-law exponent of 1.9 was found.

2.3.3 Extensibility

We then performed uniaxial stretching experiments to characterize the nonlinear (large strain) behavior of the dual crosslink gels, in order to clarify the effect of chemical and physical crosslink densities on the extensibility of the gel. Tensile stress - strain curves of the dual crosslink gels (with $C_{\text{borax}} = 1 \text{ mM}$) and of the corresponding chemical gels with different GA concentration at the same stretch rate $\dot{\lambda} = 0.01\text{s}^{-1}$ are shown in **Figure 13a**. For all GA concentrations the dual crosslink gels have higher moduli (expected from linear viscoelastic data) but have also higher extensibilities than the respective chemical gels, which is less obvious.

In particular, the extensibility of the dual crosslink gels with $C_{GA} = 0.2$ mol% dramatically increases with the introduction of physical crosslinks, with a value of λ at break close to 6. For other C_{GA} tested, we observed little differences in extensibility between the chemical and dual crosslink gels (data not shown). It should be noted that for these unnotched samples the fracture typically occurs in the clamps for sample fixation allowing us only qualitative discussion about the absolute value of the stretch at rupture. However experiments on notched samples give similar results for the gels with $C_{GA} = 0.2$ mol%²⁶.

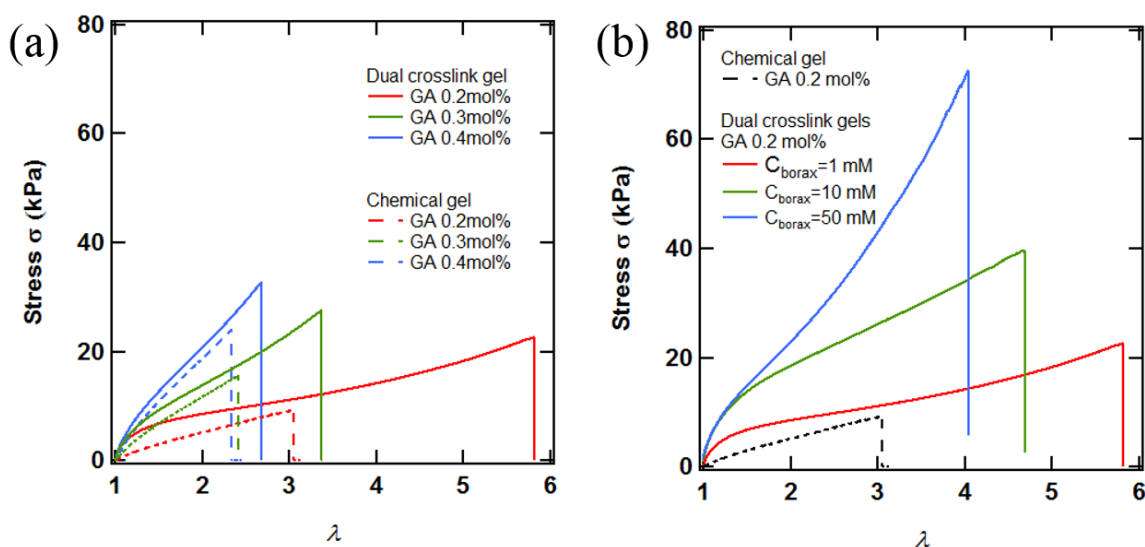


Figure 13. Stress - strain curves of the PVA dual crosslink gels compared with the corresponding chemical gels at a stretch rate of 0.01 s^{-1} . (a) at $C_{borax} = 1 \text{ mM}$, (b) at $C_{GA} = 0.2 \text{ mol\%}$.

The remarkable extensibility for the dual crosslink gel at $C_{GA} = 0.2 \text{ mol\%}$ is presumably explained by the loosely crosslinked network structure of the chemical gel. **Figure 14** shows the viscoelastic moduli of the chemical gels at different chemical crosslinking density (as prepared, $C_{PVA} = 12 \text{ wt\%}$). For all the gels tested, we observed a well-defined elastic plateau. On the other hand for G'' , only the chemical gel at $C_{GA} = 0.2 \text{ mol\%}$ shows measureable values of G'' , giving $\tan \delta$ of the order of $0.1 - 0.01$. For the other more crosslinked gels G'' is not measureable within the resolution of the instrument and $\tan \delta < 0.01$. In **Figure 14b** the value

of G' at the plateau was plotted as a function of C_{GA} . For the gels with $C_{GA} \geq 0.4$ mol%, a linear relation was found with an extrapolated value of 380 Pa at $C_{GA} \geq 0$ mol%, presumably corresponding to the entanglements of the PVA solution at this concentration. The value of the plateau for the chemical gel at $C_{GA} = 0.2$ mol% shows a slightly lower value than that expected from the linear regression for the other crosslinking densities, suggesting the network is loosely crosslinked, with dangling chains and long strands.

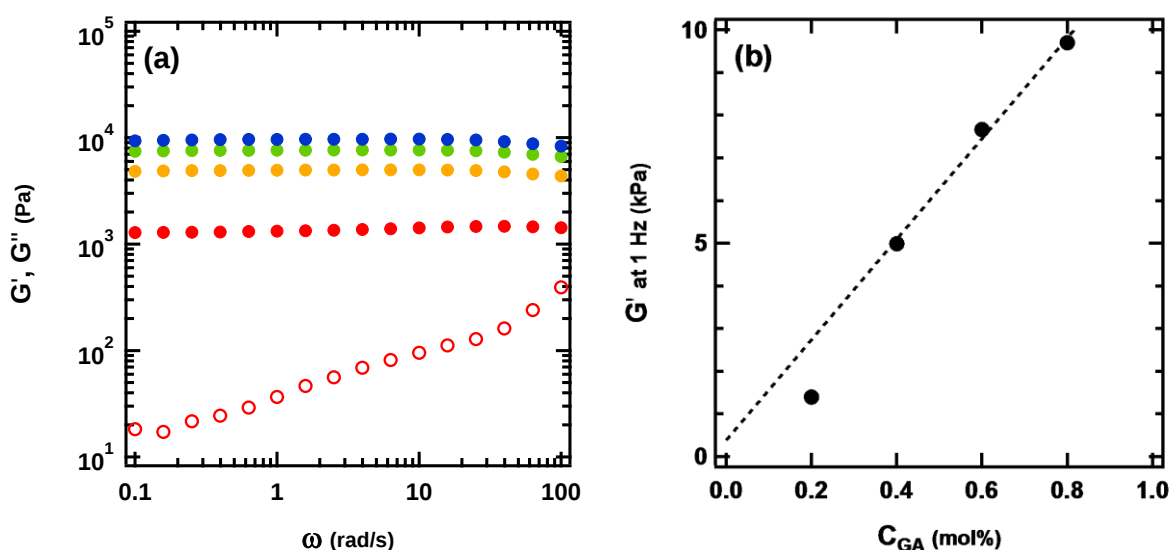


Figure 14. (a) Viscoelastic moduli of chemical gels at various chemical crosslinking density. Closed circles: G' , open circles: G'' . Red: $C_{GA} = 0.2$ mol%, yellow: 0.4 mol%, green: 0.6 mol%, blue: 0.8 mol%. (b) G' at 1 Hz as a function of C_{GA} . The dashed line shows linear regression of 0.4, 0.6 and 0.8 mol%.

The effect of the physical crosslinking density on the extensibility was also studied for a fixed density of chemical crosslinks. For $C_{GA} = 0.2$ mol% we observed a very significant increase in modulus and extensibility for all concentrations of borax relative to the chemical gel. The increase in stiffness was more pronounced for the high C_{borax} as expected from the results shown in **Figure 13b**. However the increase in extensibility showed a more complex borax concentration dependence. From the chemical gel to the dual crosslink gel at $C_{borax} = 1$ mM, the extensibility dramatically increased, while at higher borax concentration than 1 mM, the

extensibility decreased with the borax concentration. The dual crosslink gel with $C_{GA} = 0.2$ mol% and $C_{borax} = 1$ mM, which has been extensively investigated in previous studies^{19,26}, had the largest strain at break.

Comparisons between different dual crosslink gels at the same strain rate should be made with caution, since the extensibility for the dual crosslink gel ($C_{GA} = 0.2$ mol% and $C_{borax} = 1$ mM) showed a strong strain-rate dependence attributed to the breaking and healing of the physical crosslinks²⁶. The extensibility of this gel decreased significantly with increasing strain rate for both unnotched and notched samples. For the dual crosslink gels of this study, we found that the relaxation time decreased with increasing density of physical crosslinks as shown in **Figure 10b**. The Weissenberg number defined as the product of the strain rate and the sample relaxation time can be a relevant parameter to compare the different gels. For the same gel ($C_{GA} = 0.2$ mol%, $C_{borax} = 1$ mM) stretched at various strain rates, one finds a *decrease* in the extensibility with increasing Weissenberg number²⁶. However for different gels having different values of the relaxation time and stretched at a constant strain rate, **Figure 13** shows an *increase* in extensibility with increasing the Weissenberg number. Therefore, the reduced extensibility with increasing physical crosslinking density (**Figure 13b**) is not consistent with the strain-rate dependency of the extensibility observed for the dual crosslink gel ($C_{GA} = 0.2$ mol% and $C_{borax} = 1$ mM) and suggests that there are other factors important for fracture or in other words the strain rate giving optimum toughness cannot be described by a simple Weissenberg number²⁶. Although this is speculative at this stage it is possible that the strain hardening which is clearly affected by the density of physical crosslinks (**Figure 13b**), plays also an important role in fracture.

Let us comment also on the strain stiffening observed at large deformation. As previously discussed²², the value of the stress measured at high λ tends to be higher than that expected from the Neo-Hookean model. Models taking into account strain stiffening such as the

exponential model can predict this strain hardening behavior²⁷. Similarly to many associating polymer systems, physical gels of PVA-borax system show shear thickening^{28,29}. During steady shear tests, at high strain rates the viscosity increases due to the increase in the density of effective elastic chains (transition from intra- to inter-chain association) and/or non-Gaussian nonlinear chain stretching. From our experimental results at one strain rate we cannot separate the variation in the number of effective elastic chains from the intrinsic non-linearity of the chain itself due to finite extensibility. Detailed experiments at different strain rates would be necessary in order to obtain better insight on the origin of the strain stiffening.

2.3.4 Separability

Separability of the time-dependent and strain-dependent terms of the tensile stress is a major feature of the dual crosslink gels. As shown previously for one dual crosslink gel, the stress σ measured in uniaxial extension as a function of stretch ratio λ showed a strong strain rate dependence but the reduced stress $\bar{f}^* = \sigma/(\lambda - \lambda^{-2})$ plotted as a function of time at various strain rates, superposed well on a master curve²⁰. Thus the stress could be separated into a strain-dependent Neo-Hookean contribution term, and a time dependent term $\bar{f}^*$ deriving from the dynamics of the physical crosslinks.

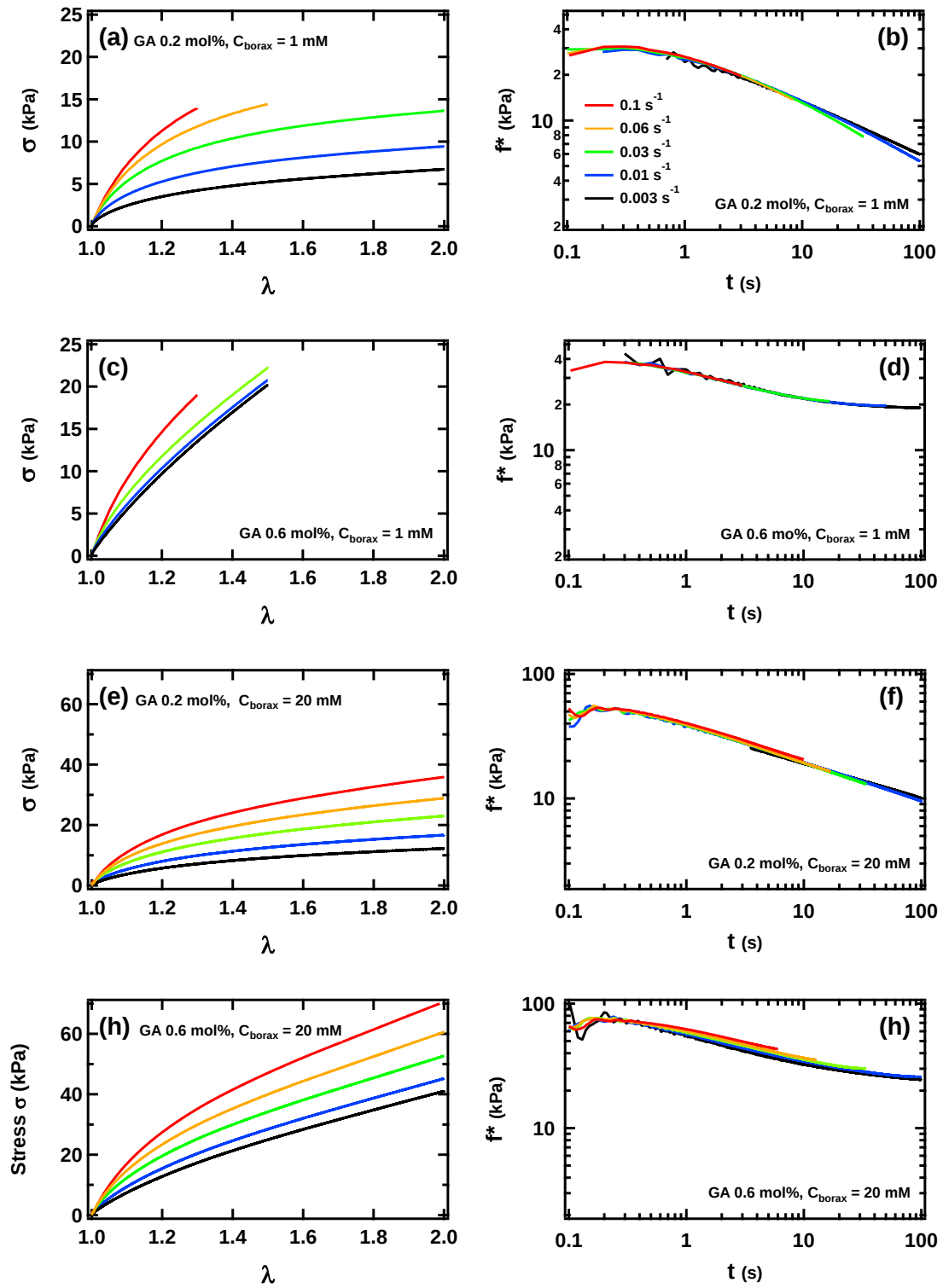


Figure 15. a,c,e,g) Stress σ as a function of stretch λ , and b,d,f,h) reduced stress f^* as a function of time, for various chemical and physical crosslinking densities. The samples were not stretched to rupture.

In order to investigate the applicability of this separability to dual crosslink gels having various chemical and physical crosslink densities, we performed tensile tests at five different stretch rates: 0.003, 0.01, 0.03, 0.06 and 0.1 s^{-1} . As an example, results for four dual crosslink gels are shown in **Figure 15a,c,e,g** (for $C_{\text{borax}} = 1$ and 20 mM and for $C_{\text{GA}} = 0.2$ and 0.6 mol%). In this test, in order to reduce experimental errors (due to the sample batches, sample fixation repeatability, etc), the gel samples were not stretched to rupture, and the same sample was stretched repeatedly at different stretch rates after a sufficiently large recovery time of 30 min. We obtained better reproducibility than the previously reported results²⁰ and found that all the dual crosslink gels studied here showed higher stresses when deformed at higher stretch rates. In order to highlight the separability, we plotted in **Figure 15b,d,f,h** the reduced stress f^* as a function of time. At all the investigated crosslinking densities, a master curve of f^* vs t was obtained for all the strain rates studied, demonstrating that the separability of the time-dependent and strain-dependent terms holds well for different crosslinking densities. This separability indicates that the time-dependent stress term is nearly independent of the strain level and thus has the same time-dependence than the absolute modulus measured by shear rheometry in the linear domain. **Figure 16** shows the comparison between f^* and the linear relaxation modulus $|G^*(t)| = [G'(\omega)^2 + G''(\omega)^2]^{1/2}$ obtained from using the Cox-Merz rule on oscillatory data. The master curve of f^* obtained from the tensile tests and the shear modulus showed the same time dependence, though the value of the shear modulus was about half the value of f^* . This difference of a factor of about 2 is believed to arise from the fact that the shear rheology test is performed in a parallel plate geometry (not in a cone plate geometry). Empirically, we find often good agreement between the moduli of gels measured by tensile tests with those measured by torsion tests in cone-plate geometries when the gel is prepared in that geometry.

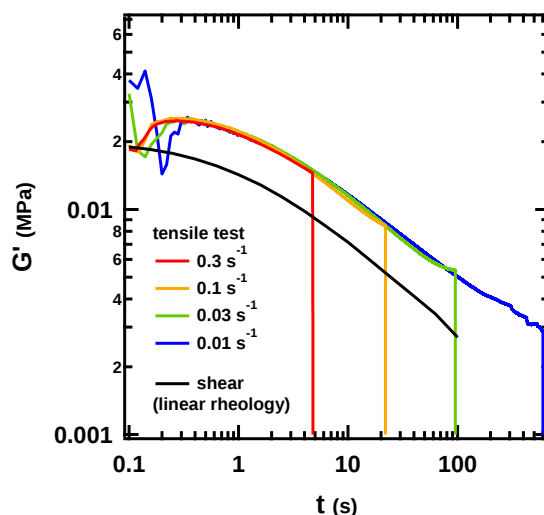


Figure 16. Comparison between the reduced stress f^* from tensile tests and modulus from applying the Cox-Merz rule to oscillatory tests as a function of time. $C_{GA} = 0.2 \text{ mol\%}$, $C_{borax} = 1 \text{ mM}$.

The separability of stress into strain- and time-dependent terms for physical gels without chemical crosslinking is not obvious or generally accepted. For example, relaxation moduli for solutions of triblock associating copolymers or hydrophobically modified ethoxylate urethanes show strain rate dependency^{30,31}. Luo et al. found a similar separability to our system for their polyampholyte hydrogel with low water content (52 wt%)³². It was believed that the strength of the reversible association by electrostatic interactions had a wide distribution, and certain amount of *strong* bonds served as permanent crosslinks while *weak* bonds served as transient reversible crosslinks³³. Suppression of terminal relaxation by permanent crosslinks can be a key to observe the separability.

2.4 Conclusions

In order to investigate the effects of the chain association/dissociation dynamics on the polymer network mechanics in a wide range of strains and strain rates without plastic terminal flow, we developed associating polymer hydrogels having a large amount of transient physical crosslinks and a small amount of permanent chemical crosslinks. The former bring to the network strain rate dependency and self-recovery properties while the latter deliver a reference state of deformation and prevent the network from irreversible flow. We rheologically studied a series of poly(vinyl alcohol) “dual crosslink” hydrogels, permanently crosslinked by glutaraldehyde and transiently crosslinked by borate ions, at various crosslinking densities, in comparison with the corresponding chemical gels. Our main conclusions are the following:

(1) Additivity:

The contribution of the chemical and physical crosslinks to the dynamic moduli was determined in small strain oscillatory torsion tests and the additivity (independent and additive contributions of the two types of crosslinks to the elastic and viscous moduli) was confirmed for all investigated systems. The dependence of the relaxation time on the physical crosslinking ratio was explained by the incomplete relaxation of the chains between two adjacent crosslinks for low crosslink densities. When the healing time (reassociation of open crosslinks) is shorter than the Rouse relaxation time of the chain, the rheological relaxation time slows down. Thus the relaxation time can increase with decreasing physical crosslinking density due to the concomitant increase in the Rouse time and decrease in the healing time.

(2) Extensibility:

Thanks to its high extensibility the dual crosslink gel is considered as a tough hydrogel. In all cases, extensibility of the dual crosslink gels was found higher than that of the corresponding

chemical gels. However the benefit of adding physical crosslinks decreased for higher physical crosslink densities and the extensibility also decreased at fixed chemical crosslink density with increasing physical crosslinking density suggesting that the effect of the physical crosslinks on the strain hardening may also play a role in fracture.

(3) Separability:

The strong strain rate-dependent behavior of the stress measured in tensile tests could be simplified by separating its strain-dependent and time-dependent terms. The strain-dependent term was described by the neo-Hookean model, while the time-dependent term reflected the breaking and reforming dynamics of the physical bonds. A master curve of the reduced stress as a function of time was obtained. We validated this separability for all the crosslinking densities tested and a constitutive model for the PVA-borax system will be discussed in Chapter 3.

(4) Limitations:

There are several limitations inherent to the PVA-borax hydrogel, such as a relatively slow dynamics, a narrow relaxation time range, no access to stable gels with low physical crosslinking ratio, and a time-consuming preparation. To overcome these limitations, we developed a new dual crosslink hydrogel based on a different type of physical crosslinking chemistry, with relatively fast and controlled kinetics, and a wider range of accessible physical crosslinking ratio. This new dual crosslink gel will be discussed in Chapter 4.

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Chapter 3: PVA–borax system: **constitutive model**

3.1 Introduction

Tough hydrogels having reversible crosslinks can show strain rate-dependent mechanical properties governed by the dissociation/re-association dynamics of the transient physical crosslinks, and it is still a challenge to develop quantitative constitutive descriptions of the mechanical behaviors in the linear and nonlinear domains by taking into account the dissociation and re-association characteristic times. The difficulties also come from the materials, many hydrogels with such dynamic crosslinks have a broad distribution of relaxation times^{1,2}. Hui and Long proposed a 3D finite strain constitutive model for self-healing gels containing reversible physical crosslinks. The model was inspired by and meant to simulate the mechanical behavior of an ionically crosslinked triblock copolymer hydrogel^{3,4}.

The dynamics of the PVA dual crosslink gel has a well-defined main relaxation time stemming from the physical bond dissociation and re-association(see chapter 2), providing a reasonable platform for quantitative modeling^{5,6}. In view of the experiments done on this simpler system, Long et al. further improved their constitutive model to fit the transient nonlinear tensile behaviors of a PVA dual crosslink gel containing a certain concentration of chemical and physical crosslinks⁷. That version of the model was later modified to account for the steady-state behavior more common in oscillating shear rheology in the linear domain. This physically grounded parameter was able to fit the tensile tests, using only four parameters (as opposed to 7 in the previous version) to describe the mechanical behavior of the dual crosslink gel^{8,9}.

In this chapter, the validity of the model for PVA dual crosslink gels with different chemical and physical crosslinking ratios is evaluated. The results of the tensile tests and parallel plates shear rheology tests of the dual crosslink gels studied in Chapter 2 will be used to validate the model.

3.2 Continuum theory

3.2.1 Continuum theory

First we briefly describe the latest version of the rate-dependent finite three-dimensional continuum theory validated for a PVA dual crosslink gel having a chemical crosslinking ratio of 0.2 mol% prepared with C_{borax} of 1 mM. This model is developed with the following key assumptions^{7,9}:

1. The chemical crosslinks are assumed to be unbreakable while the physical crosslinks can undergo a rate-dependent breaking and reforming process.
2. The physical bond breaking and reforming process has achieved a dynamic equilibrium after the gel is synthesized.
3. The stress sustained by a temporary chain is instantaneously relaxed when it breaks; after a temporary chain is reattached, it is in the relaxed state immediately and carries no strain energy. The reattached temporary chain experiences the deformation history from its birth at time τ (s) to the current time t (s).
4. Macroscopically the gel is incompressible and isotropic. For both permanent and transient chains the Neo-Hookean model is used to specify the strain energy of a chain under deformation.
5. We assume that the rates of chain breaking and reattaching are independent of the imposed strain history.

3.2.2 Model for tensile tests

For uniaxial tension, the stress σ (Pa) is written as⁹:

$$\sigma = \mu[\rho + n(t)] \cdot \left(\lambda(t) - \frac{1}{\lambda^2(t)} \right) + \mu\bar{\gamma}_\infty \cdot \int_0^t \phi_B \left(\frac{t-\tau}{t_B} \right) \cdot \left(\frac{\lambda(t)}{\lambda^2(\tau)} - \frac{\lambda(\tau)}{\lambda^2(t)} \right) \cdot d\tau, \quad (1)$$

with

$$n(t) = \bar{\gamma}_\infty \cdot \int_{-\infty}^0 \phi_B \left(\frac{t-\tau}{t_B} \right) d\tau, \quad (2)$$

$$\bar{\gamma}_\infty = \frac{1-\rho}{t_H + \frac{t_B}{2-\alpha_B}}, \quad (3)$$

$$\phi_B \left(\frac{t}{t_B} \right) = \left[1 + t \frac{\alpha_B - 1}{t_B} \right]^{\frac{1}{1-\alpha_B}}, \quad (4)$$

where, μ (Pa) is the small strain shear modulus, ρ is the molar fraction of the permanent chains relative to the total number of chains, $\lambda(t)$ is the applied stretch ratio. $n(t)$ is the molar fraction of the temporary chains formed before $t = 0$, t_B (s) is the characteristic breaking time for the physical bonds, $\bar{\gamma}_\infty$ (s⁻¹) is a steady state rate parameter considering a dynamic equilibrium of breaking and reforming processes. t_H (s) is the characteristic time of the physical crosslink reattachment. The function ϕ_B denotes the probability of breaking the chain, $1 < \alpha_B < 2$ is a dimensionless material constant that specifies the rate of decay.

The five parameters, μ , ρ , t_B , t_H and α_B can be reduced into four parameters (**Figure 1**):

- (1) $\mu\rho$, the elastic modulus due to the chemically crosslinked chains only (Pa),
- (2) $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$, the elastic modulus due to the physically crosslinked chains (Pa),
- (3) t_B , the breaking time (s),
- (4) α_B , is a material constant.

3.2.3 Model for steady-state torsion tests

The theory also predicts the steady state shear modulus with the same set of parameters. The complex modulus $G^*(\omega)$ is written as⁸:

$$G^*(\omega) = \mu \left\{ \rho + \bar{\gamma}_\infty \frac{t_B}{2-\alpha_B} \left[1 - \frac{2-\alpha_B}{\alpha_B-1} \cdot I(\omega) \right] \right\}, \quad (5)$$

$$I(\omega) = \int_0^\infty \exp\left(-i \frac{t_B}{\alpha_B-1} \omega\right) (1+x)^{-\frac{1}{\alpha_B-1}} \cdot dx. \quad (6)$$

And the expressions for $G'(\omega)$ and $G''(\omega)$ are given as:

$$G'(\omega) = \text{Re}[G^*(\omega)] = \mu \left\{ \rho + \bar{\gamma}_\infty \frac{t_B}{2-\alpha_B} \left[1 - \frac{2-\alpha_B}{\alpha_B-1} \cdot \text{Re}[I(\omega)] \right] \right\}, \quad (7)$$

$$G''(\omega) = \text{Im}[G^*(\omega)] = -\mu \bar{\gamma}_\infty \frac{t_B}{2-\alpha_B} \cdot \frac{2-\alpha_B}{\alpha_B-1} \cdot \text{Im}[I(\omega)]. \quad (8)$$

The integral $I(\omega)$ which is a function of the angular frequency ω , is numerically evaluated.

It is useful to verify the high and low frequency behavior of the equations above. In the low frequency limit, we have:

$$G'(\omega \rightarrow 0) = \mu \rho + \left[\frac{\mu(1-\rho)t_B}{(2-\alpha_B)t_H+t_B} \Gamma\left(\frac{2\alpha_B-3}{\alpha_B-1}\right) \cos\left(\frac{2-\alpha_B}{2(\alpha_B-1)}\pi\right) \right] \left(\frac{t_B\omega}{\alpha_B-1}\right)^{\frac{2-\alpha_B}{\alpha_B-1}}, \quad (9)$$

thus $G'(0) = \mu\rho$,

$$G''(\omega \rightarrow 0) = \frac{\mu(1-\rho)t_B}{(2-\alpha_B)t_H+t_B} \left[\frac{\pi}{2\Gamma\left(\frac{2-\alpha_B}{\alpha_B-1}\right)} \sec\left(\frac{2-\alpha_B}{2(\alpha_B-1)}\pi\right) \right] \left(\frac{t_B\omega}{\alpha_B-1}\right)^{\frac{2-\alpha_B}{\alpha_B-1}}, \quad (10)$$

thus $G''(0) = 0$.

And for the high frequency limit, we have:

$$G'(\omega \rightarrow \infty) = \mu \rho + \frac{\mu(1-\rho)t_B}{(2-\alpha_B)t_H+t_B} \left[1 - \frac{2-\alpha_B}{b t_B^2} \frac{1}{\omega^2} \right], \quad (11)$$

$$\text{thus } G'(\infty) = \mu\rho + \mu(1 - \rho) \frac{\frac{t_B}{2-\alpha_B}}{t_H + \frac{t_B}{2-\alpha_B}} = \mu\rho + \mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}, \quad (12)$$

$$G''(\omega \rightarrow \infty) = -\frac{\mu_0(1-\rho)}{t_H + t_B/(2-\alpha_B)} \frac{1}{\omega}, \quad (13)$$

$$\text{thus } G''(\infty) = 0.$$

It should be noted that the model assumes a dynamic equilibrium between the closed and open physical crosslinks. And the values of G' corresponding to the closed and open physical crosslinks are written as:

$$G'^{closed}_{phys}(\omega) = \mu(1 - \rho) \frac{\frac{t_B}{2-\alpha_B}}{t_H + \frac{t_B}{2-\alpha_B}}, \quad (14)$$

$$\text{and } G'^{open}_{phys}(\omega) = \mu(1 - \rho) \frac{t_H}{t_H + \frac{t_B}{2-\alpha_B}}, \quad (15)$$

It is not possible to determine the value of t_H by fitting, without independently measuring ρ (from the binding isotherm, for example), since G'^{open}_{phys} is not rheologically accessible.

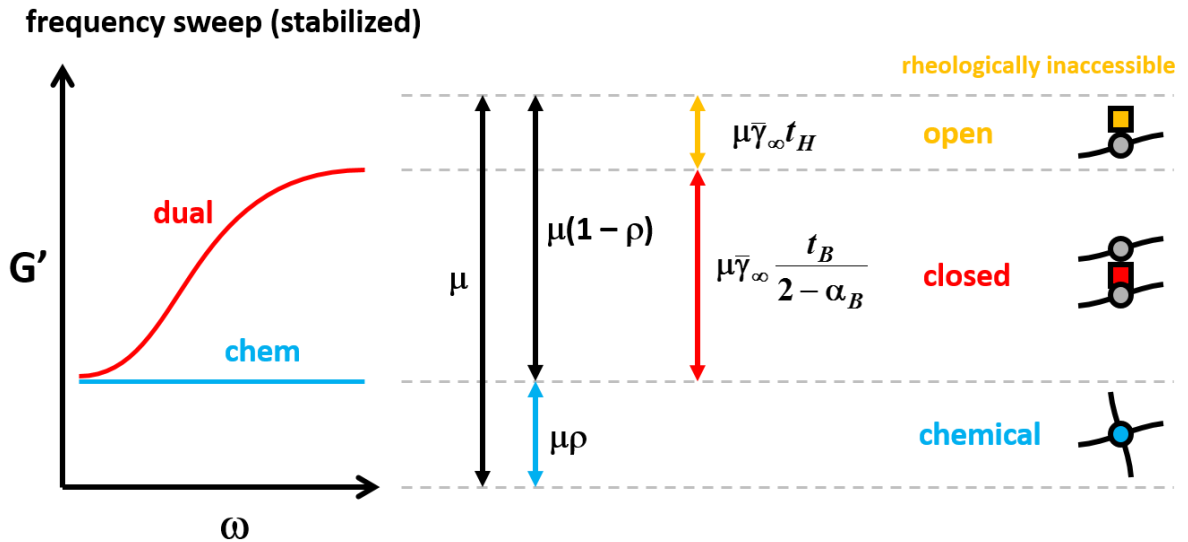


Figure 1. Schematic presentation of the model.

3.2.4 Parameters determination by fitting

The four parameters were determined by fitting the experimental data of the tensile and torsion tests with the equations corresponding to each test.

3.2.4.1 Tensile test

Determination of the parameters was done by fitting the data of a stress relaxation test following the procedure described in the literature⁹. Here we briefly state the experimental and fitting procedures. The relaxation test starts from a rapid stretching to a desired fixed stretch ratio λ_0 . We used 0.1. With an ideal stress relaxation test the stretch increases from 0 to the desired value λ_0 at $t = 0$ (or the stretch rate is infinite), while for real tests any apparatus requires a certain time $t = t_1$ to reach λ_0 . For the tensile test performed by our Instron tensile tester, we used $t_1 = 1$ s. Then the stress starts to relax and is recorded (during 60 s). To prepare for fitting, first, the value of the stress σ_∞ at the long time is used to determine the contribution of the chemical crosslinks to the elastic modulus, $\mu\rho$, as $\sigma_\infty = \mu\rho[\lambda_0 - \lambda_0^{-2}]$. Second, the stress relaxation part was fitted with the following relation:

$$\ln[\sigma(t) - \sigma_\infty] = \left[\ln\left(\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}\right) - \frac{2-\alpha_B}{\alpha_B-1} \ln\left(\frac{\alpha_B-1}{t_B}\right) \right] + \ln\left(\lambda(t) - \frac{1}{\lambda^2(t)}\right) - \frac{2-\alpha_B}{\alpha_B-1} \ln t. \quad (16)$$

By plotting $\ln[\sigma(t) - \sigma_\infty]$ as a function of $\ln t$, the value of α_B was determined from the slope. Finally, the initial stretch part considered as continuous loading with a strain rate of $\dot{\lambda} = \lambda_0/t_1$, is fitted with eq.(1) to determine t_B and $\mu\bar{\gamma}_\infty$. The results of the second and third steps were shown in **Figure 2**. As example, two dual crosslink gels having different physical crosslinking densities were shown. Both fits were satisfactory, the four parameters were successfully determined for all the dual crosslink gels tested.

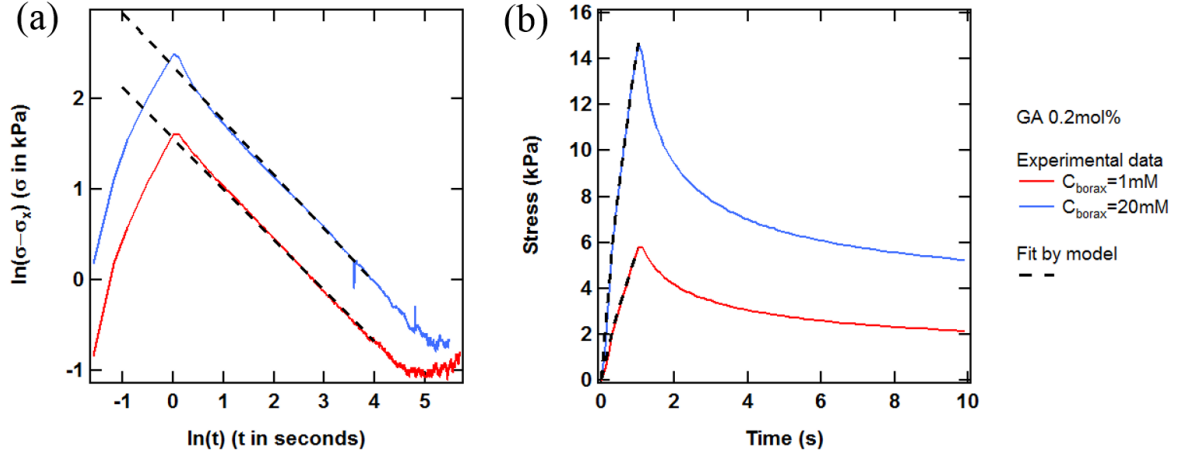


Figure 2. Fitting the tensile stress relaxation tests with the model eq1.

3.2.4.2 Torsion test

Similarly to the tensile tests, for the torsion tests also the stress relaxation test can be used to fit the model. In general the shear rheometer can apply a step shear much faster than the tensile tester ($t_1 \sim 0.01$ s), and when the relaxation is not too fast (as for the case of the PVA dual crosslink gels), the plateau modulus at high frequencies can be observed and fitted. The relaxation modulus can be fitted with the following equation to determine all the four parameters $\mu\rho$, $\mu\bar{\gamma}_\infty$, $\frac{t_B}{2-\alpha_B}$, and α_B :

$$G(t) = \mu\rho + \mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B} \left[1 + (\alpha_B - 1) \frac{t}{t_B} \right]^{(2-\alpha_B)/(1-\alpha_B)}. \quad (17)$$

Figure 3 shows the results of the fitting procedure for two dual crosslink gels as example. For all the samples tested over the whole frequency range measured, the fit was found to be reasonable.

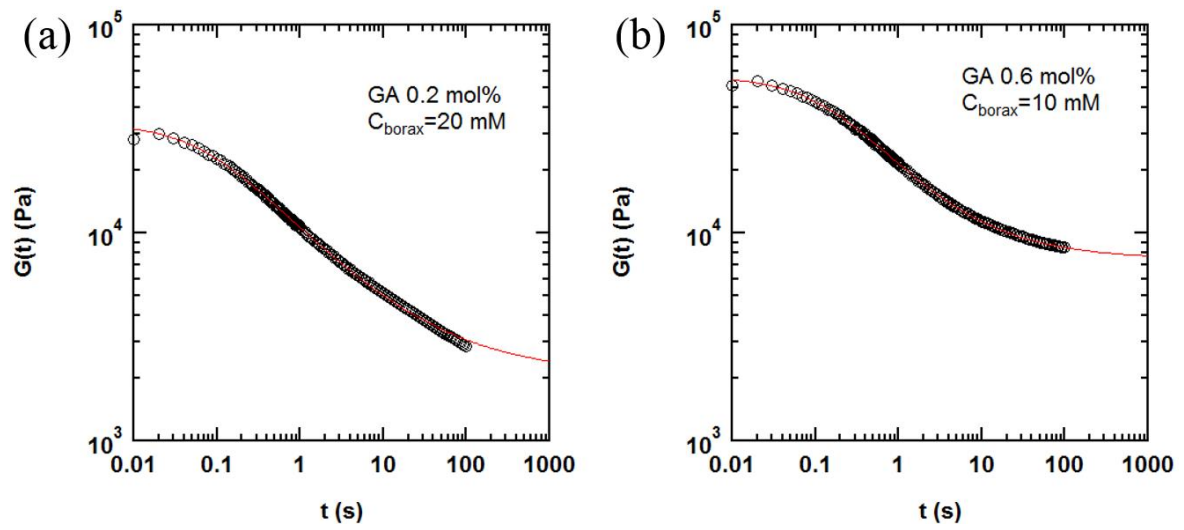


Figure 3. The torsion relaxation test and the fitting based on the model.

3.3 Results and discussion

Here we discuss the dependence of the four parameters determined by both the tensile and torsion tests for two series of data at two different chemical crosslinking ratio (0.2 and 0.6 mol%).

3.3.1 $\mu\rho$ and $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$

First we evaluate the values of the two parameters $\mu\rho$ and $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$. The value of $\mu\rho$ corresponds to that of the elastic modulus at zero frequency, and that of $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$ corresponds to the elastic modulus of the closed physical crosslinks. **Figure 4** shows the borax concentration dependence of the value of $\mu\rho$. The value of $\mu\rho$ is practically independent of the borax concentration except for $C_{\text{borax}} = 50$ mM where the fitted value of $\mu\rho$ has a much higher value than for the other concentrations. Those determined by the tensile test for $C_{\text{GA}} = 0.2$ mol% (red open circles in **Figure 4**) slightly increased with borax concentration. Those determined by the fit for the tensile tests are systematically higher than those determined by the fit for the torsion tests. This point is discussed later in this subsection.

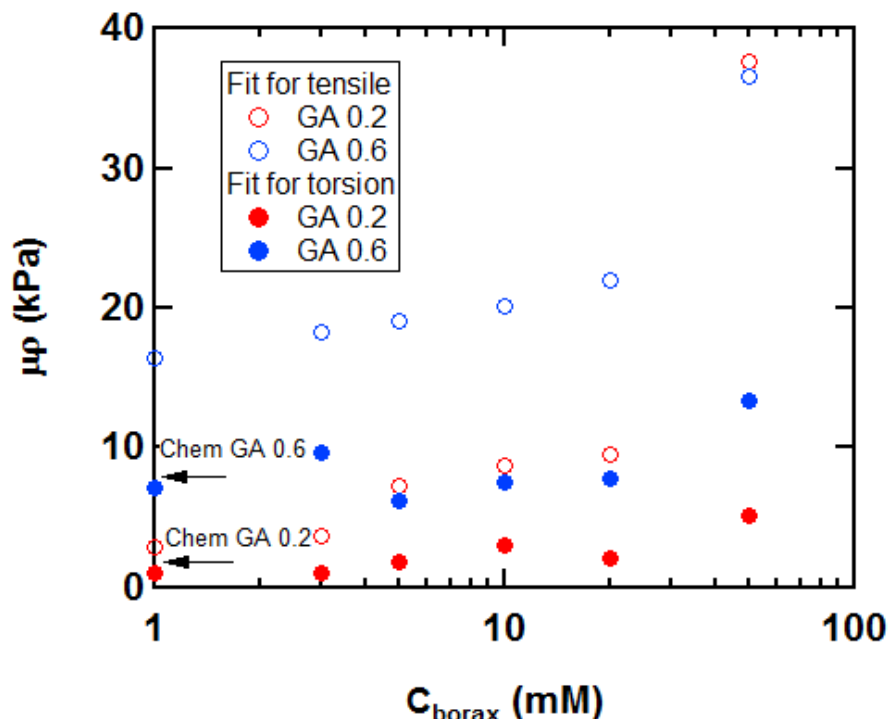


Figure 4. The borax concentration dependence of the value of μ_p . The red circles represent gels for $C_{\text{GA}} = 0.2$ mol%, blue ones for $C_{\text{GA}} = 0.6$ mol%; open circles for μ_p determined by the fit of the tensile tests, filled circles for μ_p determined by the fit of the torsion tests.

The value of μ_p is expected to correspond to the fraction of the elastic modulus due to the chemical crosslinks since the physical crosslinks dissociate and re-associate freely at low frequency and the stress should be fully relaxed. The values of the elastic modulus of the corresponding chemical gels measured by torsion tests are indicated by the arrows in the figures. The value of μ_p at the low borax concentration corresponds well to the elastic modulus of the chemical gel. All the dual crosslink gels at the different physical crosslinking densities were prepared from the same chemical gel, so the value of μ_p should indeed be independent of C_{borax} . However, since we determined the value of μ_p from the long time behavior of the stress, we interpreted this increase in μ_p as due to the existence of a slowly relaxing physical crosslinks component. Experimentally the dissociation of a physical crosslink does not necessarily mean immediate chain relaxation especially at high crosslinking density. With increasing crosslink

density, the chain length between neighboring crosslinks decreases and there are less available binding sites near a physical crosslink. The probability to reform a physical crosslink with the same binding site without relaxing the chain is expected to increase with physical crosslinking density¹⁰. As a consequence of this imperfect relaxation, a fraction of physical crosslinks may not dissociate and would then be counted as permanent chemical crosslinks and contribute to the increase in $\mu\rho$ at long time scales.

In **Figure 5**, $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$ is plotted as a function of borax concentration. The values of $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$ increase with borax concentration then seems to saturate at 10 mM (except for those at 50 mM of borax in the tensile test). Similarly to $\mu\rho$, the values determined by fit for tensile tests are systematically higher than those determined by fit for torsion tests.

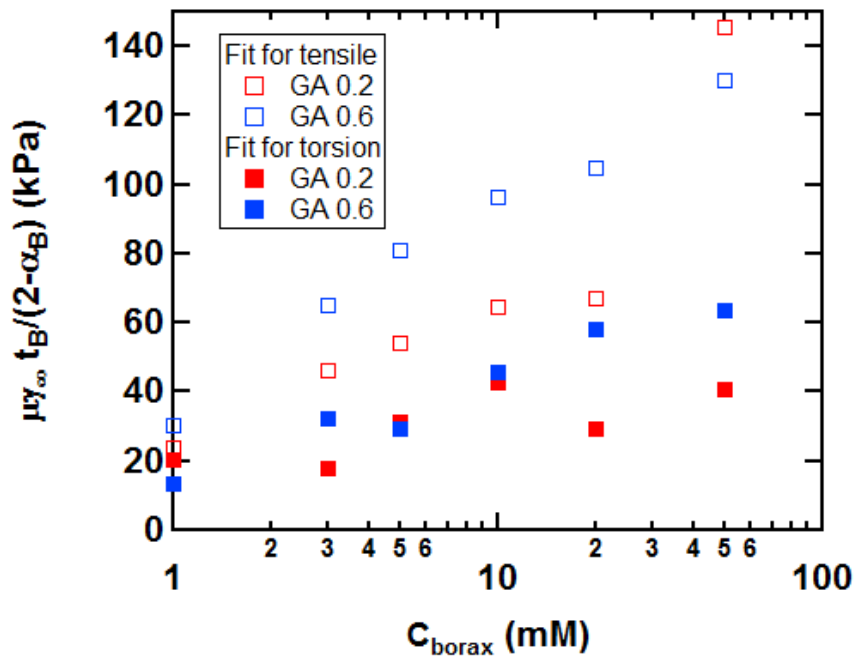


Figure 5. The borax concentration dependence of the value of $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$. The red squares represents gel for $C_{\text{GA}} = 0.2$ mol%, blue ones for $C_{\text{GA}} = 0.6$ mol%; open squares for $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$ determined by the fit for the tensile tests, filled squares for $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$ determined by the fit for the torsion tests.

The systematic difference found between the values of $\mu\rho$ and $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$ between the tensile and torsion tests should be discussed. In **Figure 6** the values of $\mu\rho$ and $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$ determined by the tensile tests are plotted against those determined by torsion tests for both chemical crosslinking ratios (0.2 and 0.6 mol%). All the data series (both $\mu\rho$ and $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$, for the two chemical crosslinking ratios) collapse on the same proportional relation, with a slope of about 2.

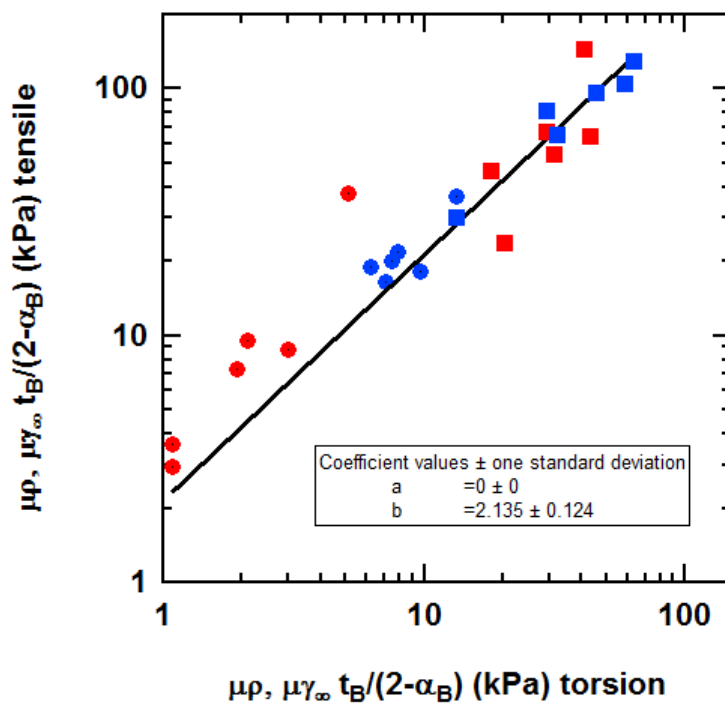


Figure 6. The values of $\mu\rho$ and $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$ determined by the tensile tests as a function of those determined by torsion tests for both chemical crosslinking ratios.

As discussed in Chapter 2, this factor of 2 is believed to arise from the fact that the torsion test is performed in a parallel plate geometry (not in the cone plate geometry). After shifting the values of $\mu\rho$ determined by the torsion tests by this factor of 2, they are comparable with those determined by the tensile tests. **Figure 7** shows the borax concentration dependence of $\mu\rho$ and $\mu\bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}$. Despite the large dispersion due to the experimental errors, the two methods show a

good agreement. The values of $\mu\bar{\gamma}_{\infty} \frac{t_B}{2-\alpha_B}$ show little dependence on the chemical crosslinking ratio for all the four series of data.

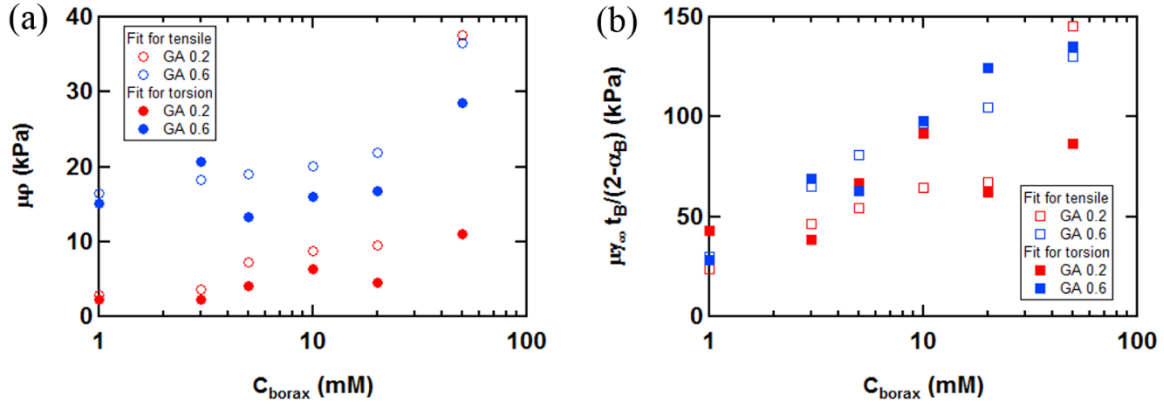


Figure 7. The borax concentration dependence of μp (a) and $\mu\bar{\gamma}_{\infty} \frac{t_B}{2-\alpha_B}$ (b).

3.3.2 α_B

The values of α_B determined by fit for tensile and torsion tests for the two chemical crosslinking ratios are plotted as a function of the borax concentration in **Figure 8**. We do not find particular chemical nor physical crosslinking density dependence. The tensile tests and the torsion tests give roughly the same results. This material constant mathematically signifies the concentration dependence of a reversible physical crosslink breaking rate. This result suggests that the simple model description of the single physical bond dissociation is sufficient to predict the polymer network relaxation due to the physical crosslink dissociation.

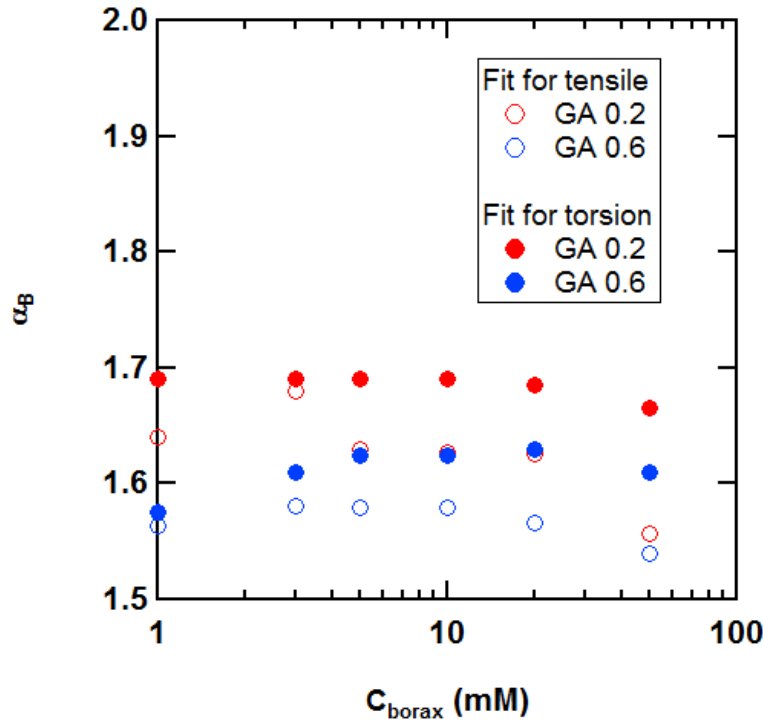


Figure 8. The values of α_B determined by fit for tensile and torsion tests for the two chemical crosslinking ratios. The red circles represents gel for $C_{GA} = 0.2$ mol%, blue ones for $C_{GA} = 0.6$ mol%; open circles for α_B determined by the fit for the tensile tests, closed circles for μ_p determined by the fit for the torsion tests.

3.3.3 t_B

Finally the bond breaking characteristic time t_B is discussed. The value of $\frac{t_B}{2-\alpha_B}$ is used as the relevant form of the dissociation time as expected from the equations. It is plotted as a function of the borax concentration in **Figure 9** for both tensile and torsion tests, as well as for 0.2 and 0.6 mol% chemical crosslinking ratios. The values of the relaxation times τ_R determined from the peak of G'' (**Chapter 2 Figure10**) are also plotted for comparison. The values of $\frac{t_B}{2-\alpha_B}$ and τ_R are reasonably close to each other, suggesting the relevance of the characteristic time $\frac{t_B}{2-\alpha_B}$. Globally the values of $\frac{t_B}{2-\alpha_B}$ decrease with increasing borax concentration, the values of $\frac{t_B}{2-\alpha_B}$ determined by the tensile tests and those determined by torsion tests show slightly different

behaviors. For the tensile tests (open circles) the values of $\frac{t_B}{2-\alpha_B}$ do not strongly depend on the borax concentration in the low concentration range and those for the gels with 0.2 mol% chemical crosslinking show slightly higher values. For the torsion tests (filled circles), the values continuously decrease with borax concentration and practically no effect of the chemical crosslinking is observed. For all the gels except for the gels crosslinked with $C_{GA} = 0.6$ mol% at $C_{borax} = 1$ and 3 mM, when the values from the tensile tests and those from the torsion tests are compared for the same gels, the difference is within a factor of 2, thus we consider that the fits for the two different experiments give the same results. Still the ratio of the values tensile/torsion can be as high as 4.3 (for $C_{GA} = 0.6$ mol% at $C_{borax} = 1$ mM), we do not have a clear explanation of this discrepancy which may be due however to the uncertainties of the fitting.

Let us comment on another characteristic time, the physical bond healing time t_H . In the model t_H is integrated in $\bar{\gamma}_\infty$ which is a function of ρ and of $\frac{t_B}{2-\alpha_B}$. Thus without knowing the value of ρ which can be written as $\rho = C_{chem}/(C_{chem} + C_{phys}^{open} + C_{phys}^{closed})$, it is not possible to determine t_H . The model assumes a steady state bond breaking/healing controlled by the thermodynamic equilibrium. As expected from Eq 14, the ratio between the concentration of open and closed physical crosslinks can be written as $C_{phys}^{open}/C_{phys}^{closed} = t_H(2 - \alpha_B)/t_B$, indicating that it is essential to experimentally determine the concentration of open physical crosslinks. Unfortunately, for the PVA borax system it is difficult to accurately measure the binding isotherm in gels due to the complex equilibrium of borate ions.

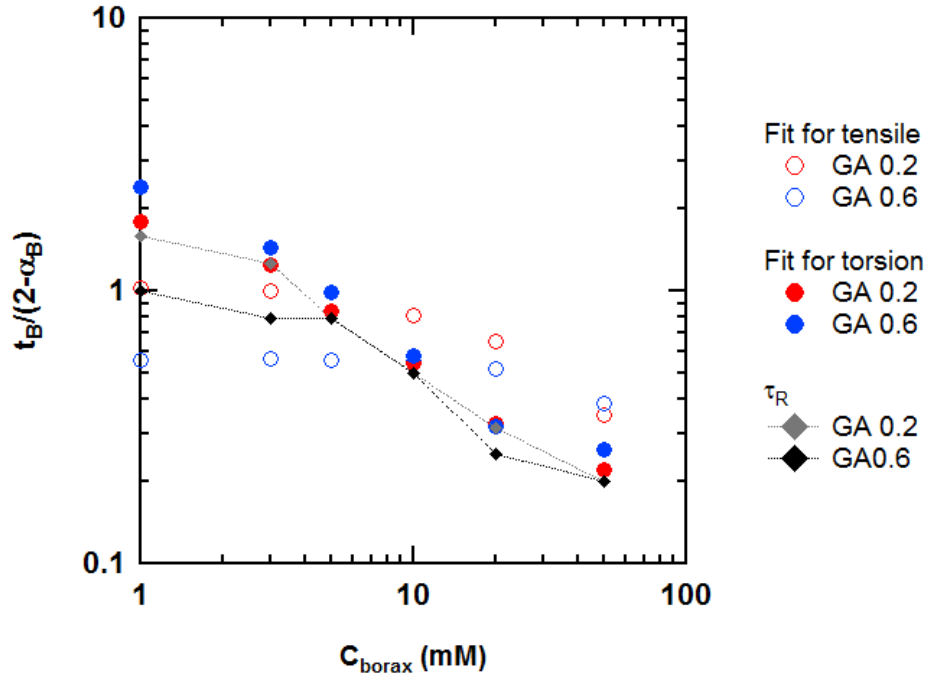


Figure 9. The value of $\frac{t_B}{2-\alpha_B}$ as a function of of the borax concentration for both tensile and torsion tests, and the values of the relaxation time τ_R determined from the peak of G'' , for 0.2 and 0.6 mol% chemical crosslinking ratios.

3.4 Conclusion

In this Chapter, the validity of the continuum theory for the PVA dual crosslink gels at various crosslinking ratios was studied. The theory predicts the stress-strain behaviors in both tensile and torsion tests and has been validated for a PVA dual crosslink gel having a chemical crosslinking ratio of 0.2 mol% prepared with C_{borax} of 1 mM.

For the two values of chemical crosslinking ratios, $C_{\text{GA}} = 0.2$ and 0.6 mol%, PVA dual crosslink gels at different physical crosslinking ratios were prepared, and we successfully determined a set of the four parameters of the model by fitting the experimental data of the tensile relaxation tests. Another set of the parameters was also determined by fitting the torsion relaxation tests. The two experiments are supposed to give the same values of the parameters, we discussed the crosslinking ratio dependence of the two sets of the four parameters.

$$(1) \mu\rho \text{ and } (2) \mu\bar{\gamma}_{\infty} \frac{t_B}{2-\alpha_B}$$

These parameters correspond to the elastic modulus of the chemical and physical crosslinks respectively. We observed a systematic difference between the values of the two parameters determined by the tensile tests and those determined by the torsion tests (in the parallel plate geometry): those determined by the tensile tests are higher than those by the torsion tests with a factor of about 2. A similar result was discussed in Chapter 2. As expected, the value of $\mu\rho$ was found to increase with chemical crosslinker concentration but we also found that it increases with borax concentration, suggesting the presence of slowly relaxing physical crosslinking component. The values of $\mu\bar{\gamma}_{\infty} \frac{t_B}{2-\alpha_B}$ increases with borax concentration while no significant chemical crosslinker concentration dependence was observed.

$$(3) \alpha_B$$

Chapter 3: PVA–borax system: constitutive model

α_B , which is a material constant expressing the concentration dependence of the physical crosslink dissociation rate, shows no strong chemical or physical crosslinking dependence over the concentration range studied.

(4) t_B

The characteristic time of the physical bond dissociation t_B decreases with increasing physical crosslinker concentration. When this characteristic time is expressed as $\frac{t_B}{2-\alpha_B}$, it shows values close to those of the macroscopic relaxation time determined from the peak frequency of G'' in a frequency sweep (Chapter 2). The best fits of the tensile and torsion tests, resulted in values of $\frac{t_B}{2-\alpha_B}$ that had a slightly different dependence on the physical crosslinking concentration and a weak dependence on the chemical crosslinker concentration except for the low physical crosslinker concentration.

As a conclusion, the continuum model describes well both tensile and torsion behaviors of the dual crosslink gels at various crosslinking ratios with only four parameters.

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Chapter 4: Dual crosslink hydrogels **with metal-ligand coordination**

4.1 Introduction

4.1.1 Why do we need a second system?

In the previous two chapters, we studied the chain association/dissociation dynamics of PVA dual crosslink hydrogels. Rheological additivity, tensile extensibility, strain rate-dependent behavior and separability were discovered for hydrogels with different crosslinking densities. The characteristic time of the relaxation process by physical crosslink dissociation was studied by applying a continuum theory.

However, there are several limitations of this system:

- (1) The value of the average relaxation time τ_R is relatively high (~ 1 s), which indicates a relatively slow dynamics, and results in the difficulty in investigating the mechanical behavior at very slow strain rate relative to the inverse of τ_R .
- (2) The value of τ_R varies by about 1 decade in the investigated borax concentration range, and changing the crosslinking density is not an efficient way to tune the dynamics of the dual crosslink gels.
- (3) To prepare PVA dual crosslink hydrogels at a constant polymer concentration, chemical gels were immersed in a borax solution, with NaCl to maintain the swelling ratio in its preparation conditions ($W_2/W_0 = 1$). However, for $C_{\text{borax}} < 1$ mM, W_2/W_0 cannot be maintained at 1 (**Chapter 2, Figure 8**). Therefore, it's not possible to study gels with a very low physical crosslinking ratio.
- (4) The presence of non-crosslinking boric acid makes it different to determine the crosslinking ratio.

To overcome these limitations, a new system with fast and tunable dynamics, accessible low physical degree of crosslinking, and reliable measurement of the crosslinking ratio is needed.

Inspired by mussel byssus¹⁻³, in this chapter, we propose a dual crosslink gel based on a metal-ligand coordination bond to create physical crosslinking. Similarities and differences between these two systems will be discussed.

4.1.2 Mussel byssus

The investigation of the properties of the mussel byssus has recently been the focus of more detailed investigations in particular because of its toughness and water-resistant adhesion to rock^{4,5}. The underlying chemistry inside the byssus has been the inspiration for the design of artificial self-healing materials^{3,6}. In order to understand the connection between the living organism and the bioinspired synthetic materials, it is useful to describe the structure of the mussel byssus.

Marine mussels attach to intertidal coastal surfaces via byssus, a bundle of 50 to 100 individual threads that are extensible up to over 100% strain^{2,3,7}, and terminate in adhesive plaques (**Figure 1a**). These threads are covered by a thin cuticle (**Figure 1b**) with a granular morphology⁸⁻¹⁰, which hinders the crack propagation and results in a high breaking strain and a hardness of ~ 0.4 GPa⁶. The mechanical role of coordination bonds in the thread has been intensely studied. The thread is able to partially recover even when stressed beyond its yield point (**Figure 1c**)¹, due to a high content of histidine and dopa (3,4-dihydroxyphenylalanine), which has the ability to bind reversibly metal ions such as Zn^{2+} , Cu^{2+} and Fe^{3+} in the thread (**Figure 1d**), creating sacrificial bonds that act as an energy dissipating mechanism^{3,11}.

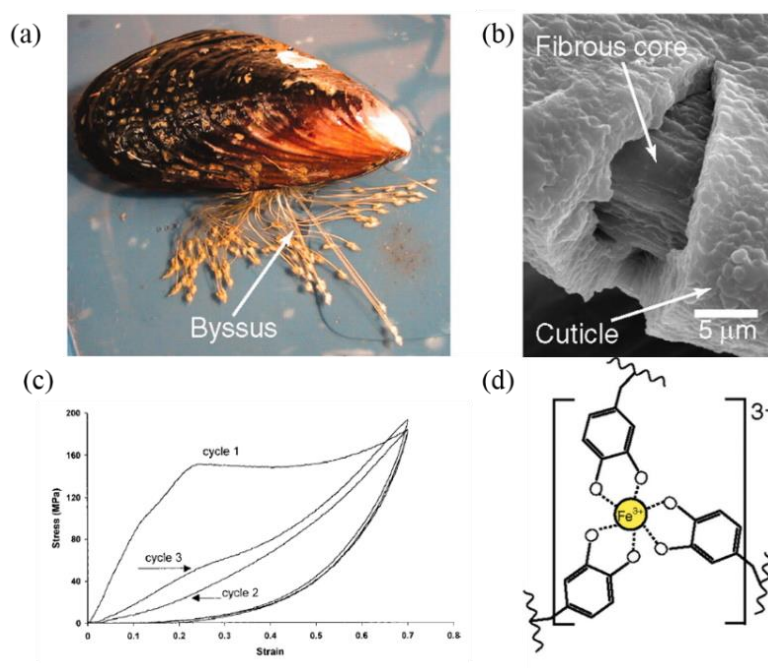


Figure 1. (a) Mussels produce byssus. Threads are made by the mussel foot and attached to hard surfaces by adhesive plaques. (b) Strain-induced macro-tearing of cuticle exposing the underlying fibrous core is evident in the SEM. (c) Stress-strain curves for a thread sample.¹ (d) Dopa-ion coordination complex.⁷

4.1.3 Bio-inspired metal-ligand coordination physical hydrogels

The mussel byssal thread provides a model for the development of self-healing biomaterials with good mechanical properties. Inspired by the reversible metal-ligand coordination in the mussel byssus, various tough self-healing biomaterials have been developed.

4.1.3.1 Catechol-Fe³⁺ crosslinked hydrogels

The catechol-Fe³⁺ ligand coordination bond has been correlated to the hardness and high extensibility of the mussel byssus cuticle⁷. Following this study, the authors developed a new hydrogel by introducing catechol-Fe³⁺ crosslinks into dopa-modified polyethylene glycol polymer (PEG-dopa) (**Figure 2b**), which displays high elastic moduli and self-healing properties⁶.

The equilibrium ratio between catechol-Fe³⁺ complexes (mono-, bis-, tris-) is controlled by the pH (**Figure 2a**), the relative fractions of these complexes in solution of PEG-dopa-Fe³⁺, show that the mono-species dominate at low pH, tris- at high pH, and bis- in between (**Figure 2c**).

The mechanical properties of the tris-catechol-Fe³⁺ crosslinked gels was compared with that of covalently crosslinked gels. Both types of gels have similar elastic moduli (G') at high strain rates, while the tris-catechol-Fe³⁺ crosslinked gels dissipated more energy (G'') than the covalently crosslinked gels at low strain rates (**Figure 2d**). Failure was induced by tearing or shear strain to study the recoverability of the elastic modulus G' as a function of time. As shown in **Figure 2e**, the tris-catechol-Fe³⁺ crosslinked gels recovered G' in a very short time while the covalent gels did not.

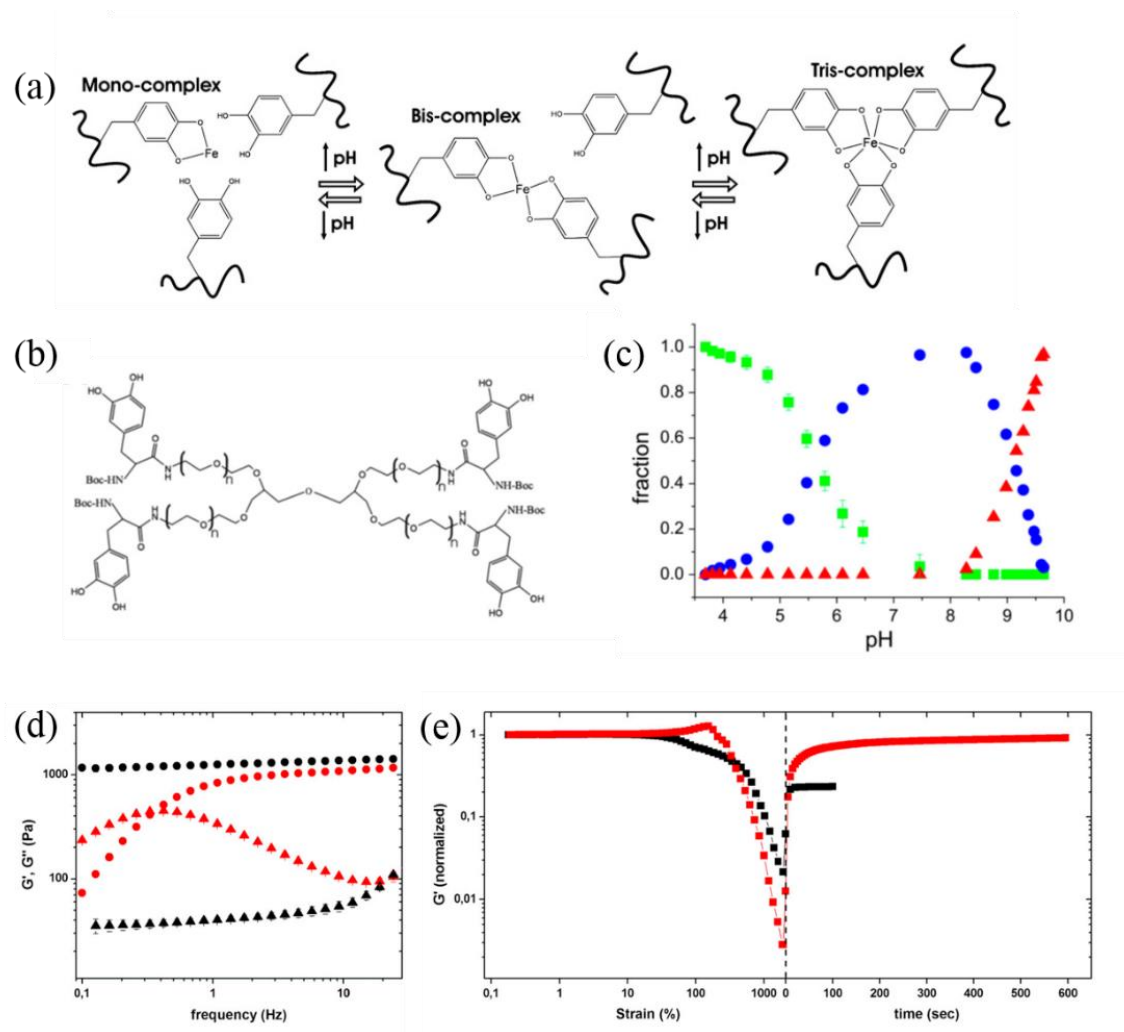


Figure 2. (a) The pH-dependent stoichiometry of Fe^{3+} -catechol complexes. (b) Dopa-modified polyethylene glycol (PEG-dopa). (c) Relative fractions of mono- (green), bis- (blue), and tris-catechol- Fe^{3+} (red) complexes in solution of PEG-dopa with FeCl_3 as a function of pH. (d) Comparison of gels cross-linked with tris-catechol- Fe^{3+} complexes (red) or with covalent bonds (black) (G' and G'' , circles and triangles, respectively). (e) Recovery of stiffness and cohesiveness after failure of tris-catechol- Fe^{3+} gels (red curve) and covalent gels (black curve).⁶

4.1.3.2 Metal-coordination physical hydrogels with tunable rheological properties

The rheological properties of polymers are traditionally tuned by changing the spatial elements, such as polymer molecular weight, architecture or persistence length^{5,12,13}, while another dimension of scale, time, is neglected. The time element focuses on multiple hierarchical time

scales like kinetic effects or reptation time. Grindy *et al* designed physically crosslinked hydrogels with both spatial (controlled by polymer architecture) and temporal (controlled by crosslink kinetics) hierarchy so that both dimensions could be used as mechanical design elements (**Figure 3a**)⁵. The linear viscoelastic properties of hydrogels crosslinked by reversible metal-coordination bonds are primarily dictated by the metal-ligand exchange kinetics, which can vary by several orders of magnitude in time^{3,4,14}.

Histidine-modified star PEG polymers were synthesized to mimic the histidine-rich regions of the mussel byssal thread collagen^{3,5}. 4-arm-PEG-Histidine (4PEG-His) crosslinked with metal ions was used to produce hydrogels with relaxation times accessible by oscillatory rheometry, due to its ability to vary the relaxation times of the physical gel in a controlled way¹⁵. The scheme of the hypothesized crosslinking reaction is shown in **Figure 3a**, with the stoichiometric ratio of 2:1 (histidine end group: metal), one single metal ion bridging two polymer arms³.

Figure 3b shows the linear viscoelastic properties of these hydrogels with different ions at 5 °C, pH = 7. The pattern is very close to the Maxwell-like relaxation, and the relaxation times of these gels follow the order $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$, which correlates with the divalent metal complexation and de-complexation kinetics^{16,17}. His- Ni^{2+} gels have long relaxation times while His- Cu^{2+} and His- Zn^{2+} gels relax much faster. A change of metal ion in single metal-ion hydrogels can change the timescale by several orders of magnitude.

The viscoelastic properties of these single metal-ion hydrogels can be tuned only at one level of temporal hierarchy (one relaxation time). To gain multi-level control over molecular relaxation times, hydrogels with two different His- M^{2+} complex crosslinks ($\text{Ni}^{2+}:\text{Cu}^{2+}$, $\text{Ni}^{2+}:\text{Zn}^{2+}$) were studied. For example, 50 % Ni^{2+} :50 % Zn^{2+} gel (**Figure 3c**) displays two relaxations: one slow ($\omega \sim 10^{-2} - 1$ rad/s) and one fast ($\omega \sim 10 - 10^2$ rad/s) dissipation modes.

These double-metal networks contain controllable concentrations of slow His-Ni²⁺ crosslinks and fast His-Cu²⁺ or His-Zn²⁺ crosslinks (**Figure 3a**).

Instead of changing metal ions, different ligands also show temporally hierarchal mechanical behavior. 4PEG gels crosslinked with both dopa: Ni²⁺ and His: Ni²⁺ complexes were synthesized and characterized (**Figure 3d**). The rheological data indicates two distinct relaxation timescales.

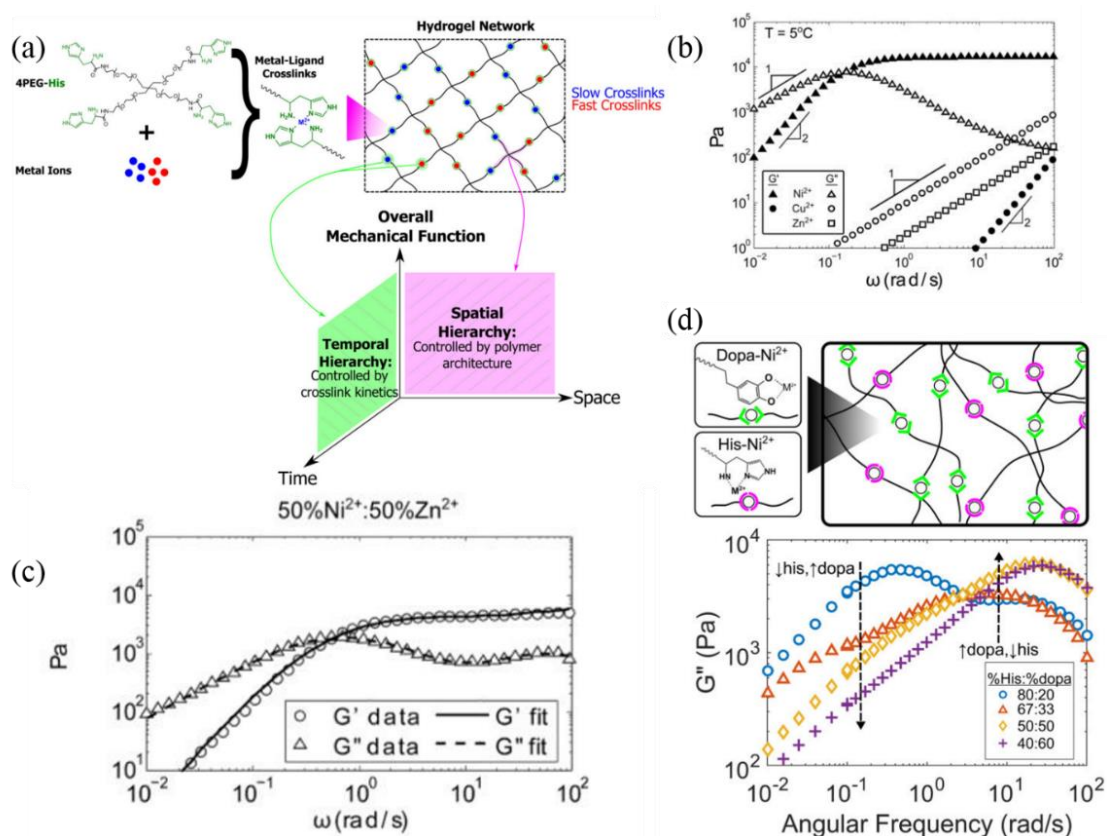


Figure 3. (a) Model materials systems with orthogonally tunable mechanical temporal hierarchy. (b) Rheological properties of single metal-ion hydrogels. (c) Rheological properties of double metal-ion coordinate networks. (d) The effects of temporal mechanical hierarchy in systems beyond model 4PEG-His hydrogels.⁵

4.1.4 Dual crosslink hydrogels with metal coordination

Metal-coordination physical hydrogels have been investigated intensively in the last decade, however, there are few studies about dual crosslink hydrogels with metal-coordination.

Built upon Sakai's homogeneous tetra-arm hydrogel¹⁸ and the following work on mechanical 'fuse link' hydrogels¹⁹, Seiffert *et al* developed covalent gels including physical crosslinks, based on terpyridine-metal complexation²⁰. Linear PEG is functionalized with azide (N_3) and terpyridine (TPy) functional groups at each end, while tetra-arm PEG is functionalized with cyclooctynes (CyOct) capped to each arm (**Figure 4a**). A homogeneous covalent tetra-PEG-type network is formed by mixing these two PEG compounds and reacting cyclooctene with the azide groups. Additional metal-complexation-based physical crosslinks are formed²¹ by adding metal ions such as Co^{2+} , Zn^{2+} , or Mn^{2+} that form complexes with terpyridine.

The elastic and viscous shear moduli, G' and G'' , were determined by using oscillatory shear rheology. The elastic modulus G' of the chemical gel is independent of the frequency and larger than G'' (**Figure 4b**), while the Zn^{2+} -based dual-crosslink gel has a larger G'' with a peak at $\omega = 0.25$ rad/s (k_{diss} , **Figure 4c**), which matches the dissociation rate constant k_{diss} of the Zn^{2+} -terpyridine complex.

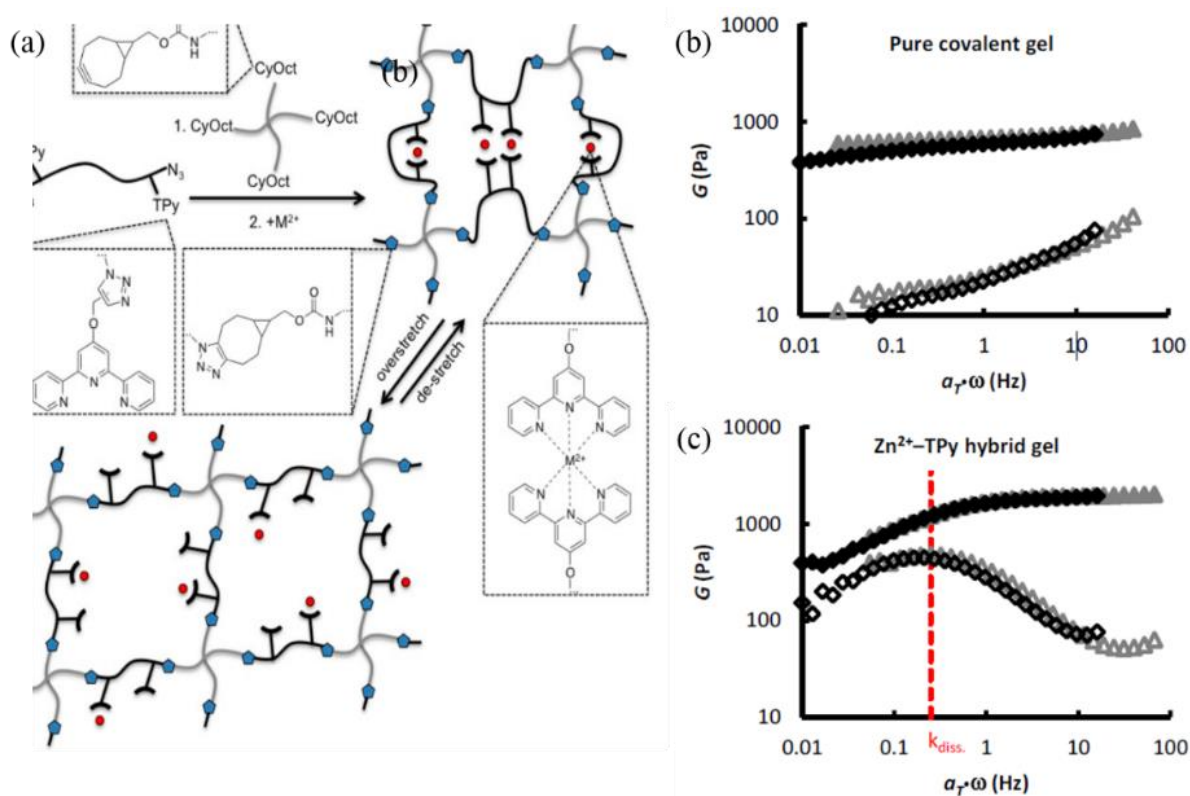


Figure 4. (a) Formation of hybrid polymer-network gels. Frequency-dependent shear moduli of (b) the purely covalent gel and (c) the Zn²⁺-terpyridine-enforced hybrid gels. G'-full symbols; G'': open symbols; gray triangles: 10 °C; black diamonds: 25 °C. All data are superimposed by shifting the 10 °C along the frequency axes to obtain master curves, referenced to 25 °C.²⁰

4.2 Dual crosslink gels based on AAm-VIm-M²⁺ system

Transient hydrogels crosslinked through dopa and histidine based metal coordination complexes have been investigated^{3,6}, and a few dual crosslink hydrogels with metal coordination have been reported²⁰. While the rheological properties of these dual crosslink gels have been investigated the mechanical properties in the non-linear regime and the fracture properties has not been investigated.

As mentioned at the beginning of this chapter, there are several limitations inherent to the PVA-borax hydrogel, such as relatively slow dynamics, narrow relaxation time range, no access to gel with low physical crosslinking ratio, and time-consuming preparation. To overcome these limitations, it is necessary to develop a new dual crosslink hydrogel, with a relatively fast and controlled kinetics, and a wider range of accessible physical crosslinking ratios. An easy and relatively fast synthesis procedure is also important, since the mechanical tests, especially the fracture experiments, require large amounts of samples.

Here, we propose to investigate a dual crosslink gel, with covalent crosslinks and metal-ligand coordination as physical crosslinks. This AAm based imidazole group-containing gel can bind transition metal ions, in particular Ni²⁺ and Zn²⁺ (**Figure 5**). This metal-ligand bonding between metal ions and the imidazole ligand can be explained by hard soft acid base principles (HSAB)²². Imidazole is categorized as a borderline base, a moderate σ -donor and a weak π -acceptor, while Ni(II) and Zn(II) are borderline acids¹⁵.

In this chapter, the synthesis and mechanical properties of this dual crosslink gel, in both the linear and non-linear domain will be discussed.

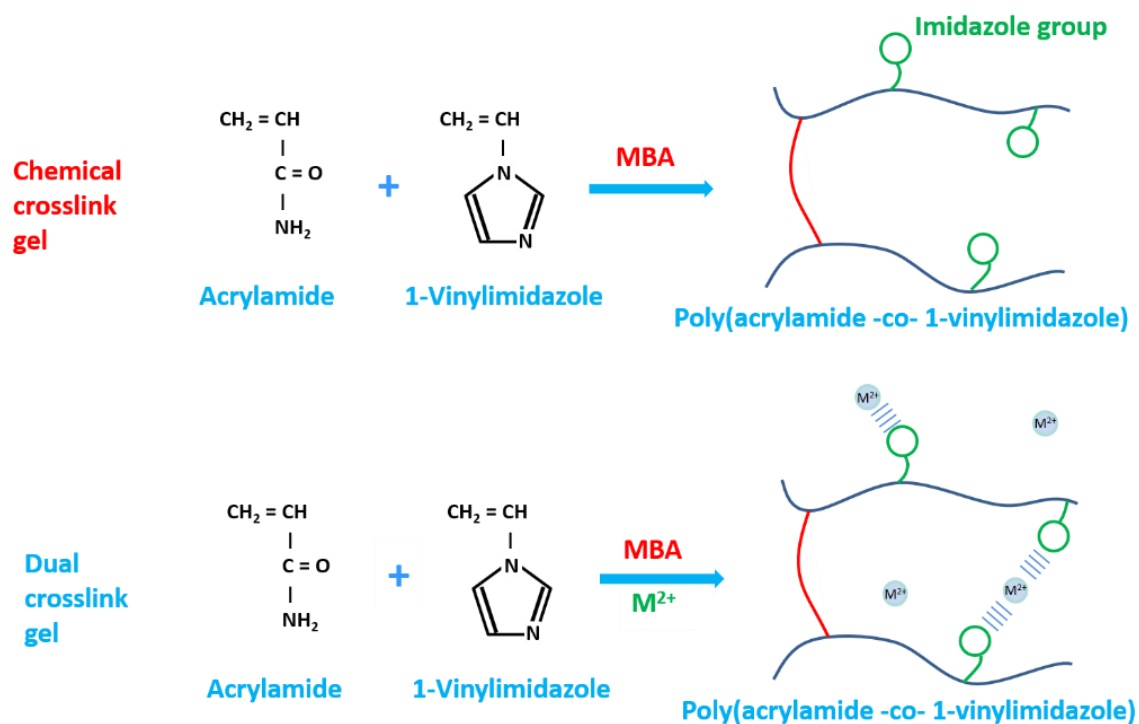


Figure 5. Schematic presentation of the formation of the chemical gel and the dual crosslink gel.

4.3 Experimental section

4.3.1 Sample preparation

Chemical gels were prepared by mixing Acrylamide, AAm (purchased from Aldrich) (1.8 M) and 1-Vinylimidazole, VIm (purchased from Aldrich) (0.2 M) in aqueous solution with N,N'-Methylenebisacrylamide, MBA (purchased from Aldrich) and Potassium persulfate, KPS (purchased from Aldrich) (6 mM), under nitrogen flow at low temperature (in ice bath). The solution was then transferred in a glovebox, N,N,N',N'-Tetramethylethylenediamine, TEMED (purchased from Aldrich) (20 mM) was then added. The MBA concentration in the feed varied from 2 to 10 mM, corresponding to 0.1 – 0.5 mol% of the monomer units of AAm and VI. After the overnight crosslinking reaction, the obtained AAm-VI chemical gels were used for measurements as prepared.

AAm-VIm-M²⁺ dual crosslink gels were prepared by adding extra Nickel chloride, NiCl₂ (purchased from Aldrich) or Zinc chloride ZnCl₂ (purchased from Aldrich) in the solution, the concentration of MBA was fixed at 3 mM (0.15 mol%). After the overnight crosslinking reaction, the obtained AAm-VI-M²⁺ dual crosslink gels were used for measurements as prepared.

4.3.2 Linear viscoelastic properties

In order to characterize the linear viscoelastic properties of the dual crosslink gels, small strain oscillatory shear measurements were performed in a parallel plates geometry with roughened surfaces (20 mm in diameter) with the ARES LS1 rheometer (TA instruments). The sample thickness was 1.5 mm. Frequency sweep tests with a dynamic range varying from 0.1 to 100 rad/s were carried out at 25 °C within the linear viscoelasticity regime (0.2 – 0.8 % strain).

4.3.3 Uniaxial tensile tests

The large deformation behavior of the gels was studied by uniaxial tensile test to fracture and step-cycle loading – unloading tests on an Instron 5565 tensile tester with a 10 N load cell. Samples were rectangular in shape with 5 mm width, 1.5 mm thickness, and 15 mm length (length between clamps). We kept the samples in paraffin oil during all the tests to prevent them from drying following a previously published procedure²³.

4.4 Results

4.4.1 Polymerization process

For PVA-borax dual crosslink gels, the PVA chemical gel was prepared by crosslinking PVA polymer with glutaraldehyde, then the physical crosslink was added by diffusion of the physical crosslinker borate ion. To keep the polymer concentration constant, the equilibrium swelling was adjusted by addition of NaCl in the borax solution. For this AAm-VIm- M^{2+} system, a ‘one-pot synthesis’ method starting from monomers was used for the polymerization. This synthesis method consists of the simultaneous copolymerization and chemical and physical crosslinking, thus the whole synthesis procedure can be carried out in just one reactor, which improves the efficiency and avoids waste during preparation.

4.4.1.1 Chemical gel polymerization

AAm and VIm were polymerized by using MBA as chemical crosslinker, this free radical polymerization was triggered by KPS as initiator and TEMED as catalyst. The obtained Poly(acrylamide-co-vinylimidazole) hydrogel was completely transparent.

4.4.1.2 Dual crosslink gel polymerization

The polymerization of the dual crosslink gel was the same as that of the chemical gel, except for the existence of the metal ions. As shown in **Figure 6a**, the $NiCl_2$ solution (100 mM, containing no other chemicals for gel synthesis as reference) has a distinct green color. The addition of VIm to the $NiCl_2$ solution (100 mM) induced an immediate color change to blue (**Figure 6b**), due to the complexation between Ni^{2+} and the imidazole ligand. This results suggest that the complexes which can serve as physical crosslinkers exist during the polymerization thus it may influence the kinetics of the polymerization and chemical

crosslinking process and hence the chemical network structure. When the KPS-TEED initiator system was introduced the solution became turbid and took a dark color (**Figure 6c**), but changed to almost transparent blue (not 100% transparent) during the polymerization process (**Figure 6d**). Since the same mixture without Ni^{2+} (thus for the corresponding chemical P(AAm-co-Vim)gel) did not show any change in turbidity, the interactions between persulfate radical and Ni^{2+} are involved. For the preparation of Zn^{2+} gel, the ZnCl_2 solution (100 mM) had no color (**Figure 6e**); the complexation between Zn^{2+} and the imidazole ligand didn't cause any color change (**Figure 6f**); after adding KPS, however, the solution became turbid and white (**Figure 6g**), and no color or turbidity change occurred during the polymerization process (**Figure 6h**).

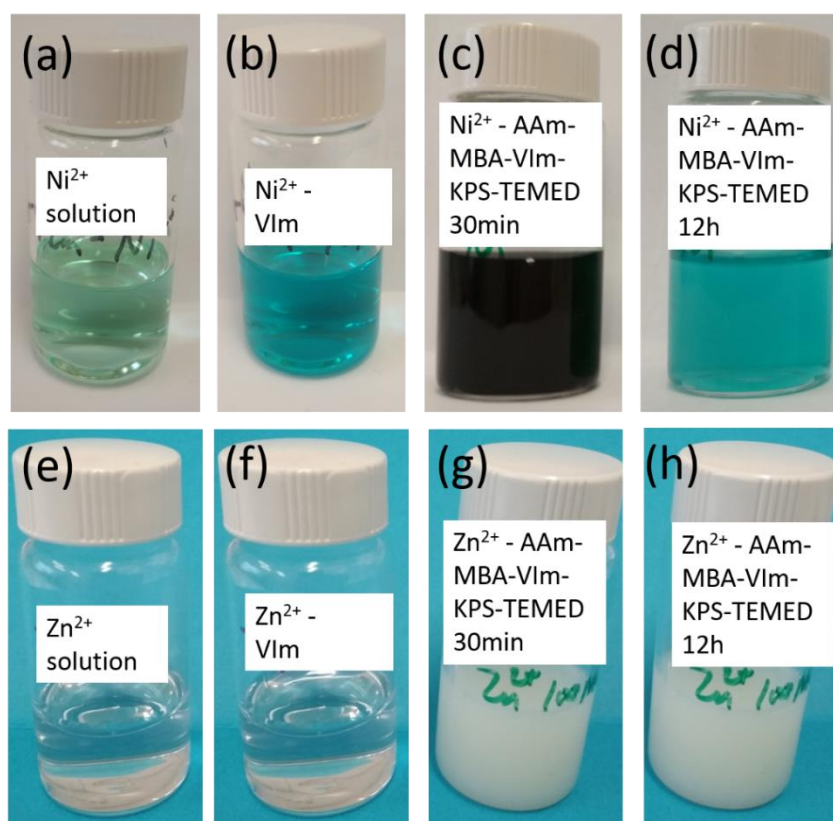


Figure 6. The color and turbidity change during polymerization.

In order to investigate the reason of the change in turbidity, a series of complementary experiments were carried out, and the reaction between KPS and metal ions was found to be responsible. **Figure 7a, b, c** show the reaction between KPS and the Ni^{2+} solution, once KPS and TEMED are added (to accelerate the polymerization reaction, and to keep the same reaction speed as the preparation of gels) in the Ni^{2+} solution, a black precipitate appeared (**Figure 7b**). Though this black precipitate has not been analyzed, from the appearance, it was suggested to be Nickel(III) oxide or Nickel oxide hydroxide NiOOH , due to the interaction between Ni^{2+} and the strongly oxidizing radical produced by KPS²⁴. The precipitate did mostly disappear in several hours (**Figure 7c**) due to the slightly acidic environment ($\text{pH} = 6.8$). This can be the explanation for the appearance and disappearance of the turbidity during polymerization. As for Zn^{2+} , a white precipitate was observed after adding KPS and TEMED, which was suggested to be Zinc oxide ZnO . Unlike the black precipitate in Ni^{2+} solution, this precipitate didn't disappear, which is the reason why the Ni^{2+} gel is white.

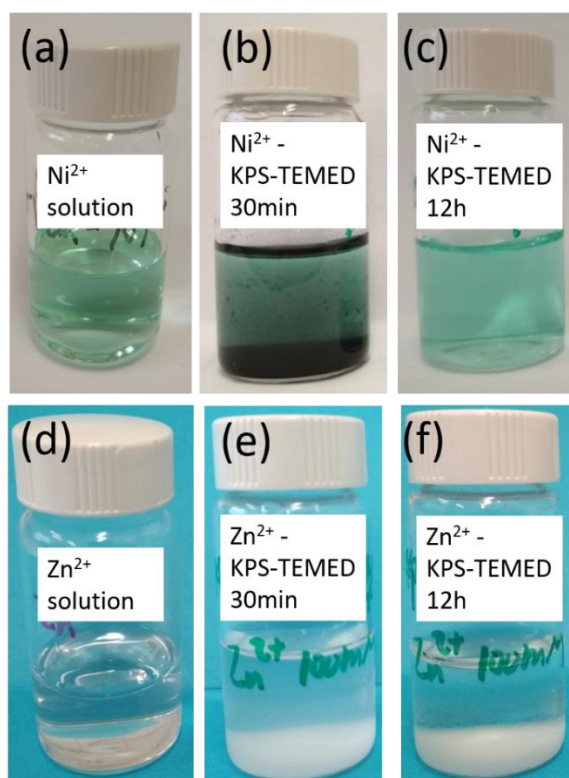


Figure 7. The precipitate during polymerization.

The existence of metal oxide in the gels (ZnO and a small amount of NiOOH) can be a second reinforcing mechanism for the dual crosslink gels. These metal particles might interact with imidazole groups with a different affinity. Persulfate radicals are consumed for oxidation thus less available for the radical polymerization which could also lead to a different chemical crosslinking density in dual crosslink gels than in the pure chemical gels. For the following work, we used the AAm-VIm- M^{2+} system, as prepared, initially assuming that the majority of metal ions were not oxydated and could serve as physical crosslinks as expected. The impact of the secondary reaction with KPS will be discussed in the following sections when necessary.

4.4.2 Chemically crosslinked hydrogels

Uniaxial stretching experiments were performed to characterize the nonlinear behavior of the chemically crosslinked gels, in order to clarify the effect of the chemical crosslink density on the extensibility of the gel, and to choose the most appropriate chemical crosslink density for the dual crosslink gels. Tensile stress-strain curves of the chemical crosslink gels with different MBA concentrations at the same strain rate $\dot{\lambda} = 0.03 \text{ s}^{-1}$ are shown in **Figure 8**. The extensibility dramatically increases with decreasing concentration of MBA, with the value of λ at break increasing from 2 to over 5. The moduli show the opposite trend as expected, with a decreasing value of E with decreasing [MBA]. The highest extensibility and lowest modulus gel (presumably explained by the loosely crosslinked network structure) is in principle ideal for dual crosslink gels, by analogy with the PVA-borax dual crosslink hydrogels. The chemical gel with [MBA] = 0.1 mol% has the highest extensibility, however, with such an extremely low modulus, it was hard to manipulate and perform experiments on it.

The linear viscoelastic properties of the chemical gels were studied by oscillatory shear measurements. **Figure 9a** shows the frequency dependence of the elastic modulus $G'(\omega)$. The

chemical gels with the higher MBA concentration $[MBA] = 0.2, 0.3 \text{ mol\%}$) exhibit a typical elastic solid behavior, while the moduli of gels with $[MBA] = 0.1, 0.15 \text{ mol\%}$) varies slightly with frequency (less than 0.5 kPa). The value of the modulus at the elastic plateau (for gels with low MBA concentration, the value was taken at $\omega = 100 \text{ rad/s}$) increases with MBA concentration (**Figure 9b**) and the gelation limit is expected to be around 0.05 mol%.

Combining the tensile and rheological properties, the chemical gel with $[MBA] = 0.15 \text{ mol\%}$, and stretch at break λ_b close to 5 and $G' = 1 \text{ kPa}$, was chosen as base composition to further study the properties of the dual crosslink hydrogels.

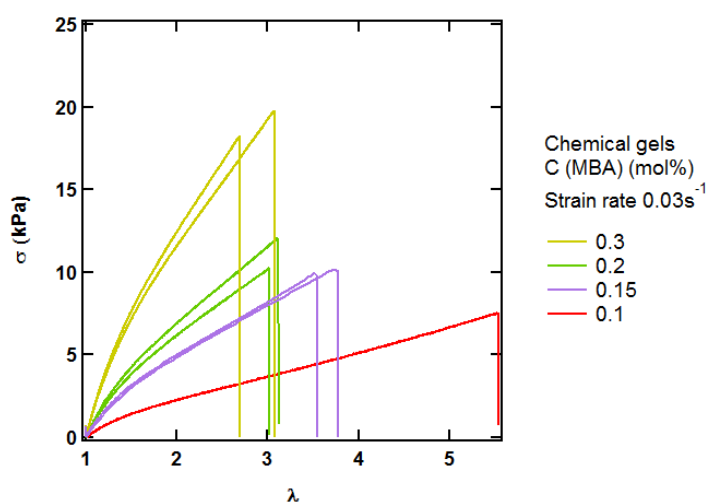


Figure 8. Stress-strain curves of the AAm-VIm chemical crosslink gels with different concentration of chemical cross-linker MBA.

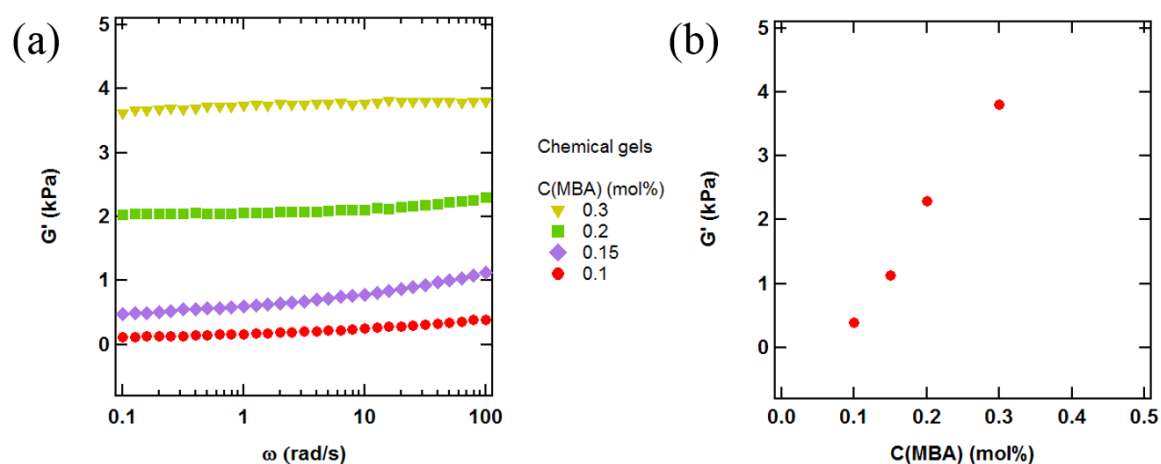


Figure 9. Rheological properties of the AAm-VIm chemical crosslink gels with different concentrations of chemical cross-linker MBA.

4.4.3 Effect of the concentration of physical crosslinks

The effect of the physical crosslink density was studied for a fixed chemical crosslink density $[\text{MBA}] = 0.15 \text{ mol\%}$. Both rheological (linear) and tensile (non-linear) properties of dual crosslink hydrogels with Ni^{2+} were investigated.

4.4.3.1 Rheological properties

The linear viscoelastic properties of dual crosslink gels with different Ni^{2+} concentrations ($[\text{Ni}^{2+}] = 5, 20 \text{ and } 100 \text{ mM}$) at a fixed $[\text{MBA}]$ were investigated. To compare the moduli of dual crosslink gels with different $[\text{Ni}^{2+}]$, **Figure 10** shows the values of G' and G'' at 5°C (the results at 5°C are chosen for clarity, and those at 25°C and other temperature are shown later in this subsection). For chemical gels with $[\text{MBA}] = 0.15 \text{ mol\%}$, we found a very weak frequency dependency of G' . The value of the modulus at the elastic plateau was measured as around 1 kPa. The value of G'' was very low (0.05 – 0.4 kPa). For dual crosslink gels with $[\text{Ni}^{2+}] = 100 \text{ mM}$, we found an elastic plateau at high frequency over 20 rad/s and G' decreased with

decreasing frequency, approaching the value of G' of the chemical gel. Gels with $[\text{Ni}^{2+}] = 5$ and 20 mM, follow the same trend as the gel with $[\text{Ni}^{2+}] = 100$ mM, though no clear elastic plateau was observed in the accessible frequency range. Over the whole frequency range, the value of G' increased with Ni^{2+} concentration relative to the corresponding chemical gels. For G'' shown in Figure 10b, we found single large peaks for all the Ni^{2+} concentration tested, correlated with the decrease in G' . This result indicates that the dissociation of the physical crosslinks by Im-metal ion interactions induce a large dissipation at this frequency. The values of G''_{peak} increased with $[\text{Ni}^{2+}]$. Globally the linear rheological responses of this gel system corresponds to the physical picture of the dual crosslink gel: the physical crosslinks contribute to the moduli additively to the chemical crosslinks and the dynamics of the physical crosslink breaking is observed as a single peak in G'' over the observable frequency range.

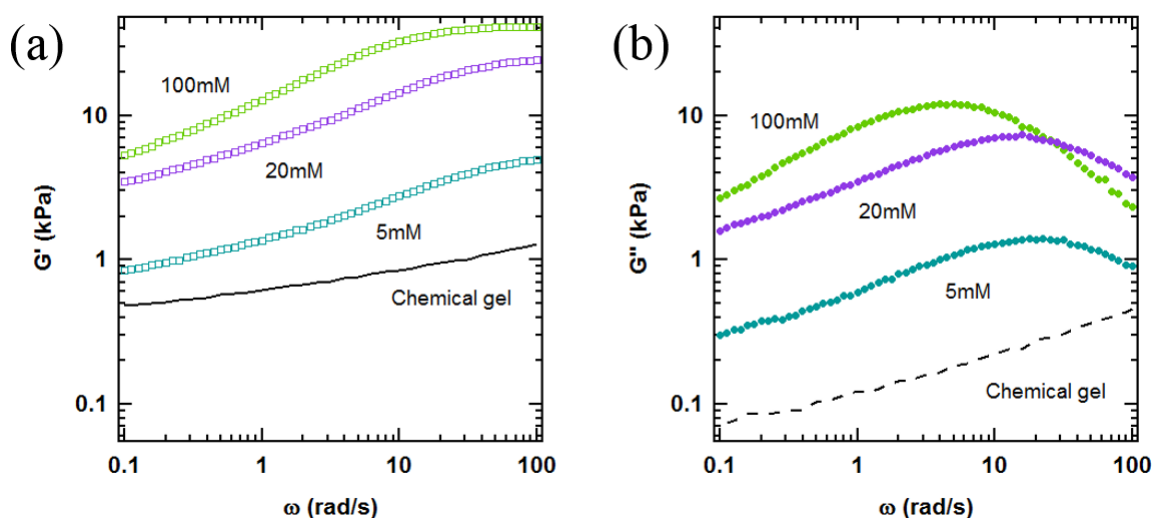


Figure 10. Angular frequency dependence of $G'(\omega)$ (a) and $G''(\omega)$ (b) of the dual crosslink gels with different Ni^{2+} concentrations and compared with the chemical gel at 5 °C.

Let us now comment on the Ni^{2+} concentration dependence of the moduli. **Figure 11a** shows the value of G'' at the peak. It increases clearly with $[\text{Ni}^{2+}]$, indicating that the number of effective physical crosslink increased with $[\text{Ni}^{2+}]$. The vinylimidazole concentration in the feed being 200 mM, if we assume that two imidazole groups complex with one Ni^{2+} ion, at $\text{Ni}^{2+} =$

100 mM, the physical crosslinking should saturate. Consistently, the same gel prepared at Ni^{2+} = 200 mM did not show particular differences with that at 100 mM.

The relaxation time τ_R of gels with $[\text{Ni}^{2+}]$ = 5, 20, 100 mM is 0.045, 0.063 and 0.251 s, respectively (**Figure 11b**) indicating that τ_R increases with Ni^{2+} concentration.

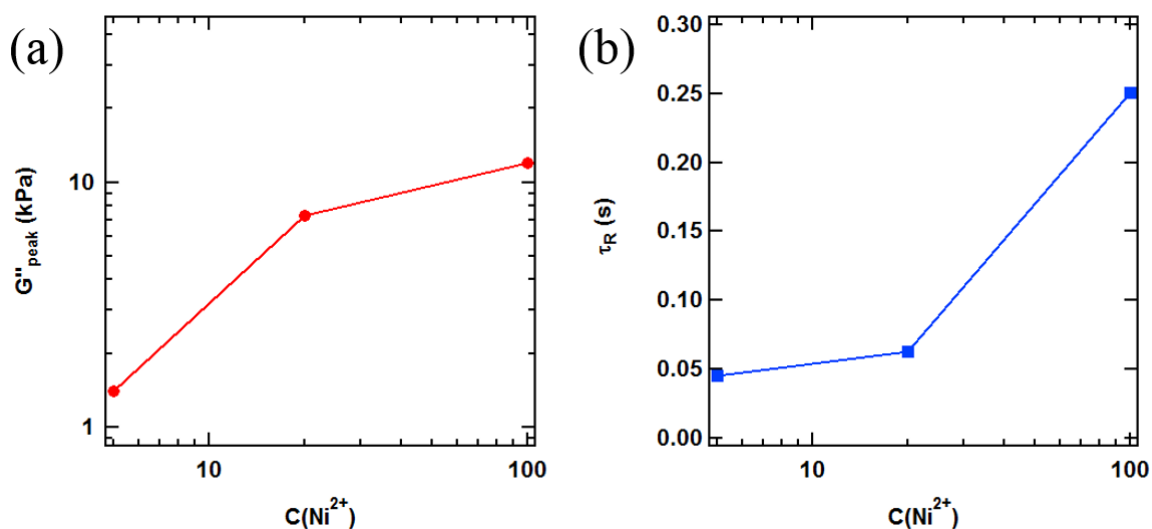


Figure 11. G''_{peak} (a) and relaxation time τ_R (b) of dual crosslink gels as a function of Ni^{2+} concentration at 5 °C.

The frequency dependence of G' and G'' for dual crosslink gels and for the corresponding chemical gel were also investigated at different temperature (5, 10, 15, 20, 25°C) (**Figure 12a, c, e**). For gels with low Ni^{2+} concentration, the peaks at high temperature are located out of the accessible range ($\omega > 100$ rad/s), which is the reason why 5 °C was chosen to discuss the effect of ion concentration (**Figure 10**). Time-temperature superposition curves are shown in **Figure 12b, d, f**, from which, the values of the energy barrier activation energy E_a were obtained: 64.0 kJ/mol for $[\text{Ni}^{2+}]$ = 5 mM), 60.8 kJ/mol for $[\text{Ni}^{2+}]$ = 20 mM), 80.9 kJ/mol for $[\text{Ni}^{2+}]$ = 100 mM). For the same polymer in solution (without chemical crosslinks) the activation energy was measured to be 86 kJ/mol (for a polymer concentration of 4 %, $[\text{Ni}^{2+}]$ = 2 mM)²⁵.

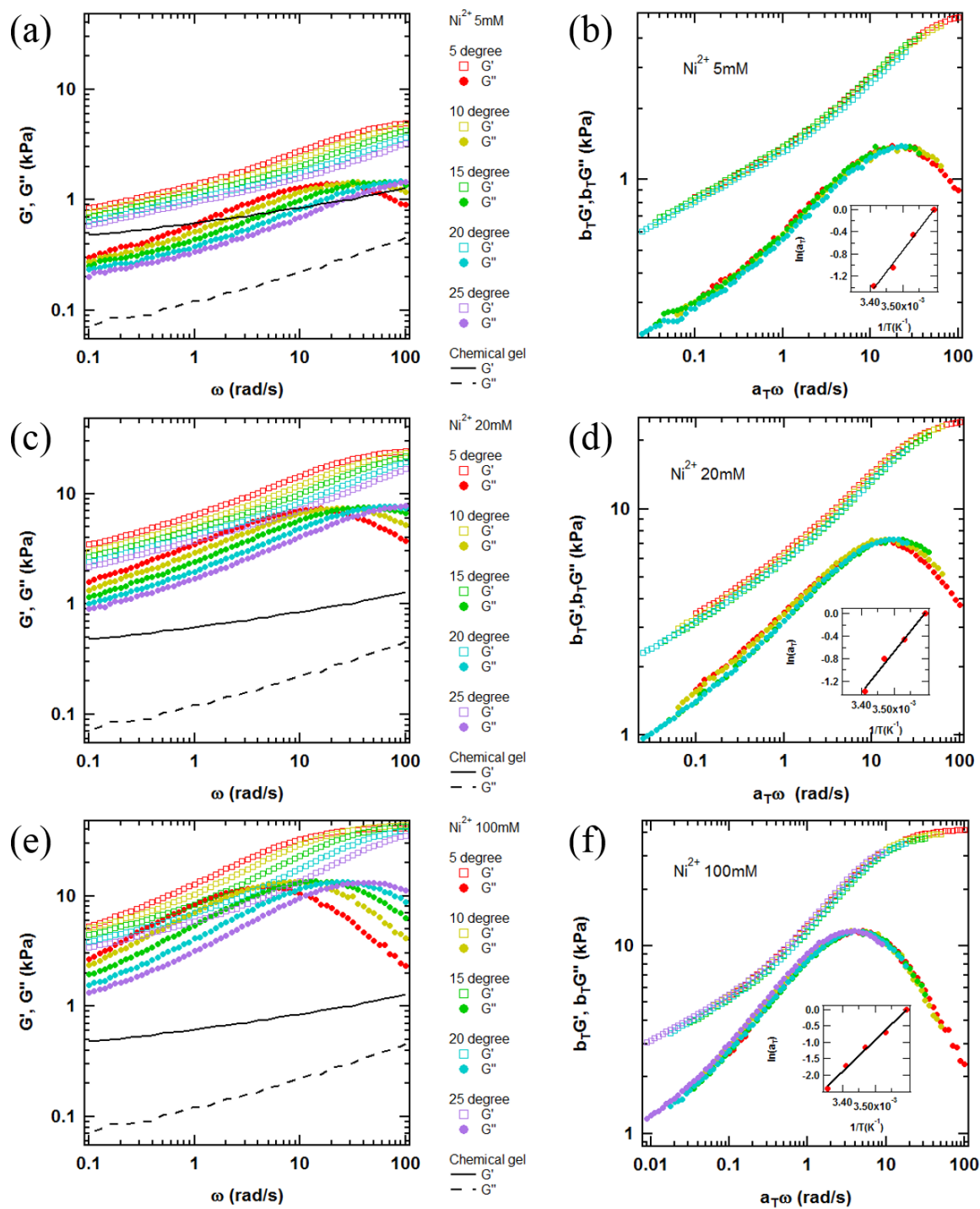


Figure 12. (a, c, e) Angular frequency dependence of $G'(\omega)$ and $G''(\omega)$ of the dual crosslink gels with different Ni^{2+} concentrations and compared with the chemical gel at different temperature. (b, d, f) Time-temperature superposition of these dual crosslink gels.

4.4.3.2 Large strain properties

We then performed uniaxial stretching experiments at room temperature to characterize the nonlinear (large strain) behavior of the dual crosslink gels, in order to clarify the effect of physical crosslinking density on the extensibility and modulus. Tensile stress - strain curves of the dual crosslink gels with different values of $[\text{Ni}^{2+}]$ and of the corresponding chemical gel at the same stretch rate $\dot{\lambda} = 0.06 \text{ s}^{-1}$ are shown in **Figure 13**. For all values of $[\text{Ni}^{2+}]$, the dual crosslink gels have higher extensibilities than the chemical gel, the extensibility dramatically increases with the introduction of physical crosslinks, with a value of λ_b varying from less than 4 for the chemical gel to over 6. λ_b also increases significantly with $[\text{Ni}^{2+}]$ from 6 to close to 9. The moduli showed a more complex $[\text{Ni}^{2+}]$ dependence. The increase of $[\text{Ni}^{2+}]$ leads to a significant increase of the stiffness over the whole range. For gels with high $[\text{Ni}^{2+}]$, the ‘S-shaped’ curves resemble more those of a strain crystallizing rubber such as natural rubber or a pressure-sensitive-adhesive: softening at intermediate strains, which indicates the breakup of a network structure, and strain hardening at large strain indicating finite extensibility of the polymer chains. For gels with low Ni^{2+} concentration (5 mM), the stress-strain curve is similar to that of the chemical gel, but with much higher extensibility.

It should be pointed out however that the modulus of the dual crosslink gel with $[\text{Ni}^{2+}] = 5 \text{ mM}$ is lower than that of the chemical gel. We assume that this discrepancy is due to the presence of nickel ions during the polymerization and therefore to the existence of small amounts of nickel oxide which reduces the chemical crosslinking density in the dual crosslink gel.

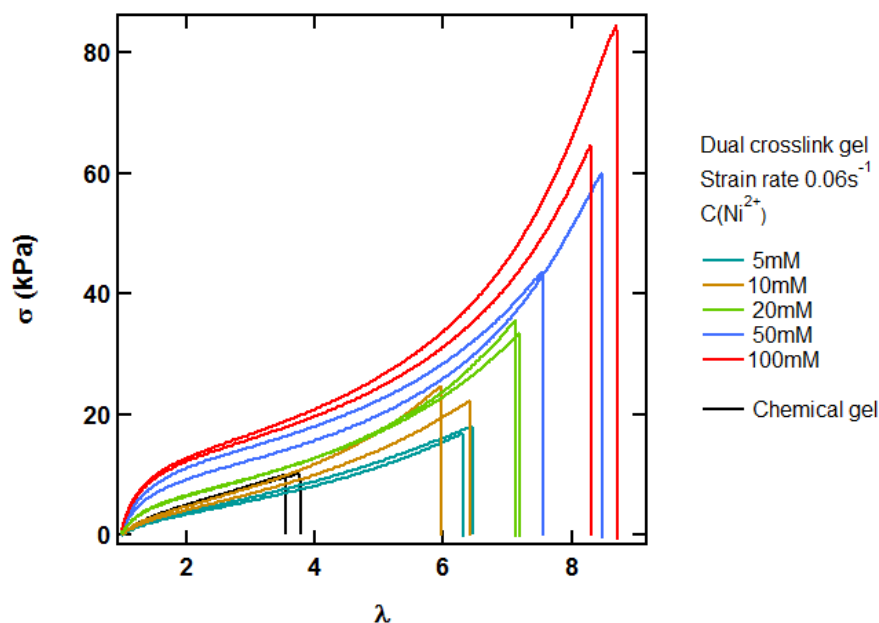


Figure 13. Stress - strain curves of the dual crosslink gels with different Ni^{2+} concentrations compared with the corresponding chemical gels at a stretch rate of 0.06 s^{-1} .

4.4.3.3 Strain rate dependent behavior

To observe the recovery of the physical crosslinks, tensile tests with loading and unloading cycles were performed. The energy dissipation, which is responsible for enhanced toughness in soft materials, can be identified by the hysteresis exhibited between loading and unloading tests. The loading and unloading cycles were conducted at a constant strain rate of $\pm 0.03 \text{ s}^{-1}$. During a cycle, the gel specimen was stretched to $\lambda = 2$ and returned to $\lambda = 1$, then the cycle was repeated after 30 min of rest time¹. **Figure 14** shows two consecutive cycles in the dual crosslink gel with $[\text{Ni}^{2+}] = 100 \text{ mM}$ and it is clear that the sample recovered completely: the loading and unloading curves for the first and second cycle lie right on top of each other. This result proves the complete healing of the physical crosslinks. All the dual crosslink gels with different

¹ 30min is sufficient for the gels to recover, but it's not the minimum time to fully recover. The minimum recovery time for each gel is different, so I used the same time in all experiments, which is sufficient for every gel.

physical crosslinking concentrations were tested and showed the same result. Based on this full recovery behavior, cyclic tests with different strain rates were conducted to further investigate the effect of the physical crosslinking density on the time-dependent dissipative and recovery processes.

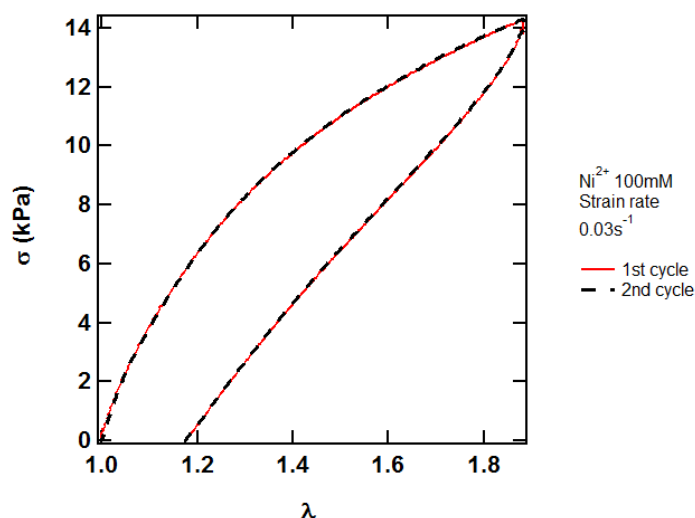


Figure 14. Stress-strain curves in repeated tests with loading and unloading cycles of the same dual crosslink gel sample.

The loading and unloading cycles were performed at different strain rates (0.03 , 0.01 , 0.003 s^{-1}), on the chemical gel and its corresponding dual crosslink gels with three different Ni^{2+} concentrations (5 , 20 , 100 mM) (**Figure 15**). The dissipated strain energy during the cycle, corresponding to the area within the loop, is induced by the physical crosslinking. The chemical gel behaves like a purely elastic system (**Figure 15a**), while the dissipated strain energy significantly increases with $[\text{Ni}^{2+}]$. For each dual crosslink gel, the curves show a strain rate dependent behavior, and higher modulus with higher strain rate. It is less obvious for dual crosslink gel with $[\text{Ni}^{2+}] = 5 \text{ mM}$, which has similar behavior with chemical gel, due to its very fast exchange rate.

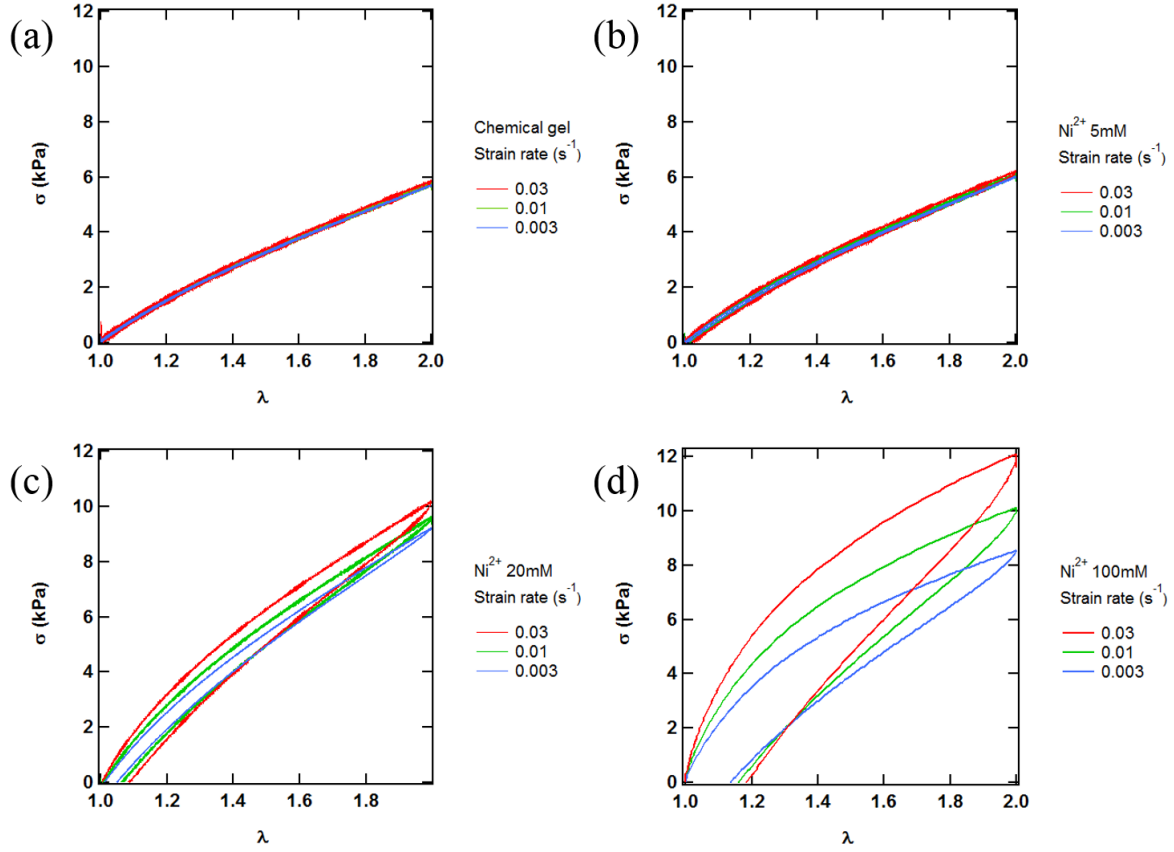


Figure 15. Stress-strain curves of loading and unloading cycles with different strain rate.

4.4.4 Tunable mechanics

As shown in the rheological results, by changing the concentration of nickel, the relaxation time can only be tuned within one decade. As mentioned in the introduction, according to the divalent metal kinetics^{16,17}, these transient metal ions have very different relaxation times, Cu^{2+} and Zn^{2+} for example, are much faster than Ni^{2+} . The rate-limiting step for coordination is usually the dissociation step, which follows the same order. By changing ions, we expect to control the active crosslinks and modulate the relaxation time of the dual crosslink gel and their corresponding energy dissipation modes.

Here, we choose Zn^{2+} as a relatively fast transient metal ion to study the tunable mechanics of dual crosslink hydrogels with metal-ligand coordination.

4.4.4.1 Rheological properties

The linear viscoelastic properties of dual crosslink gels with Zn^{2+} ($[\text{Zn}^{2+}] = 100 \text{ mM}$) at a fixed $[\text{MBA}] = 0.15 \text{ mol\%}$ were investigated. **Figure 16a** shows the frequency dependence of G' and G'' for dual crosslink gels and for the corresponding chemical gel, at different temperature (5, 15, 25 °C), G' is higher than G'' , both G' and G'' decrease over the whole range. **Figure 16b** shows the comparison of the linear viscoelastic properties of Ni^{2+} and Zn^{2+} dual crosslink gels at 5°C. Compared to the Ni^{2+} gel, the Zn^{2+} gel has a lower G' in the whole frequency range, and no elastic plateau at high frequency. Since the dissociation kinetics of $\text{Zn}^{2+} - \text{Im}$ is much faster than that of $\text{Ni}^{2+} - \text{Im}$, the peak of G'' is not accessible on the rheometer time scale. From the curves, we can deduce that the relaxation time of Zn^{2+} gel is about 400 times faster than Ni^{2+} gel, confirming that the goal of changing relaxation time by a wide range can be achieved.

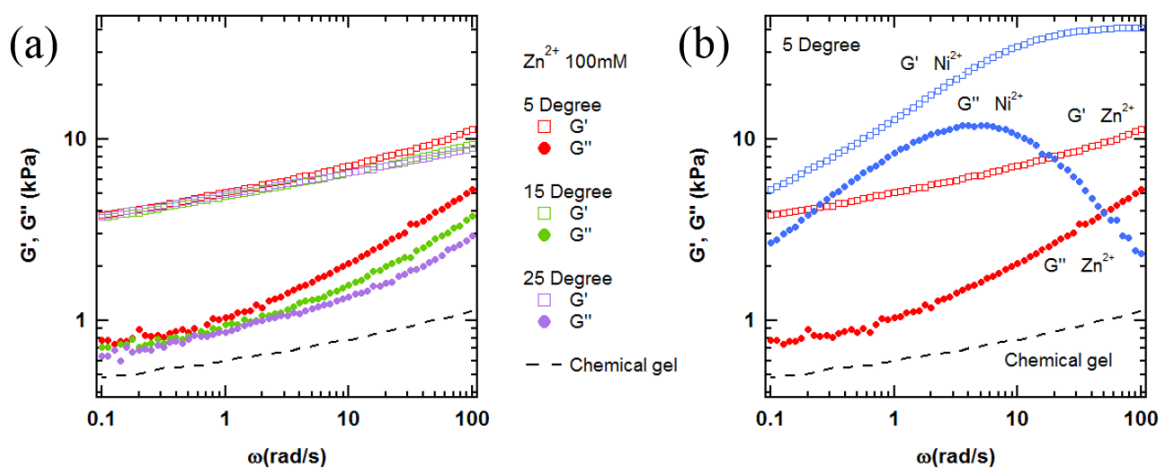


Figure 16. (a) Angular frequency dependence of $G'(\omega)$ and $G''(\omega)$ of the dual crosslink gels with different $C(\text{Zn}^{2+}) = 100 \text{ mM}$ at different temperatures. **(b)** Comparison of dual crosslink gels with same concentration of Ni^{2+} and Zn^{2+} (100 mM), at 5 °C.

4.4.4.2 Strain rate dependent nonlinear properties

Uniaxial stretching experiments with different strain rates were then performed, to characterize the nonlinear (large strain) behavior of the dual crosslink gels, in order to clarify the effect of

different ions on the extensibility and modulus, and the strain rate dependency. Tensile stress - strain curves of the dual crosslink gels with the same concentration (100 mM) of Ni^{2+} and Zn^{2+} at various strain rates $\dot{\lambda}$ (from 0.9 to 0.0003 s^{-1}), and of the corresponding chemical gel at the strain rate $\dot{\lambda} = 0.03 \text{ s}^{-1}$, are shown in **Figure 17a, c**. Both dual crosslink gels have a strong strain rate dependent behavior, compared to the chemical gel, both extensibility and modulus dramatically increase, the extensibility doesn't change much with strain rate. At low strain rate, both gels behave like pure elastic chemical gel, but with much higher extensibility. At high strain rate, both gels have rubber elastic behavior: softening at intermediate strains, and strain hardening at large strain. Comparing the stress-strain curves of gels with different ions, it is obvious that the Ni^{2+} gel has a much higher modulus than Zn^{2+} gel at any strain rate, while the extensibility of Zn^{2+} gel is slightly higher than that of Ni^{2+} gel.

To further analyze the details of the stress strain relationship and the contribution of crosslinks, the Mooney representation of the stress, classically used in rubber elasticity, can be used^{26,27}. This representation of the data reveals the relationship between Mooney stress (reduced stress, defined in **Eq.(1)**) and stretch λ . In the original Mooney-Rivlin model, adapted for elastic rubbers, the reduced stress (**Eq.(2)**) can be decomposed into a stretch independent term C_1 and a stretch dependent term. When $C_2 = 0$, the model corresponds to the classical neo-Hookean model; $C_2 > 0$ means a softening occurs in uniaxial tension; if a strain hardening appears, then $C_2 < 0$.

$$\sigma_{Mooney} = \frac{\sigma_N}{\lambda - \frac{1}{\lambda^2}} \quad (1)$$

$$\sigma_{Mooney} = 2C_1 + \frac{2C_2}{\lambda} \quad (2)$$

Based on these stress-strain curves, the Mooney stress (reduced stress) can be plotted as a function of λ^{-1} (**Figure 17b, d**). As we expected, the reduced stress of the chemical gel at an initial strain rate of 0.03 s^{-1} is almost independent of λ^{-1} , which indicates that, in the absence of physical bonds, there is also little effect of polymer entanglements and their uniaxial deformation is well described by the rubber elasticity model. The constant value of the reduced stress is equivalent to the modulus. For dual crosslink gels, the values of reduced stress are higher than that of the chemical gel over the whole range of λ , even at very low strain rates, which can be explained by the existence of the slow components. At almost all strain rates, a non-linear viscoelastic softening occurs in the small λ region ($\lambda^{-1} > 0.3$): with decrease in λ^{-1} (thus increase in λ) the reduced stress decreases. In the large λ region ($\lambda^{-1} < 0.2$), the reduced stress increases, or a strain hardening appears.

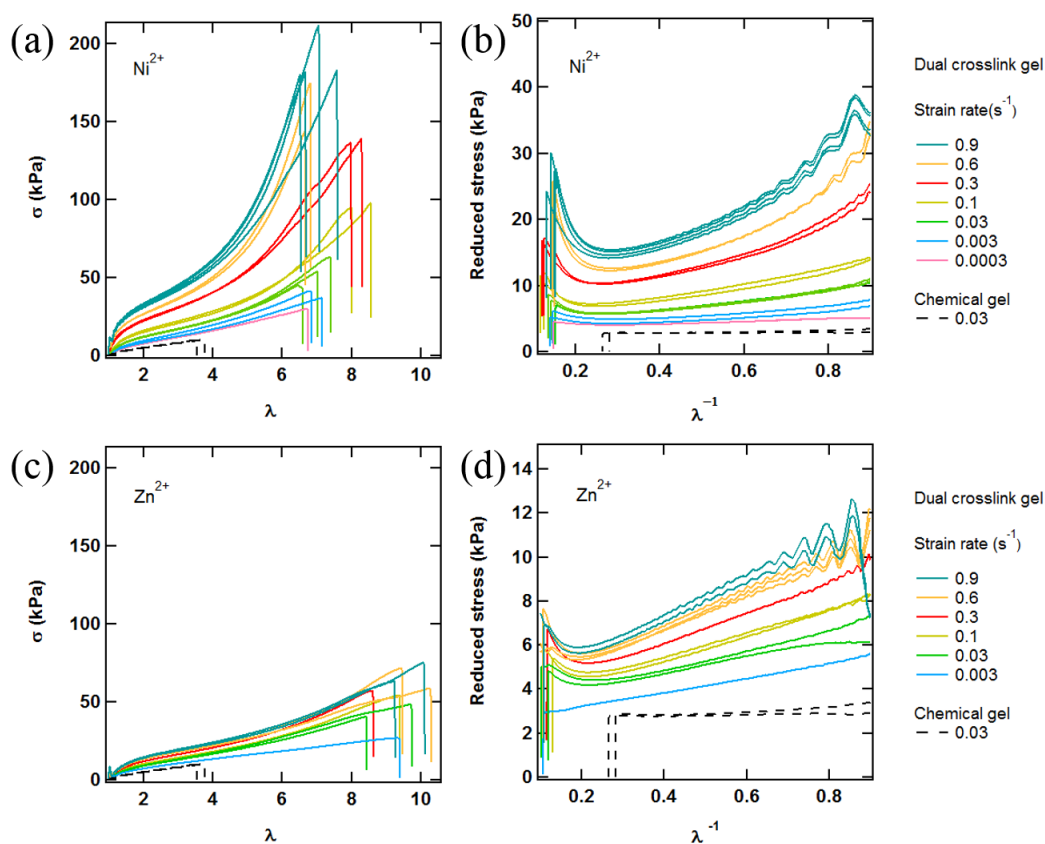


Figure 17. Stress-strain curves of dual crosslink gels with $C(\text{Ni}^{2+}) = 100 \text{ mM}$ (a), $C(\text{Zn}^{2+}) = 100 \text{ mM}$ (c), and the corresponding Mooney plots (b, d).

In order to further characterize the strain hardening behavior, the values of the stretch λ^{-1} at which the strain hardening starts to occur were studied. Based on the Mooney plots, the minimum of the reduced stress $f_{\min}^*$ before the failure of the samples, was defined as the point of onset of the strain hardening. The values of $f_{\min}^*$ and those of the corresponding stretch $\lambda_{\min}^{-1}$ are plotted as a function of strain rate in **Figure 18**. For both gels, $f_{\min}^*$ increases dramatically with strain rate (**Figure 18a**). Since this increase is due to the dynamics of the physical crosslinks, at slower stretching the physical bonds can exchange more effectively and relax the stress leading to a lower value of $f_{\min}^*$.

The values of $\lambda_{\min}^{-1}$ and $\lambda_{\min}$ are plotted as a function of the strain rate in **Figure 18b** and **c**. We observed a slight strain rate dependence of $\lambda_{\min}$ (and $\lambda_{\min}^{-1}$). As shown in the figures, for the gel with Ni^{2+} , with the decreasing of strain rate, the value of $\lambda_{\min}^{-1}$ decreases from 0.28 ($\lambda = 3.57$, $\dot{\lambda} = 0.9 \text{ s}^{-1}$) to 0.23 ($\lambda = 4.35$, $\dot{\lambda} = 0.03 \text{ s}^{-1}$), then increase back to 0.29 ($\lambda = 3.45$, $\dot{\lambda} < 0.003 \text{ s}^{-1}$) although error bars are large for these slow strain rates. For the gel with Zn^{2+} , the value increases from 0.194 ($\lambda = 5.15$, $\dot{\lambda} = 0.9 \text{ s}^{-1}$) to 0.213 ($\lambda = 4.69$, $\dot{\lambda} = 0.3 \text{ s}^{-1}$), then remains relatively constant from 0.21 to 0.215 ($\lambda = 4.76\text{-}4.65$, $\dot{\lambda} < 0.3 \text{ s}^{-1}$). This change in $\lambda_{\min}^{-1}$ indicates the possibility of the existence of a second longer relaxation time. To see this change more clearly, $\lambda_{\min}$ was plotted as a function of strain rate directly (**Figure 18c**). The corresponding $\lambda_{\min}$ for strain hardening of Zn^{2+} gel is higher than for the Ni^{2+} gel. Though the metal-radical interactions may have influenced the polymerization and therefore the structure of the network, the error bars are too big to detect a trend of each gel.

If the observed strain hardening is due the non-Gaussian stretch of the chains, the value of $\lambda_{\min}$ is expected to be related to the chain length between the effective crosslinks, thus it should decrease with increase in $f_{\min}^*$. We do not see any clear correlation between the two values. In fact each elastically active chain between physical crosslinks can have a different value of

stretch from the macroscopic value, since the physical crosslinks can break and heal during the continuous stretching and healed chains are stretched with a new reference state of deformation. If the strain hardening is due to the non-Gaussian stretch of the chains between chemical crosslinks (containing many transient physical crosslinks), then $\lambda_{\min}^{-1}$ is expected to be independent of the strain rate. Strain hardening can occur if the number of the closed physical crosslinks increases with stretch. We did not check if the corresponding physical gel can show shear thickening.

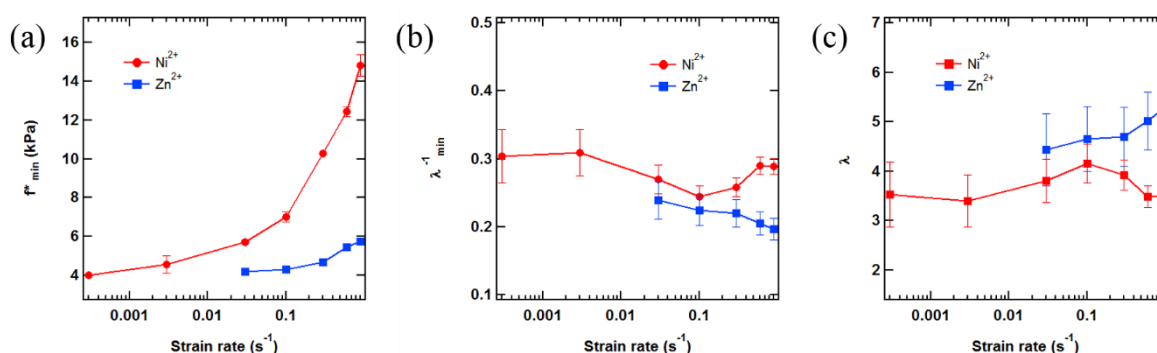


Figure 18. The minimum value of reduced stress $f_{\min}^*$ (a), the corresponding value of $\lambda_{\min}^{-1}$ (b) and λ (c) as a function of strain rate of Ni^{2+} (red) and Zn^{2+} (blue) dual crosslink gels. Error bars were calculated by increasing the value of $f_{\min}^*$ by 0.05 kPa.

4.4.4.3 Step-cycle extension

In order to investigate the energy dissipation and the potential damages of the dual crosslink gels, loading unloading step-cycle extension tests at incremental values of strain were performed at room temperature, with a constant strain rate $\dot{\lambda} = 0.3 \text{ s}^{-1}$. The samples were loaded from $\lambda = 1$ to $\lambda = 1.5$ and unloaded back to $\lambda = 1$, then the strain was increased to $\lambda = 2$ after 30 min of rest time, the stretch was increased by $\lambda = 0.5$ for each loop until the samples broke. **Figure 19** shows the step-cycle curves of dual crosslink gels with Ni^{2+} and Zn^{2+} . These two gels show similar dissipative behaviors, except that the Ni^{2+} gel has a higher modulus and lower

extensibility, consistent with the tensile uniaxial stretching result. A remaining residual extension was observed for both gels in large strain, due to a permanent change in the structure.

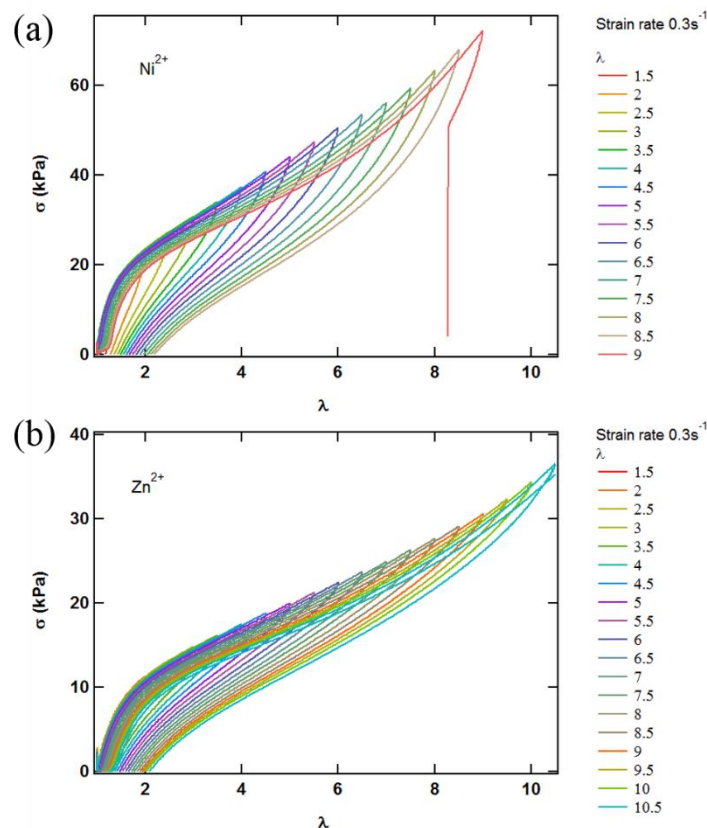


Figure 19. Step-cycle extension tests of dual crosslink gels with $C(\text{Ni}^{2+}) = 100 \text{ mM}$ (a), $C(\text{Zn}^{2+}) = 100 \text{ mM}$ (b).

The dissipation of energy is further studied to understand the dissipative behavior. As shown in **Figure 20**, the hysteresis (Hys) of each loop can be calculated by integrating the area between the loading and unloading curves, while the normalized hysteresis (Hys/W) is the ratio of the hysteresis to the total energy which can be determined by the area under the loading curve of each loop. The initial modulus of each loop E_{initial} can be determined by fitting the loading curves at low deformation.

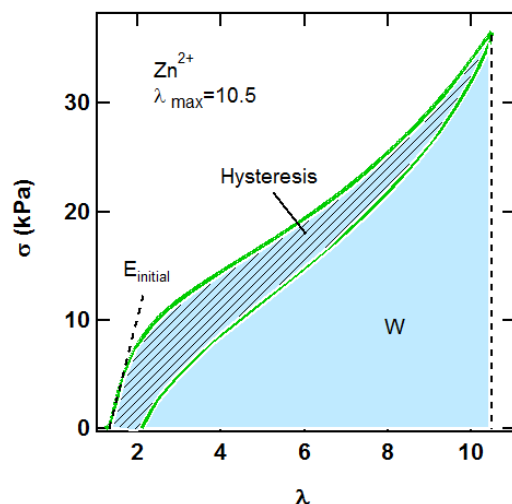


Figure 20. The calculation of the hysteresis (Hys), normalized hysteresis (Hys/W) and the initial modulus (E_{initial}).

The initial modulus and normalized hysteresis as a function of the maximum stretch ratio λ_{max} of each loop is shown in **Figure 21**. The Ni^{2+} gel has higher initial modulus (55 to 45 kPa) than the Zn^{2+} gel (20 to 15 kPa) at every λ_{max} . E_{initial} of both gels keep almost constant at small strain, then start to decrease slightly at large strain ($\lambda_{\text{max}} > 4$), which indicates the irreversible damage of the network at large strain. The values of Hys/W of both gels decrease with λ_{max} , which indicates the gels become more elastic with the increase of the maximum strain. This suggests that the strain hardening is less rate dependent than the softening and if there is a second characteristic relaxation time controlling the strain hardening it is rather long.

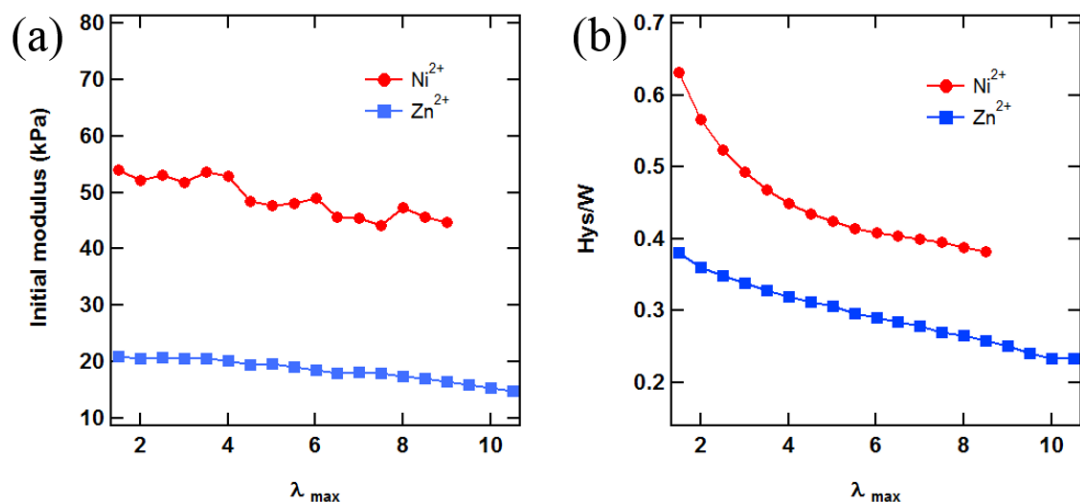


Figure 21. Initial modulus (a) and energy dissipation (b) and as a function of the maximum stretch ratio $\lambda_{\max}$ of each loop of dual crosslink gels with $C(\text{Ni}^{2+}) = 100 \text{ mM}$ (red), $C(\text{Zn}^{2+}) = 100 \text{ mM}$ (blue).

4.4.4.4 Stress-strain relationship at small strain

A series of loading and unloading cycles up to $\lambda = 2$ was performed at seven different strain rates (0.0003, 0.01, 0.003, 0.01, 0.03, 0.1 and 0.3 s^{-1}) on dual crosslink gels with Ni^{2+} and Zn^{2+} at the same concentration (100 mM) (**Figure 22a, c**). These gel samples were not stretched to rupture, and the same sample was stretched repeatedly at different stretch rates after a sufficiently large recovery time of 30 min. These curves show strong strain rate dependence, higher modulus and hysteresis with higher strain rate, but the reduced stress $f^* = \sigma/(\lambda - \lambda^{-2})$ plotted as a function of time at various strain rates, superposed well on a master curve (**Figure 22b, d**). So, at small strain, the stress could be separated into a strain-dependent Neo-Hookean contribution term, and a time dependent term f^* deriving from the dynamics of the physical crosslinks.

The gel with Ni^{2+} has a higher modulus and hysteresis than the gel with Zn^{2+} at all strain rates. The separability of the time-dependent and strain-dependent terms holds well for dual crosslink gels with different metal ions in this strain range.

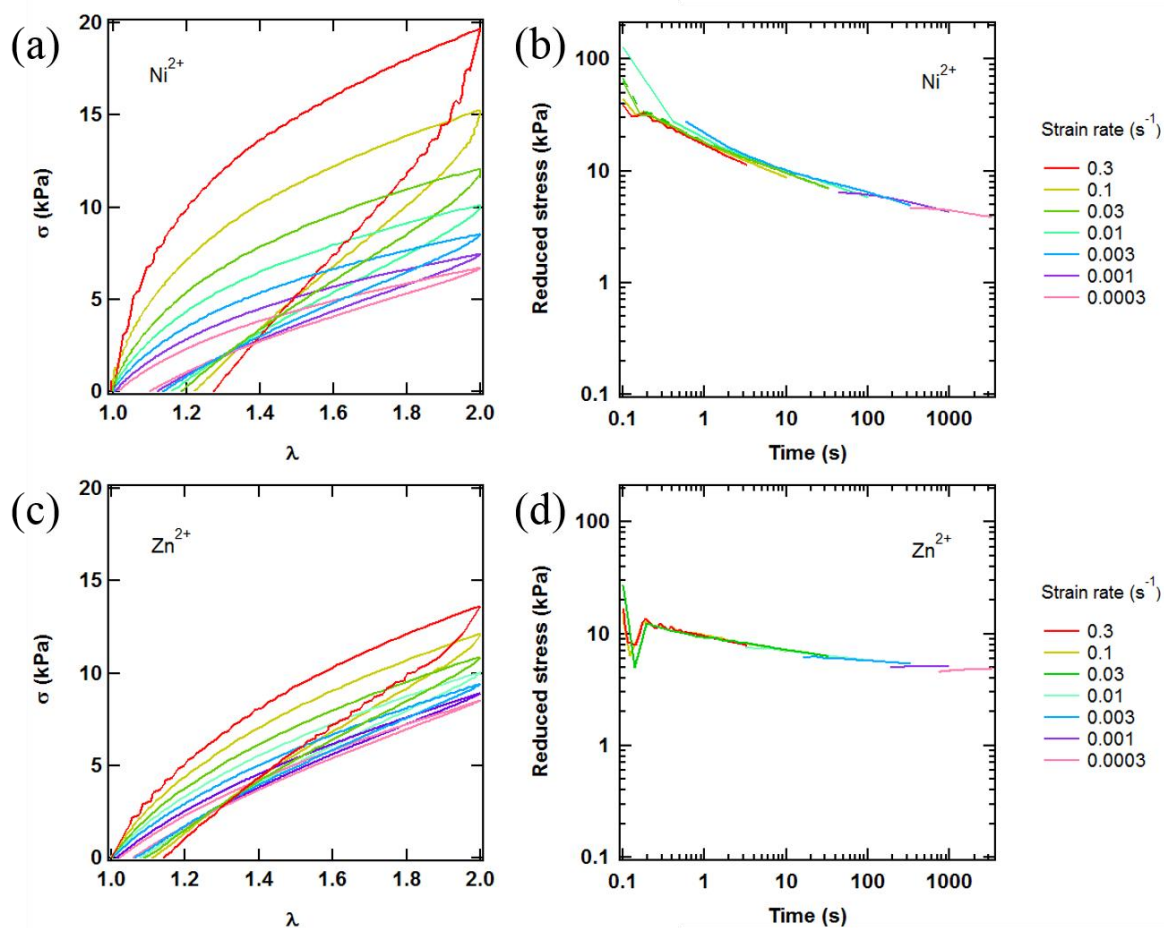


Figure 22. Stress-strain curves of loading and unloading cycles with different strain rate of dual crosslink gels with $C(\text{Ni}^{2+}) = 100 \text{ mM}$ (a), $C(\text{Zn}^{2+}) = 100 \text{ mM}$ (c), and the corresponding reduced stress from loading curves as a function of time (b, d).

4.4.4.5 Stress relaxation

To study the dynamic difference of dual crosslink gels with different ions, shear and tensile stress relaxation tests were carried out. First, the linear viscoelastic properties of Ni^{2+} and Zn^{2+} dual crosslink gels at 25°C were studied in a frequency sweep (**Figure 23a**). The same tendency as the tendency obtained at 5°C shown in **Figure 16b** was observed: G' of both gels decreases with decreasing frequency, the Ni^{2+} gel has a higher G' than the Zn^{2+} gel. At low frequency we observed a crossover ($\omega = 0.224 \text{ rad/s}$, $\tau = 4.46 \text{ s}$). For the same samples, the shear stress relaxation tests were performed at a strain of 1%. **Figure 23b** shows the relaxation modulus of

Ni^{2+} (red) and Zn^{2+} (blue) dual crosslink gels. The modulus of both gels decreases with time, the modulus of the Ni^{2+} gel is higher than that of the Zn^{2+} gel at short time region and lower than that of the Zn^{2+} gel after 3.1 s confirming the different behavior at low frequency. In order to compare the results in the frequency domain and in the time domain, the dynamic moduli $G^* = \sqrt{(G')^2 + (G'')^2}$ are also plotted as a function of t ($= 1/\omega$) (the Cox-Merz rule) in **Figure 23b** for both gels. It should be mentioned that for the dual crosslink gels the relaxation modulus and the dynamic modulus do not match: in fact during the stress relaxation, breaking and healing of the physical crosslink occurs and the healed bonds do not carry anymore the stress, while during the dynamic measurement the oscillatory deformation is continuous and the elastically active chains between healed bonds are deformed again. Thus the dynamic modulus is slightly higher than the relaxation modulus. The same result was obtained for PVA dual crosslink gel (data not shown).

With the physical picture we have of the dual crosslink gels, one would expect the modulus of the dual crosslink gel at low frequency to be equivalent to that of the corresponding chemical gel. Comparing the results on dual crosslink gels with the value of the dynamic modulus of the corresponding chemical gel, one can clearly see that even at 1000 s the dual crosslink gels do not fully relax and the existence of a slower relaxation mode is suggested. With these relaxation profiles it is not possible to apply the constitutive model discussed in Chapter 3 since it is based on a single relaxation mode.

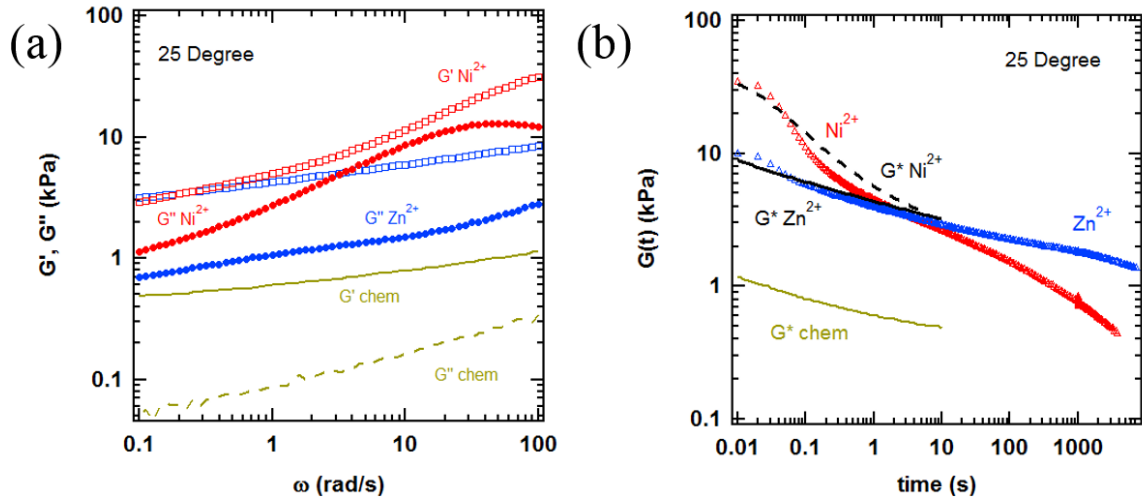


Figure 23. (a) $G'(\omega)$ and $G''(\omega)$ of the chemical gel (yellow) and the dual crosslink gels with Ni^{2+} (red) and Zn^{2+} (blue) at 25 °C. (b) Stress relaxation $G(t)$ as a function of time of the dual crosslink gels with Ni^{2+} (red) and Zn^{2+} (blue) at 25 °C, and the dynamic modulus of the chemical gel (yellow line) and the dual crosslink gels with Ni^{2+} (black dotted line) and Zn^{2+} (black solid line).

In the tensile stress relaxation experiment, a strain of 10 % was applied, and then kept constant and the reduced stress $\sigma_R = \frac{\sigma_N}{(\lambda - 1/\lambda^2)}$ as a function of time is plotted in **Figure 24a**. Comparing the values of $G(t)$ obtained from applying the Cox-Merz rule to the oscillatory shear data (Figure 23b) and the value of σ_R from the tensile relaxation data a similar qualitative trend is observed. These two methods show similar value of moduli at $t = 1$ s, but the shape of the relaxation is different, much faster in the oscillatory data than in the tensile data. It should be noted that the shear relaxation test lies in the linear region (strain 1%), while the tensile test nonlinear (10 %), suggesting that the slow mode relaxation is strain dependent. In order to verify this strain dependency, shear stress relaxation with different strains (1, 10 and 20 %) were compared in **Figure 24b** for the Zn^{2+} gel. With increasing applied strain, the modulus of the Zn^{2+} gel decreases with increasing strain, suggesting that the slower relaxation did not satisfy the separability between the strain- and time-dependent terms of the stress.

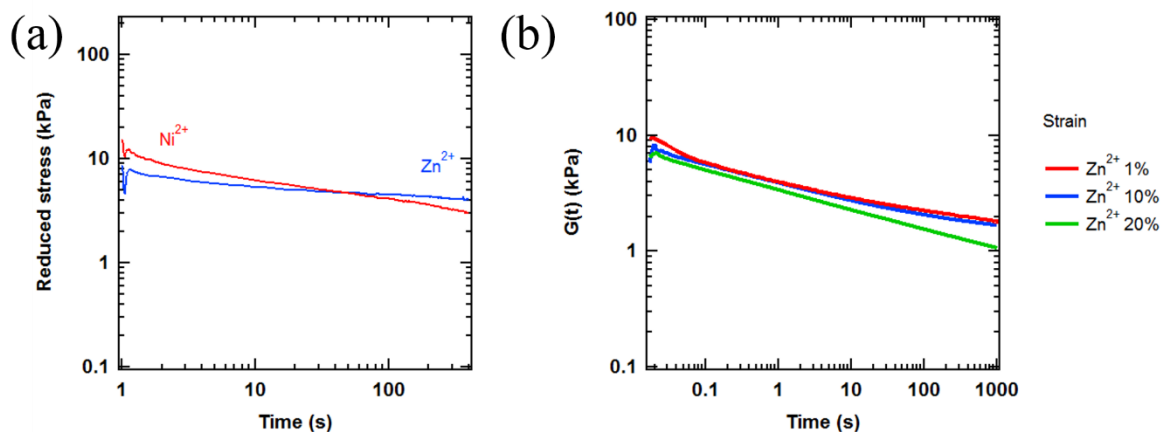


Figure 24. (a) Reduced stress f^* as a function of time of the dual crosslink gels with $C(\text{Ni}^{2+}) = 100$ mM (red) and $C(\text{Zn}^{2+}) = 100$ mM (blue) at room temperature. (b) Strain dependent of Zn^{2+} dual crosslink gel.

The relaxation curve of the Ni^{2+} gel indicates the existence of a second relaxation time, which corresponds to the hypothesis we made during the discussion of large strain properties (strain hardening and the changing of λ^{-1} in Mooney plot, **Figure 17**). The first relaxation occurs at very short times (0.01 – 0.1 s, which is similar to the relaxation time deduced from the peak of G'' at 25 °C: 0.022 s), due to the Ni^{2+} -ligand coordination. The second relaxation occurs in the longer time region (> 100 s), and could be caused by the presence of spatial heterogeneities. The characteristic time of the exchange process of the Zn^{2+} -ligand coordination is too fast to be seen in the relaxation curve.

4.5 Discussion

4.5.1 Internal consistence

4.5.1.1 Relaxation times

The loss tangent $\tan \delta$ is defined as the ratio between the viscous modulus G'' and the elastic modulus G' , which represents the dissipative character of the relaxation. **Figure 25a** shows $\tan \delta(\omega)$ of Ni^{2+} and Zn^{2+} dual crosslink gels. With increasing ω , $\tan \delta$ of the chemical gel and of the Zn^{2+} gel both increase. The Ni^{2+} gel has a clear peak in $\tan \delta$ at low frequency. As shown earlier in this chapter, the peak of G'' of Zn^{2+} gel cannot be captured by the rheology test, because of the very fast Zn^{2+} - Im ligand exchange rate, therefore its relaxation time τ_R cannot be directly measured. For further qualitative discussion, we roughly deduced the value of the relaxation time of Zn^{2+} gel by shifting the $\tan \delta$ curve to adjust it to that of Ni^{2+} gel (**Figure 25b**). Based on the relaxation time of Ni^{2+} gel (0.25 s), we found 0.00056 s for the Zn^{2+} gel.

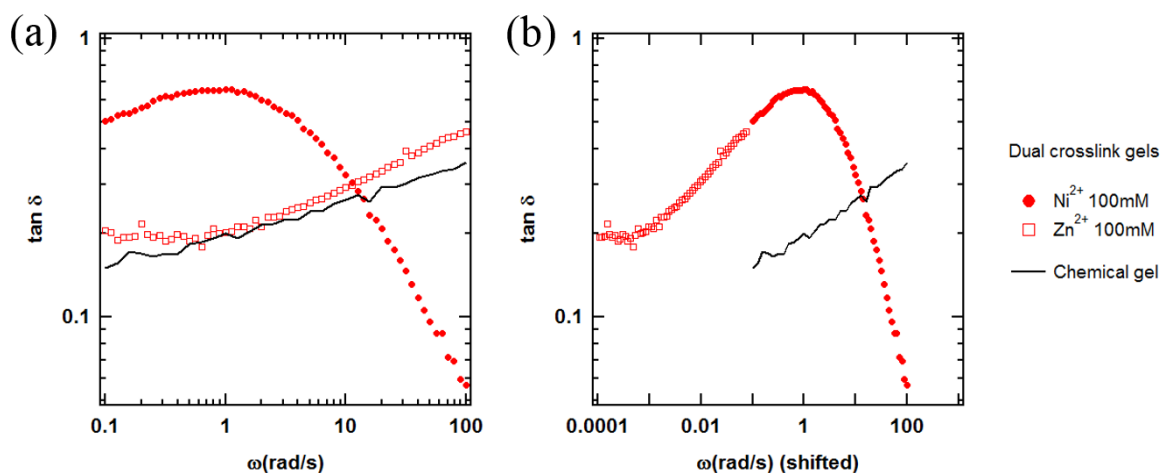


Figure 25. (a) The loss tangent $\tan \delta$ of Ni^{2+} and Zn^{2+} dual crosslink gels and the chemical gel, as a function of ω . (b) $\tan \delta$ as a function of shifted ω .

With the relaxation time of both gels known, it is possible to compare these two gels by shifting horizontally the data by τ_R . To study the large strain (nonlinear) properties, the minimum value of the reduced stress $f_{\min}^*$ was plotted as a function of stretch rate $\dot{\lambda}$ (**Figure 18a**). We can now replot $f_{\min}^*$ as a function of $\dot{\lambda} \cdot \tau_R$ (**Figure 26**). The relatively high value of $f_{\min}^*$ at high $\dot{\lambda} \cdot \tau_R$ represents the non-relaxed physical bonds, which result in more elastic gels. At low values $\dot{\lambda} \cdot \tau_R$, the physical bonds relax completely, leading to the plateau of $f_{\min}^*$ around 4 kPa. Theoretically, without a second relaxation mechanism, this plateau should be reaching the value of the chemical gel, which is not true for this system: the plateau value is still higher than that of the chemical gel (about 2.8 kPa). This is another evidence of the existence of the slower component.

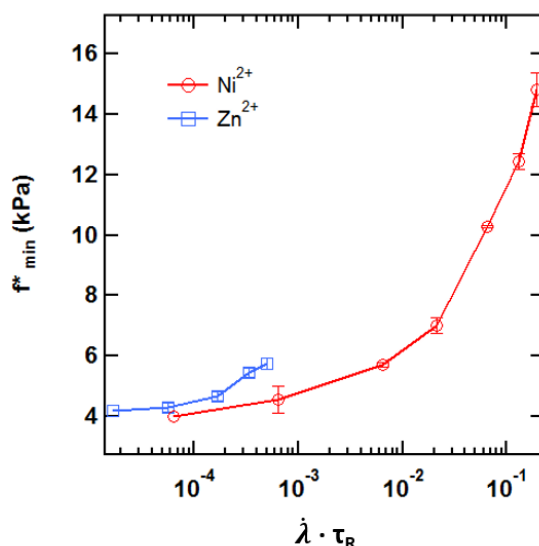


Figure 25. The minimum value of reduced stress $f_{\min}^*$ of Ni^{2+} (red) and Zn^{2+} (blue) dual crosslink gels as a function of $\dot{\lambda} \cdot \tau_R$.

4.5.1.2 Energy dissipation

A higher hysteresis represents a larger energy dissipation and it is important to assess the consistency between the large strain (nonlinear) and small strain (linear) energy dissipation. The comparison between the hysteresis of dual crosslink gels made from two different metal

ions was carried out with step-cycle extension experiment (nonlinear) (**Figure 21**). Compared to the Zn^{2+} gel, the Ni^{2+} gel has a higher W (area under the loading curve), and also a higher normalized hysteresis Hys/W . Based on the value of W , we can expect a higher fracture energy of Ni^{2+} gel, while the higher value of Hys/W may have influence on the crack propagation velocity at fixed applied energy release rate G .

The normalized hysteresis Hys/W can be seen as equivalent to the loss tangent $\tan \delta$ in large strain, the former one showing the large strain amplitude dependence while the latter one shows the frequency dependence. Comparing the $\tan \delta$ from linear rheology test with Hys/W from nonlinear tensile test at low frequency and small strain, a consistent trend can be found: Ni^{2+} gel has higher energy dissipation than Zn^{2+} gel for strain rates in the range $10^{-2} - 10^{-3} \text{ s}^{-1}$.

4.5.2 Comparison between the two dual crosslink systems

The expectation from the AAm-VIm- M^{2+} system (the second system) was a tougher, faster exchanging and tunable gel, with a controllable density of physical crosslinks all the way to low concentrations. The relaxation time of this dual crosslink hydrogel with metal-ligand coordination is much shorter than that of the PVA-borax system, and can be changed over 400 times ($0.251 - 0.00056 \text{ s}$) by simply changing the metal ion from Ni^{2+} to Zn^{2+} . For the nonlinear properties, the AAm-VIm- M^{2+} system has a higher extensibility and higher stress at break, which indicates a tougher gel.

The unexpected result is the existence of a slower relaxation process, which may come from the generation of metal oxides from the ‘one-pot’ synthesis. This results in the second relaxation time, and to a strain hardening due to the physical crosslinks in the nonlinear regime, leading to a tougher gel, with two reinforcement mechanisms.

4.5.2.1 The similarity between the two systems

The general structure of these two systems is the same: a chemical network, with physical crosslinks to reinforce these hydrogels, which results in the same mechanical reinforcement mechanism. The loss tangent $\tan \delta$ (from rheology data) of two systems, with different physical crosslinking densities, are plotted as a function of frequency ω in **Figure 26a**. By horizontally shifting the data based on the relaxation time τ_R (no vertical shift), a rough master curve can be constructed, indicating the consistency in rheological properties between these two systems. The comparison of the relaxation times of these two systems shows: Zn^{2+} 100 mM (0.00056 s) $<$ Ni^{2+} 5 mM (0.045 s) $<$ Ni^{2+} 20 mM (0.063 s) $<$ PVA-borax 50 mM (0.12 s) $<$ Ni^{2+} 100mM (0.251 s) $<$ PVA-borax 5 mM (0.794 s) $<$ PVA-borax 1 mM (1.585 s). It seems that at the low reduced frequency range the gels with 100 mM metal ions show the lower value of $\tan \delta$, presumably due to the presence of the slow mode. Interestingly the relaxation time of the PVA-borax system decreases with increasing borax concentration as discussed in chapter 3, but the opposite trend is observed for the Ni^{2+} system suggesting a different dynamics.

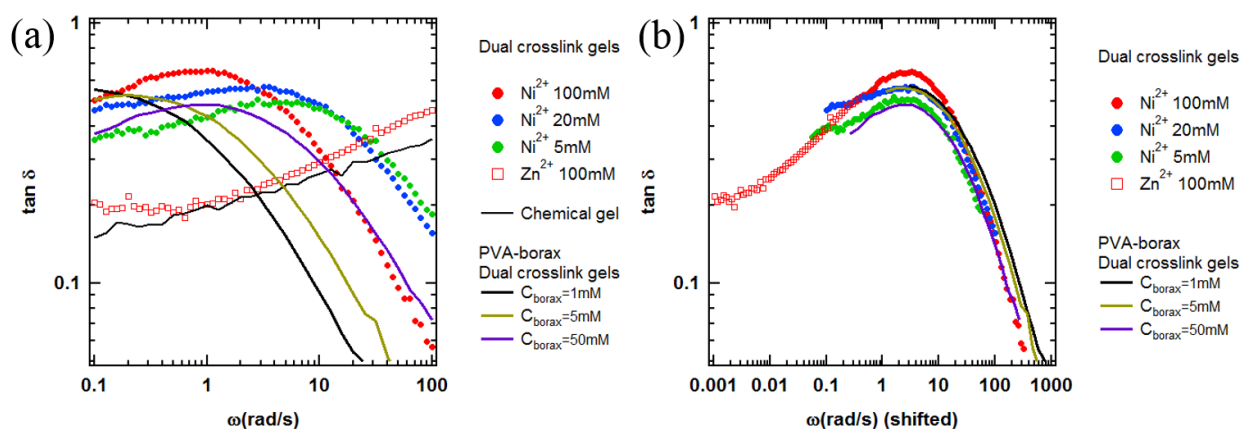


Figure 26. The loss tangent $\tan \delta$ of Ni^{2+} and Zn^{2+} , and PVA-borax dual crosslink gels, as a function of ω . (b) $\tan \delta$ as a function of shifted ω .

4.5.2.2 The differences between the two systems

The preparation methods of these two systems are different. The PVA-borax dual crosslink gel is prepared in two steps, first the preparation of the PVA chemical gel, then the physical crosslink is added by diffusion. For the AAm-VIm- M^{2+} system, a ‘one-pot synthesis’ starting from monomers is used for the polymerization.

As shown in **Figure 27**, for the PVA-borax dual crosslink gels, at a fixed stretch rate, the extensibility decreases with increasing physical crosslinking density after a dramatic increase from the chemical gel to the dual crosslink gel with the lowest physical crosslinking ratio prepared at 1 mM of borax (previously discussed in Chapter 2), while for AAm-VIm- M^{2+} gels, it monotonously increases with physical crosslinker concentration. These two systems have opposite trends for the tensile extensibility as a function of physical crosslinking ratio. In principle the extensibility should depend primarily on the ratio between the stretch rate and the relaxation time of the crosslinks themselves, the transient crosslinks are only expected to dissipate energy and prevent stress concentration at the crack tip if the applied stretch rate is about 100 times slower than the relaxation time²⁸. This argument would suggest that the extensibility should go through a peak as the parameter $\dot{\lambda} \cdot \tau_R$ changes between below 0.01 and above it. **Figure 28** shows the critical stretch ratio λ_C as a function of $\dot{\lambda} \cdot \tau_R$ for PVA-borax and AAm-VIm- M^{2+} dual crosslink gels, with different physical crosslinking density. As discussed before, these two systems have opposite trends for the tensile extensibility, and for the relaxation time, as a function of physical crosslinking ratio. Hence at a fixed stretch rate, these two systems have the same increasing trend for the λ_C as a function of $\dot{\lambda} \cdot \tau_R$.

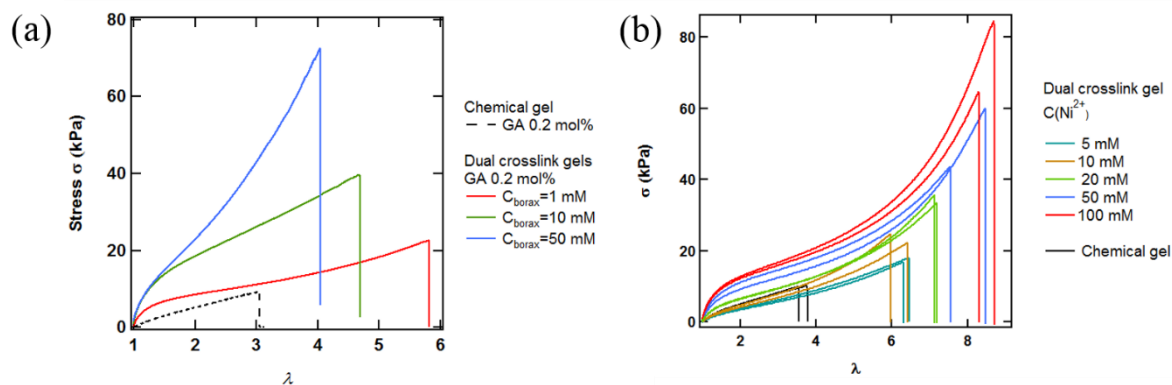


Figure 27. The different extensibility trend of two dual crosslink gels. (a) PVA-borax gels, (b) AAm-VIm- Ni^{2+} gels, with a stretch rate of 0.06 s^{-1} .

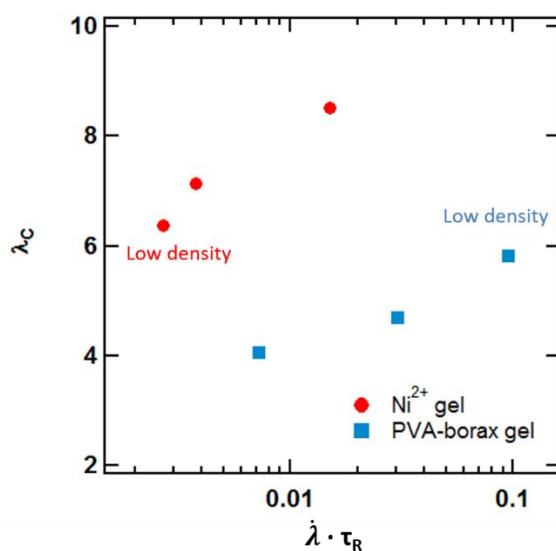


Figure 28. Extensibility as a function of $\dot{\lambda} \cdot \tau_R$ for Ni^{2+} gel and PVA-borax gel with different physical crosslinking density.

Although in principle a peak should be observed at $\dot{\lambda} \cdot \tau_R = 0.01$, the data does not show such a universal behavior suggesting that, at fixed value of $\dot{\lambda} \tau_R$ one should also observe an effect of the concentration of physical crosslinks. At low concentrations the capacity of energy dissipation should increase with physical crosslinking ratio since the dissipation is proportional to the number of the events of reversible bond breakage. This effect explains well the behavior

of AAm-VIm- M^{2+} gels, but not that of PVA-borax gels. Since the values of elastic modulus in the linear domain for both gels are similar (around 5 – 50 kPa for AAm-VIm- M^{2+} gels, 20 – 50 kPa for PVA-borax gels), the effective physical crosslinking ratio of the two system must be close. However, in the PVA-borax gels there is a large excess of borate ions which are not crosslinking (not binding or mono-diol binding). The presence of the non-crosslinking borate ions can affect the equilibrium of the breaking and healing dynamics. The heterogeneity of crosslinking could also play an important role in the fracture properties. However, it is not evident that the physical crosslinks systematically increase the heterogeneity of the network structure similarly to the chemical crosslinks, favoring therefore a crack nucleation event. How the transient crosslinks are spatially distributed in the presence of the chemical crosslinks creating the heterogeneity is an open question. Further structural characterizations are required to evaluate the heterogeneity.

Figure 29 shows the strain rate dependency of the extensibility of the two gels. The extensibility of the PVA-borax gel decreases with the increasing strain rate, while that of the AAm-VIm- M^{2+} gel is practically independent of the strain rate and always high. Based on the very different relaxation time range, the relaxation time of the AAm-VIm- M^{2+} dual crosslink gels is much shorter than the PVA-borax gels, suggesting that the general trend of the extensibility is decreasing with the increasing strain rate, these two systems reach two different regions of this general trend. We expect that at very high strain rates even the AAm-VIm- M^{2+} gels show the low extensibility brittle regime, however, due to the limitation of the apparatus used for tensile test, this regime is not easily reached.

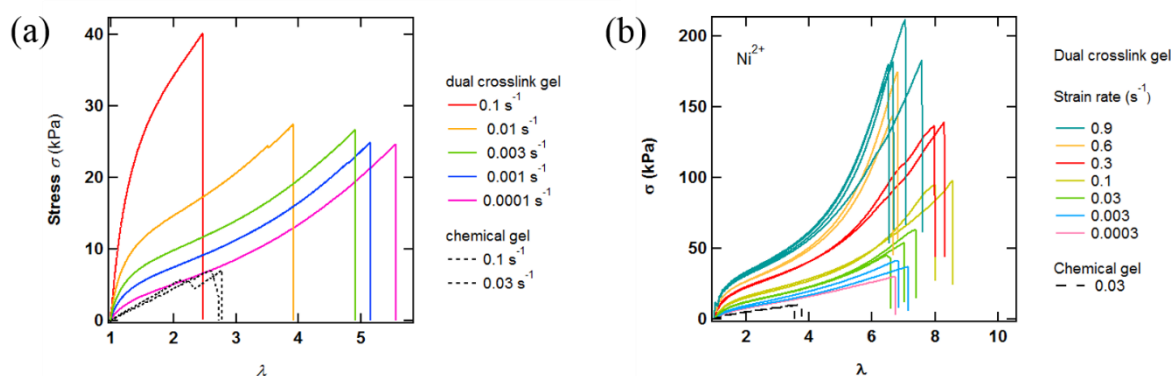


Figure 29. The different extensibility trend of two dual crosslink gels. (a²³) PVA-borax gel, (b) AAm-VIm-Ni²⁺ gel.

According to the un-notched uniaxial tensile tests, the extensibility of these two dual crosslink gels has strong physical crosslinking dependence and strain rate dependence, in which, the breaking process plays an important role. However, for un-notched samples, the crack nucleation is not controlled and the breakage always occurs in the area near the clamps, which makes it hard to extract the accurate breaking information. To understand this process, it is necessary to study their fracture properties with notched samples. In Chapter 5 we will study the fracture properties.

4.5.3 Comparison with expected behavior

As mentioned at the beginning of this Chapter, the expectation of the AAm-VIm-M²⁺ system, was to have a relatively short and tunable relaxation time, to be able to access a low physical crosslinking density, and an easy and quick synthesis process. The AAm-VIm-M²⁺ gel is easy to synthesize, tough, with high extensibility, the relaxation time varies from 0.00056 s (gel with [Zn²⁺] = 100 mM) to 0.251 s (gel with [Zn²⁺] = 100 mM). The ‘one-pot’ synthesis method is used, so that the swelling of the chemical can be avoided, and a low physical crosslinking

density is accessible. This AAm-VIm- M^{2+} system overcomes the limitation of the PVA-borax system, and corresponds to what we expected.

The unexpected behaviors of the AAm-VIm- M^{2+} system, are the strain hardening in the tensile stress-strain curve (**Figure 13, 17**), and the presence of the second relaxation (**Figure 23, 24**), which can be explained by the presence of the slow component due to the ‘one-pot’ synthesis process. This might be one reason for the good mechanical behavior, besides the M^{2+} -Im coordination bonds.

4.6 Conclusion

To overcome the limitations of the PVA-borax dual crosslink gels, inspired by the good mechanical properties of the mussel byssus, AAm-Im-M²⁺ dual crosslink gels were synthesized and their mechanical properties were investigated. This series of gels were permanently crosslinked by methylene bisacrylamide (MBA) and transiently crosslinked by the metal ion – imidazole ligand coordination, with two different ions (Ni²⁺ and Zn²⁺), at various crosslinking densities. The rheological and tensile properties were studied at different temperatures, over a wide range of strains and strain rates, in comparison with the corresponding chemical gels. Our main conclusions are following:

(1) Effect of physical crosslinking density:

For the rheological property, in all cases, the modulus of the Ni²⁺ dual crosslink gels was found higher than that of the corresponding chemical gel, the relaxation time determined from the peak of the viscous modulus increased with increasing physical crosslinking density. For the large strain properties, the extensibility of the dual crosslink gels was found much higher than that of the chemical gel, with an increasing tendency with increasing crosslinking density. A strong strain-rate dependent behavior was found for dual crosslink gels with a high physical crosslinking density, with higher dissipated energy, which was confirmed with tensile loading unloading cycles.

(2) Effect of different metal ions:

Dual crosslink gels with Zn²⁺ was confirmed to have a much faster association/dissociation dynamic than that with Ni²⁺ by torsion tests, which results in a lower hysteresis in the tensile step-cycle loops. Based on the strain-rate dependent tensile behavior at small strain, a master curve of the reduced stress as a function of time was obtained for both gels. The large strain

property was proved to be strongly strain-rate dependent, with softening at small strain and strain hardening at large strain, Mooney plot was used to characterize this strain hardening behavior, from which the corresponding $\lambda_{\min}^{-1}$ was found to be dependent of the strain rate, this indicates the presence of a second relaxation time. Same stress relaxation tendency was found in shear and tensile stress relaxation tests, with a crossover of the relaxation curves of two gels, a slower relaxation mode was suggested by the uncomplete relaxation.

(3) Comparison with the PVA-borax dual crosslink gels:

Compared to the PVA-borax dual crosslink gels, AAm-VIm- M^{2+} dual crosslink gels have relatively short and tunable relaxation time, easy and quick synthesise process, easy access to low physical crosslinking density, much higher modulus and extensibility, and two relaxation times. Despite all these differences, due to the same general structure and reinforcement mechanism, a rough master curve of loss tangent $\tan \delta$ was found, indicating the consistency in rheological properties between these two systems.

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Chapter 5: Fracture properties of two dual crosslink hydrogels

5.1 Introduction

In Chapter 2 and Chapter 4, the linear and nonlinear mechanical properties of the PVA-borax and AAm-VIm-M²⁺ dual crosslink hydrogels were presented and discussed. The existence of a crack, which can appear during the preparation or its life cycle, can dramatically change the mechanical behavior of a material, so it's very important to study a material's resistance to fracture and its ability to avoid crack propagation. In this Chapter, the fracture properties of two systems will be discussed and compared.

5.1.1 Basics of fracture mechanics

5.1.1.1 Linear elastic fracture mechanics

The most commonly known theory about fracture is the linear elastic fracture mechanics (LEFM) developed by Griffith¹. LEFM focuses on the fracture of elastic materials, with the assumption that the material remains linearly elastic except for a small region around the crack tip. The strain energy release rate $\mathcal{G}$, the elastic energy released by the system per unit surface of crack advance, equals the difference between the derivative of the external work U_w and the that of the released elastic energy U_{el} , with respect to the crack area. In the original Griffith description, the thermodynamic energy cost per area, the threshold fracture energy Γ_0 to create a new surface is equal to $\mathcal{G}$ at equilibrium² (**Eq. 1**). In real materials, the fracture energy Γ depends on the threshold fracture energy Γ_0 and the crack velocity V_P , the relationship will be discussed later in this introduction. A crack starts to propagate when the energy release rate $\mathcal{G}$ is larger than the fracture energy Γ . Note that LEFM is inadequate for soft materials, but it can serve as the basic fundamental theory for the understanding of fracture.

$$\mathcal{G} = \frac{\partial U_w}{\partial A} - \frac{\partial U_{el}}{\partial A} = \Gamma_0 \quad (1)$$

5.1.1.2 Lake and Thomas theory

As mentioned in Chapter 1, Lake and Thomas investigated the fracture of polymer networks and found that the experimental value of Γ at high temperature and very low stretch rate where viscoelastic losses can be neglected, converged toward the threshold value Γ_0 .³ A theoretical estimate of the threshold fracture energy Γ_0 to propagate a crack was proposed:

$$\Gamma_0 = N_x U_b \Sigma \quad (2)$$

where, N_x is the number of C-C bonds between crosslinks, U_b is the energy of a C-C bond (350 kJ mol⁻¹), and Σ is the areal density of chains crossing the plane. For a homogeneous network, Σ can be written as:

$$\Sigma \approx \nu_x a N_x^{1/2} \quad (3)$$

where, ν_x is the density of crosslinks, a is the size of the monomers. Combining Eq. 2 and 3, Γ_0 can be written as:

$$\Gamma_0 \approx N_x U_b \nu_x a N_x^{1/2} \approx U_b \nu_x a N_x^{3/2} \approx \frac{U_b a \rho}{M_0} N_x^{1/2} \quad (4)$$

where, ρ is the monomer density and M_0 is the monomer molar mass. For elastomers, $\rho = \rho_0$, which is the bulk un-swollen density; while for hydrogels, $\rho = \rho_0 \phi_P$, where ϕ_P is the polymer volume fraction. Therefore, this equation is valid for both elastomers and hydrogels.

The Lake and Thomas model does not take into account of the viscoelastic dissipation that happens during the fracture propagation.

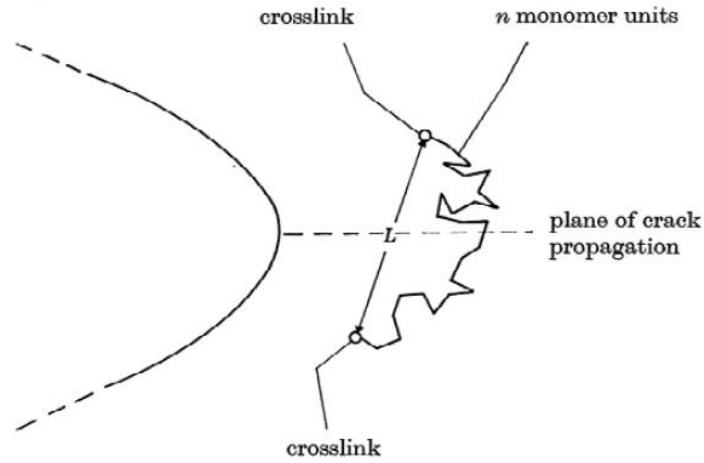


Figure 1. Schematic view showing a polymer chain lying across the plane of crack propagation.³

5.1.1.3 Crack propagation

There are several common test geometries that are used to study crack propagation in viscoelastic materials, such as the single-edge notch test geometry (**Figure 2a**), the pure shear test geometry and the trousers test geometry. Zooming in on the crack tip, **Figure 2b** shows the schematic presentation of a propagating crack in a soft material. In the blue area far from the crack tip, the dissipation of this material is dominated by the far-field loading conditions, while in the red area with a size R , the dissipation is dominated by the propagation of the crack. The local damage and molecular fracture occurs in or near the black zone with a size R_0 , the dissipated energy of which can be defined as Γ_{local} .

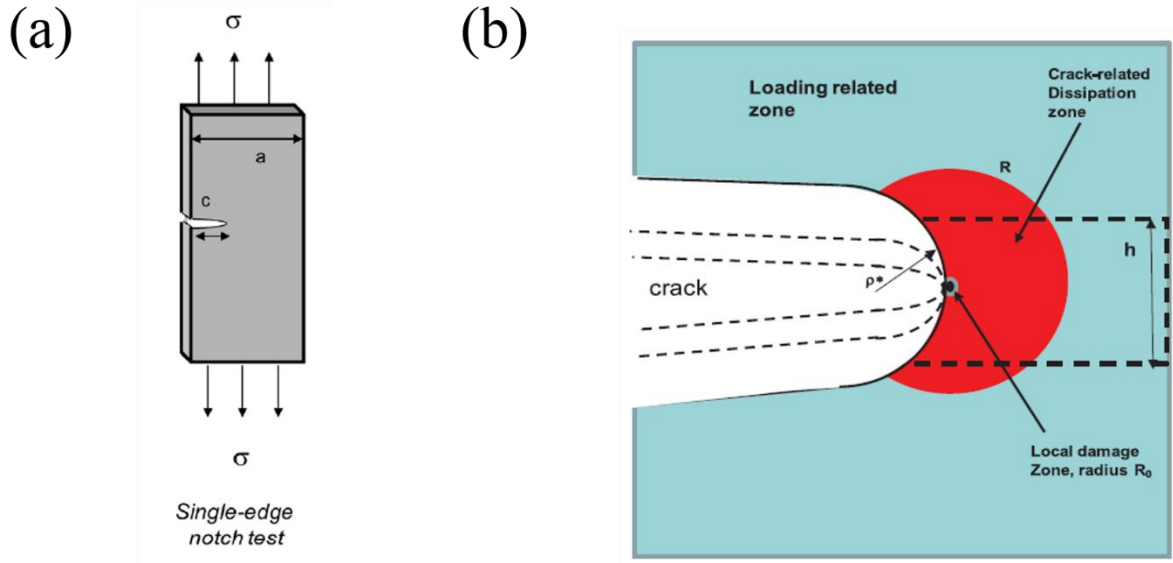


Figure 2. Schematic of (a) the single-edge notch test geometry, (b) a propagating crack in a soft material showing the radius of the dissipative zone R , the radius of the local damage zone R_0 , and several crack tip radii.²

5.1.1.4 Measurement of the fracture energy: Greensmith approximation

To characterize the ability of a material to avoid the propagation of an existing crack, it is necessary to measure the fracture energy Γ . This measurement involves choosing a well-defined geometry and introducing a crack. The knowledge of the geometry, elastic properties of the material an loading conditions and the application of Eq. 1 leads then to a value of Γ .

Common geometries to test fracture resistance are the trouser test, the pure shear test (well adapted for fatigue experiments) and the single and double edge notch geometry². Since we are not interested in fatigue experiments we chose for simplicity of testing the single edge notch geometry and the details of the experiment are described later. Based on a series of experiments with different notch lengths, Greensmith proposed a simple expression to quantify the energy release rate $\mathcal{G}$ of single edge notch samples for neo-Hookean elastomers⁴ :

$$\mathcal{G} = 2 \frac{3}{\sqrt{\lambda}} c W(\lambda), \quad (5)$$

where, c is the initial length of the notch (**Figure 2a**), $W(\lambda)$ is the stored energy density calculated from the uniaxial stress-strain curve of the un-notched sample. When $\lambda = \lambda_c$, the crack starts to propagate, and $W(\lambda_c)$ can be estimated from the area under the stress-strain curve of the un-notched sample:

$$W(\lambda_c) = \int_1^{\lambda_c} \sigma d\lambda. \quad (6)$$

When the crack starts to propagate, the energy release rate $\mathcal{G}$ equals to the fracture energy Γ :

$$\Gamma = \frac{6 c W(\lambda_c)}{\sqrt{\lambda_c}} \quad (7)$$

It is necessary to mention that this estimate of $W(\lambda_c)$ is only accurate for nonlinear elastic materials at medium strains although it also has been used for viscoelastic materials⁵⁻⁷. For elastic materials, the loading and unloading curves are identical, independent on the loading and unloading rates, therefore all the area under loading (unloading) curve is available for fracture, while for viscoelastic materials, a part of the energy is already dissipated during loading, instead of the area under the loading curve, the correct value of $W(\lambda_c)$ should be the area under the corresponding unloading curve, thus the true fracture energy Γ_{local} is lower than the Γ calculated by **eq. 5**. For example, **Figure 3** shows the calculated loading (red)/unloading (blue) curves of the PVA-borax dual crosslink gel⁸, the area in the hysteresis loop corresponds to the dissipated energy, which is not available for crack propagation. Therefore, to calculate Γ_{local} , the correct value of $W(\lambda_c)$ should be the area under the unloading (blue) curves.

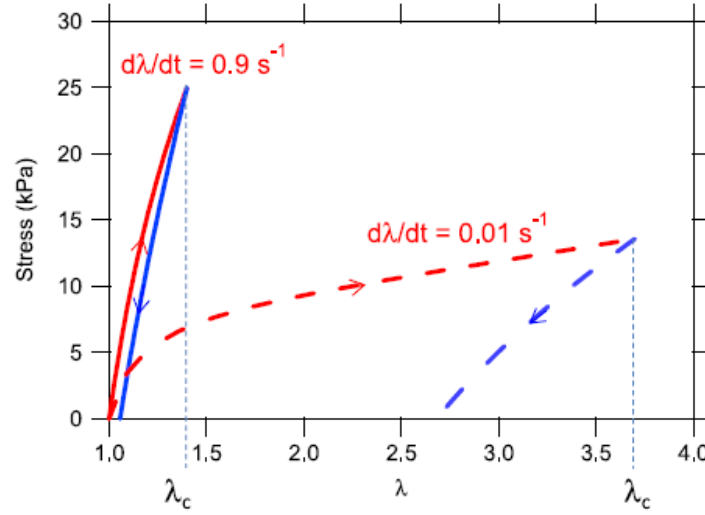


Figure 3. Calculated loading/unloading curves in uniaxial tension up to the critical stretch where the crack propagates in notched samples, at two different stretch rates and corresponding unloading rates obtained from crack velocities.⁸

5.1.1.5 The relationship between crack velocity and fracture energy

Γ depends both on the temperature and the rate, the interfacial fracture energy $\Gamma_{(v)}$ can be written as⁹:

$$\Gamma_{(v)} = \Gamma_0 (1 + \phi(a_T v)) \quad (8)$$

where $\phi(a_T v)$ is a velocity dependent dissipative factor. **Figure 4** shows $\Gamma_{(v)}$ for several typical networks (two rubbers^{10,11} and two crosslinked gels^{12,13}) as a function of rate and temperature, it shows that the fracture energy increases significantly with crack propagation velocity, the value of the exponent n varying between 0.1 and 1.

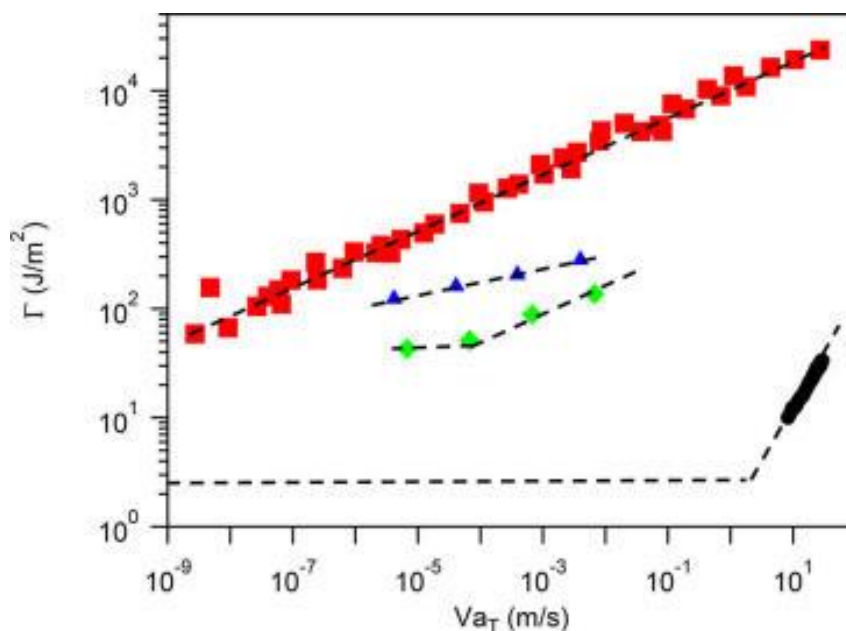


Figure 4. (a) Fracture energy Γ as a function of propagation velocity or reduced propagation velocity for different materials. (■) Master curve at 25 °C for a styrene-butadiene rubber ($T_g = -25$ °C) tested with the trouser tear geometry.¹⁰ (◆) Polyurethane rubber ($T_g = -55$ °C) at 25 °C tested with the single edge notch geometry.¹¹ (blue ▲) Double network hydrogel at 25 °C.¹² (●) Gelatin gel (5 wt % polymer) at room temperature in the pure shear geometry¹³. Horizontal lines are values of Γ_0 when reported.¹⁴

5.1.2 Fracture properties of the PVA-borax dual crosslink hydrogel

Using the method described above the fracture properties of a PVA-borax dual crosslink gel, with a chemical crosslinking ratio of $C_{GA} = 0.2$ mol% prepared at $C_{borax} = 1$ mM, was previously investigated⁸ by Mayumi et al. who carried out a series of fracture experiments with single edge notch samples at different stretch rates⁸. The critical value of the stretch rate λ_c , the fracture energy Γ , and the crack propagation velocity V_P were measured and discussed. The main results are briefly reviewed here, and the comparison with the results for the AAm-VIm- M^{2+} system will be discussed later in this Chapter.

5.1.2.1 Stretch rate dependence of the critical extension ratio

The stress-strain curves for the un-notched and notched gels, with different stretch rates are shown in **Figure 5**. The notched samples show the same stretch rate dependence as the un-notched ones, due to the presence of the transient crosslinks. As for the chemical gels, there's little effect of stretch rate for notched and un-notched samples.

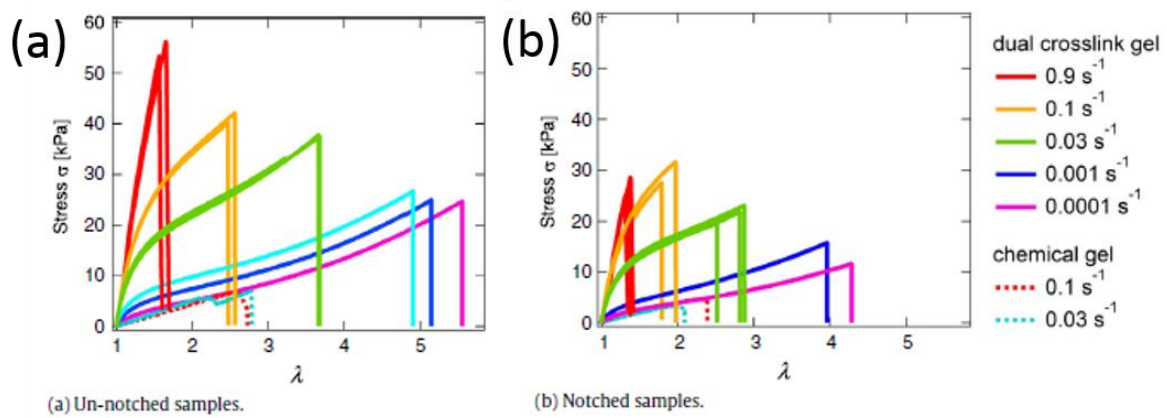


Figure 5. Stress versus stretch curves for (a) un-notched and (b) notched chemical gels and dual crosslink gels at different stretch rates.

Based on these stress-strain curves, the critical extension ratio λ_c , at which the crack starts to propagate, can be plotted as a function of $\dot{\lambda}$ (**Figure 6a**). λ_c increases with decreasing stretch rate, until it reaches a plateau at very low stretch rates ($\dot{\lambda} < 0.01$ s⁻¹), un-notched samples have higher λ_c for every $\dot{\lambda}$ but note that the difference in λ_c with notched samples is relatively small. The comparison between the extension at break of the notched dual crosslink gels and that of the notched chemical gels is shown in **Figure 6b**. The values of λ_c for the chemical gels are almost independent of $\dot{\lambda}$, while the λ_c of dual crosslink gels is lower than that of chemical gels at high stretch rates, and becomes higher at low stretch rates ($\dot{\lambda} < 0.03$ s⁻¹).

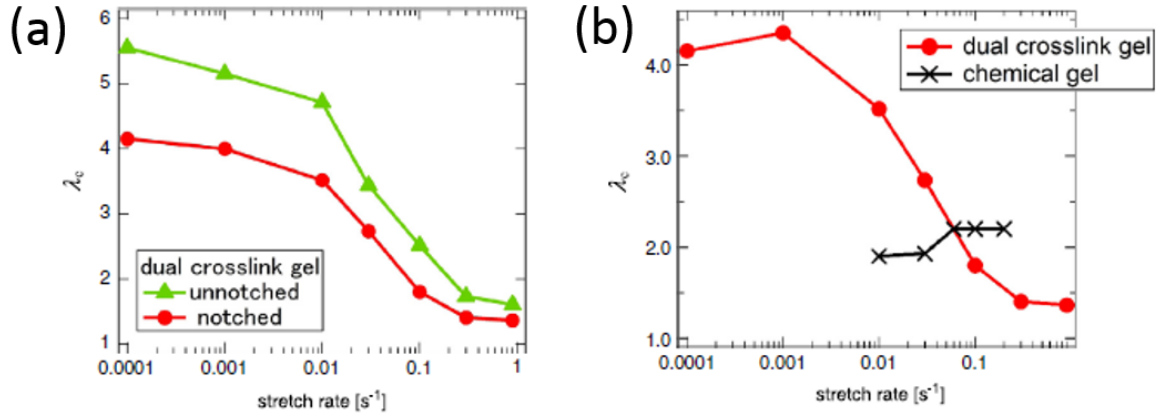


Figure 6. Stretch rate dependence of critical extension ratio λ_c at which fracture starts for (a) unnotched and notched dual crosslink gels, and (b) notched dual crosslink and notched chemical gels.

5.1.2.2 Fracture energy

Using the Greensmith approximation⁴, the fracture energy of dual crosslink gels and chemical gels is calculated and plotted as a function of $\dot{\lambda}$ (**Figure 7a**). The fracture energy Γ of the chemical gels remains almost constant and is always lower than that of the dual crosslink gels. As for the dual crosslink gels, the Γ shows a strong stretch rate dependence, with a ‘plateau’ at $\dot{\lambda}$ from 0.001 to 0.03 s^{-1} . Based on the model developed to describe the non-linear viscoelastic mechanical response of the PVA-borax dual crosslink hydrogels¹⁵, the local fracture energy Γ_{local} can be calculated and the values are shown in **Figure 7b**. The Γ_{local} of the dual crosslink gels remains nearly constant and is very close to that of the chemical gels, except for the high value at very low $\dot{\lambda}$.

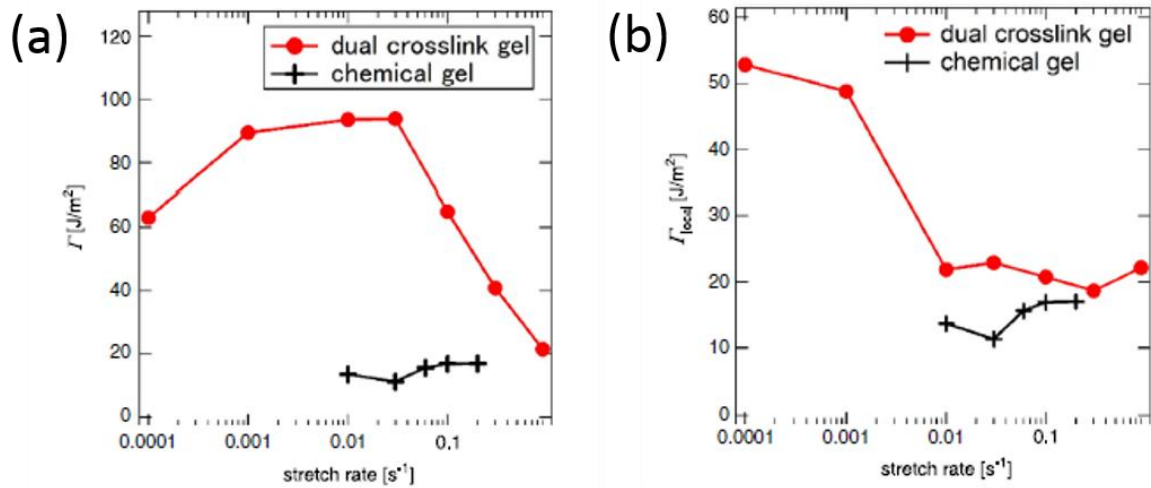


Figure 7. Plot of fracture energy Γ (a) and true fracture energy Γ_{local} (b) of the dual crosslink and the chemical gels as a function of stretch rate.

5.1.2.3 Crack propagation velocity

The crack propagation velocity V_P of the dual crosslink gels is calculated and plotted as a function of $\dot{\lambda}$ (**Figure 8**). V_P stays constant at high $\dot{\lambda}$ (over 0.01 s⁻¹), and decreases dramatically at low stretch rates. At high stretch rate the constant measured crack speed is consistent with the constant values of Γ_{local} . However it is surprising that at low stretch rate the value of Γ_{local} is high and the crack speed is very low. As mentioned in the beginning of this chapter, in general, Γ increases with V_P , with a power law relation (**Figure 4**). This suggests an interesting toughening mechanisms active at low stretch rates that is completely absent from the purely chemical gels.

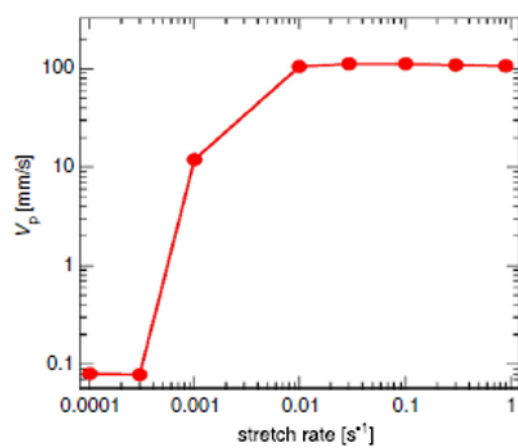


Figure 8. Stretch rate dependence of crack propagation velocity V_p for the single edge notch tests on the dual crosslink gels.

5.2 Results

5.2.1 AAm-VIm-M²⁺ system

The fracture properties of the AAm-VIm-M²⁺ dual crosslink hydrogels and those of the chemical gels were investigated. In this part, the critical extension ratio λ_c , the fracture energy Γ , and the crack propagation velocity V_P will be presented and discussed, as well as the effect of different stretch rates, of changing the physical crosslinking density, and of using different metal ions. The difference between notched and un-notched samples will also be addressed.

5.2.1.1 Experimental setup and sample geometry

As for the case of the uniaxial tensile tests mentioned in Chapter 2 and Chapter 4, the fracture tensile tests were performed on an Instron 5565 tensile tester with a 10 N load cell. Samples were rectangular in shape with 10 mm width, 1.5 mm thickness, and 20 mm length (length between clamps) (**Figure 9a**), A notch of approximately 2 mm was made with a scalpel, the actual length of the initial crack was measured for each sample from pictures of the sample with a ruler using ImageJ. The sample was then fixed in the clamps with an initial length between clamps around 20mm, force and strain were measured until failure of the sample. We kept the samples in paraffin oil during all the tests to prevent them from drying. A camera (SENTECH STC-MBCM) was used to record the crack propagation process. **Figure 9b** shows an example of the experiment setup, with the chemical gel between the clamps.

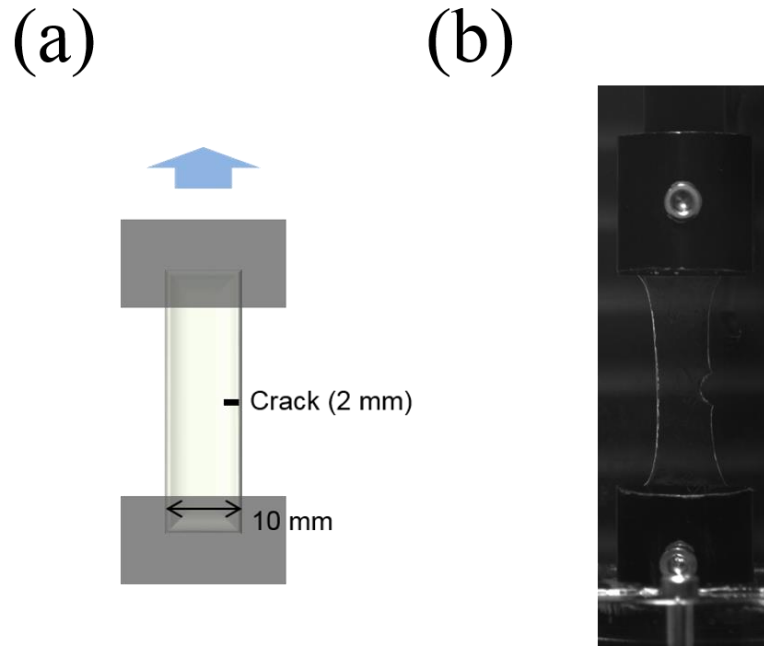


Figure 9. (a) Schematic view of sample geometry for single edge notch tests. (b) Fracture tests setup, with chemical gel.

Figure 10 shows the schematic presentation of how a crack propagates, δt represents the time that a crack takes to pass through the specimen. With δt , the width of the specimen w , and the length of the crack c , the average crack propagation velocity can be determined:

$$V_p = \frac{w - c}{\delta t}. \quad (9)$$

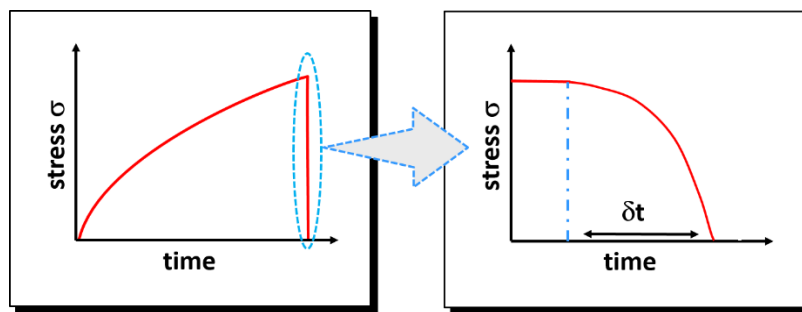


Figure 10. Schematic presentation of the calculation of the crack propagation velocity.

5.2.1.2 Crack images

Figure 11 shows a series of images of the loading and crack propagation process, of a dual crosslink gel with $[\text{Ni}^{2+}] = 20 \text{ mM}$, with a stretch rate of 0.0003 s^{-1} , the corresponding stress-strain curve is shown in **Figure 12a**. From **Figure 11a** to **11c**, the crack opens gradually, without propagation, the corresponding stress σ increases from 0 kPa to 5.4 kPa, while the stretch ratio λ increases to 2.2. Then the crack starts to propagate (**Figure 11c-f**), σ starts to decrease while the increase of λ is very small. **Figure 12b** shows the tensile curve with zoomed λ , where the crack propagation happens. Unlike the sharp drop of the PVA-borax gel, the decrease of σ is slow and uneven.

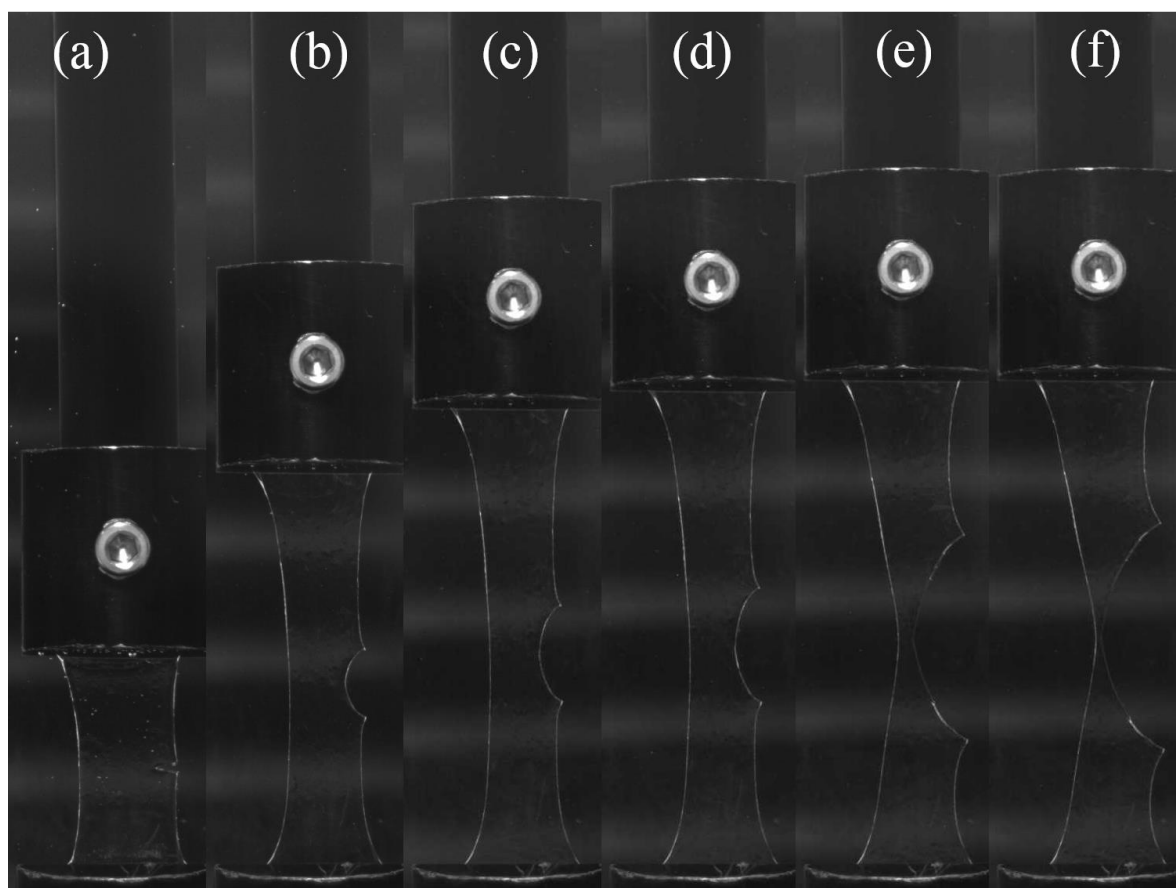


Figure 11. Images of the loading and crack propagation of dual crosslink gel with $[\text{Ni}^{2+}] = 20 \text{ mM}$, with a stretch rate of 0.0003 s^{-1} .

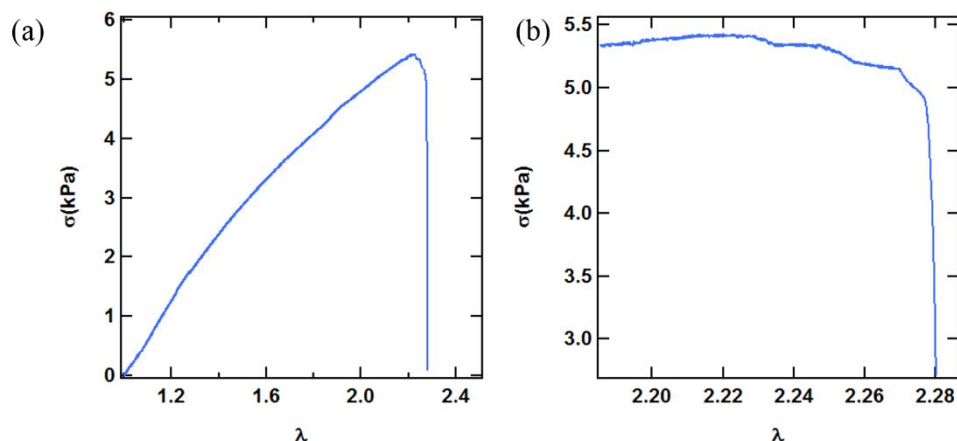


Figure 12. Stress-strain curve of the notched dual crosslink gel with $[\text{Ni}^{2+}] = 20 \text{ mM}$, with a stretch rate of 0.0003 s^{-1} .

5.2.1.3 The effect of the physical crosslinking density

Figure 13 shows the stress-strain curves for the notched chemical and AAm-VIm- Ni^{2+} dual crosslink gels, with a stretch rate varying from 0.3 s^{-1} to 0.0003 s^{-1} . For the chemical gels, there's a small effect of the stretch rate on the stiffness and the strain at break because of the low crosslink density that makes the gel slightly viscoelastic. However dual crosslink gels show a much more significant stretch rate dependence, due to the breaking and healing of the physical crosslinks. For dual crosslink gels, it is clear that for all Ni^{2+} concentrations investigated the extensibility and modulus increase with stretch rate, while at fixed stretch rate the same properties increase with Ni^{2+} concentration. The crack shape of each velocity of the gel with $[\text{Ni}^{2+}] = 100 \text{ mM}$ is shown in **Figure 14**.

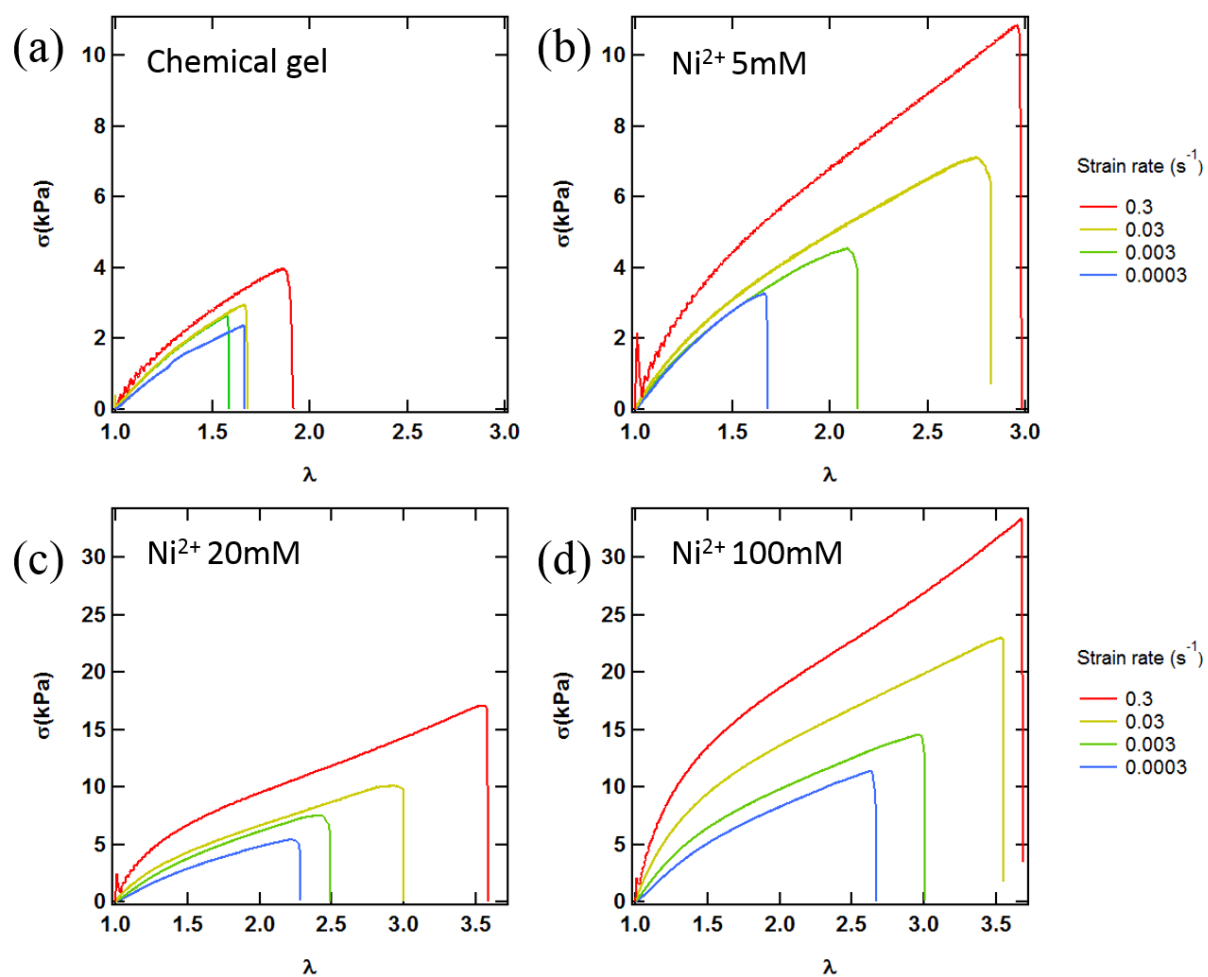


Figure 13. Stress-strain curves of notched (a) chemical gels and dual crosslink gels with different concentration of Ni²⁺ (b, c, d), with different stretch rates.

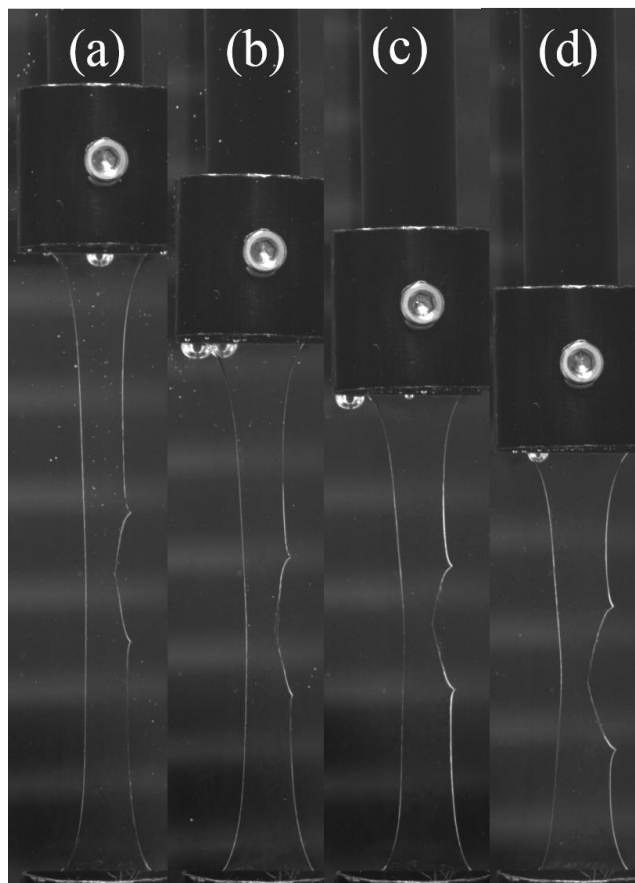


Figure 14. Images of the crack propagation of dual crosslink gel with $[\text{Ni}^{2+}] = 100 \text{ mM}$, with stretch rate of (a) 0.3 s^{-1} , (b) 0.03 s^{-1} , (c) 0.003 s^{-1} and (d) 0.0003 s^{-1} .

The critical extension ratio λ_c is plotted as a function of stretch rate for the notched chemical and dual crosslink gels (**Figure 15**). The value of λ_c of the chemical gel is clearly smaller than that of the dual crosslink gels, and remains almost for the whole range of stretch rates investigated. For all three dual crosslink gels, λ_c increases markedly with increasing stretch rate and there is no evidence of a maximum within the experimentally accessible range of stretch rates. Comparing the gels with different physical crosslinking densities, λ_c also increases with the increasing Ni^{2+} concentration although the effect is more pronounced at low strain rates where the critical strain ($\lambda_c - 1$) increases almost by a factor 3.

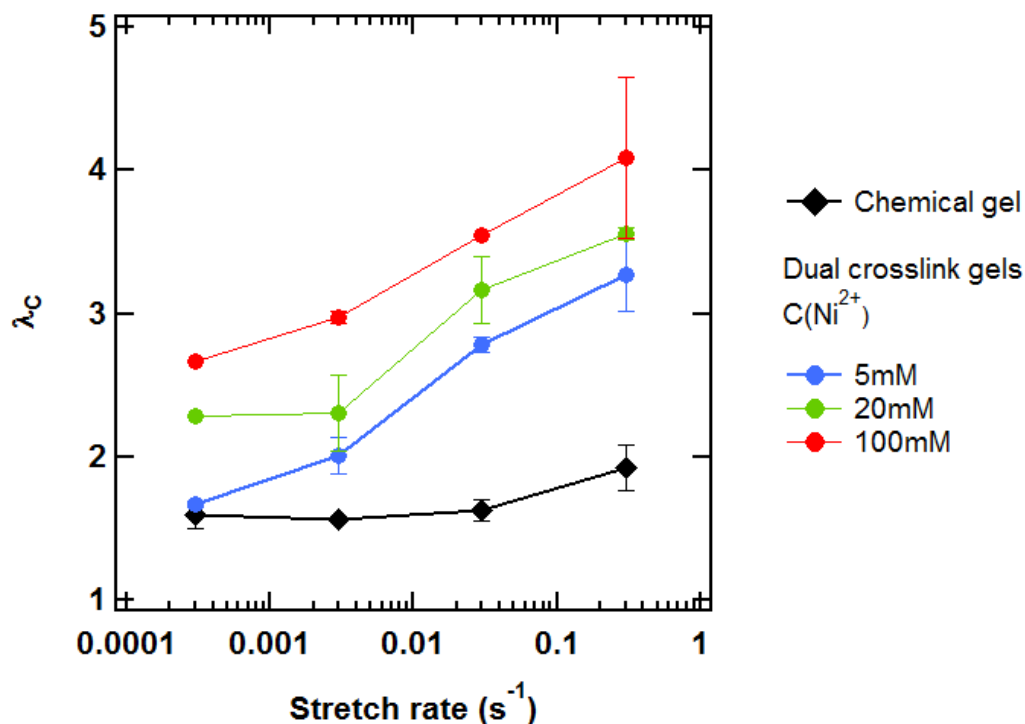


Figure 15. Stretch rate dependence of critical extension ratio λ_c at which fracture starts, for chemical gel and dual crosslink gels with different Ni^{2+} concentration.

5.2.1.4 The effect of changing the metal ions

The effect of changing the metal ions on the fracture property is investigated by comparing AAm-VIm- Ni^{2+} and AAm-VIm- Zn^{2+} dual crosslink gels at the same metal ion concentration (100mM), the stress-strain curves for both systems and at different stretch rates are shown in **Figure 16**. The Zn^{2+} gel shows the same trend as the Ni^{2+} gel: the extensibility and modulus decrease with the decreasing stretch rate. The Ni^{2+} gel has a higher initial modulus than the Zn^{2+} gel for every stretch rate (**Figure 17**).

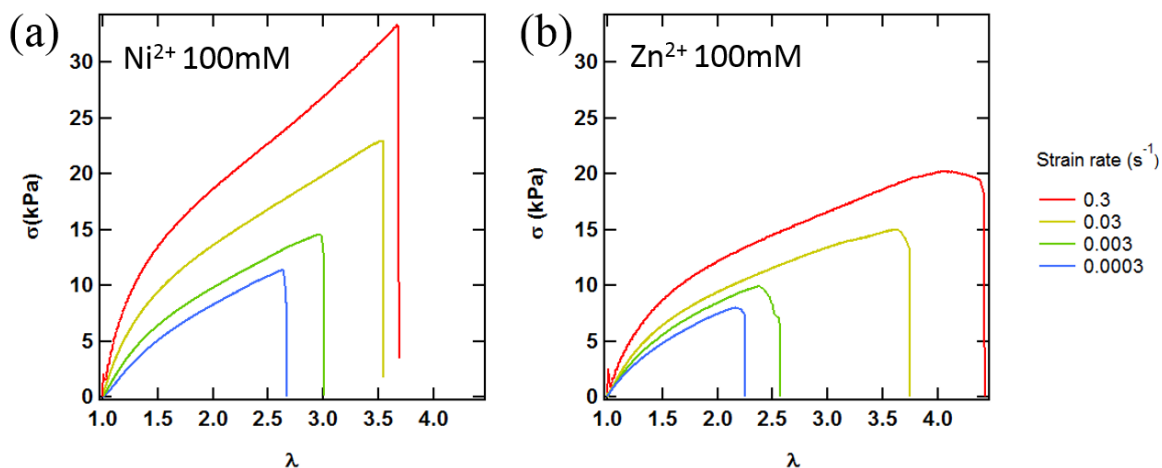


Figure 16. Stress-strain curves of notched dual crosslink gels with 100mM of Ni^{2+} (a) and Zn^{2+} (b).

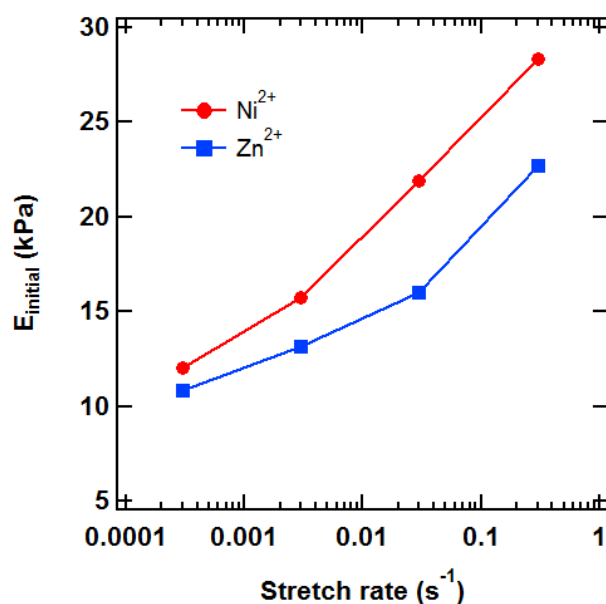


Figure 17. Initial modulus of two dual crosslink gels with Ni^{2+} and Zn^{2+} , as a function of the stretch rate.

In order to analyze the influence of the presence of an initial notch on the stretch at break λ_C , the value of λ_C is plotted vs. the stretch rate for the un-notched and notched chemical gels and for the dual crosslink gels made with different metal ions (**Figure 18**). For both dual crosslink gels, λ_C of the un-notched samples are much higher than that of the notched samples regardless of stretch rate (2 – 4 times). The λ_C of the notched samples for both gels have very close values,

both increasing with stretch rate. Comparing the λ_c of the notched chemical gel and the dual crosslink gels, the dual crosslink gels always rupture at higher strains than the chemical gel.

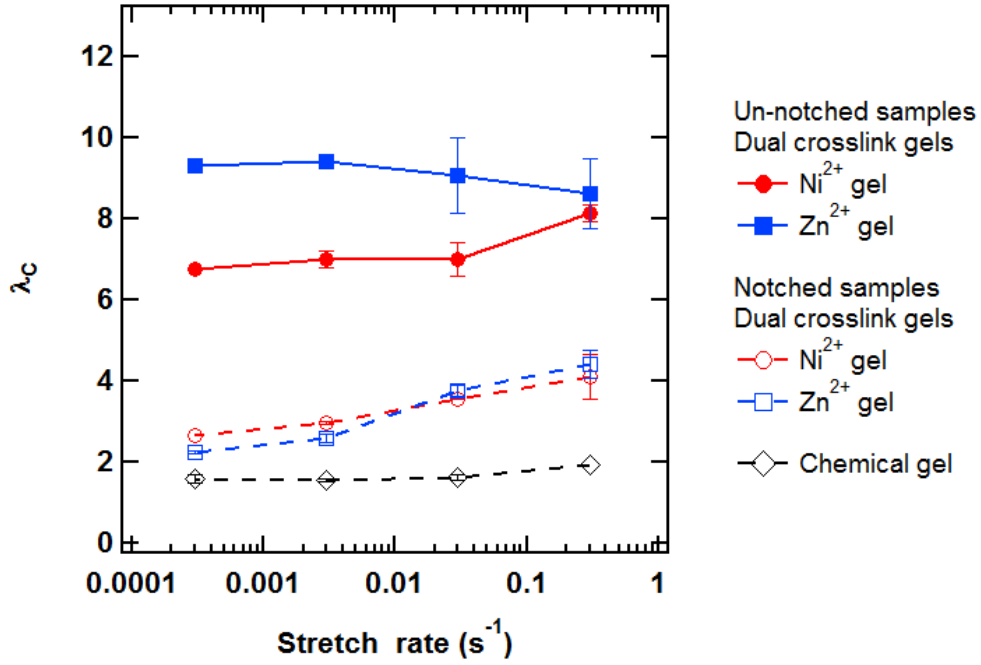


Figure 18. Stretch rate dependence of critical extension ratio λ_c at which fracture starts, for un-notched (solid) and notched (hollow) dual crosslink gels with Ni^{2+} (red) and Zn^{2+} (blue), and for notched chemical gels (black).

5.2.1.5 Fracture energy and crack propagation velocity

In order to compare quantitatively the fracture toughness of the chemical and the dual crosslink gels, the fracture energy Γ is estimated using Greensmith⁴ approximation. **Figure 19a** shows the fracture energy of the chemical gel, Ni^{2+} dual crosslink gels with different Ni^{2+} concentrations, and Zn^{2+} gel with $C(\text{Zn}^{2+}) = 100 \text{ mM}$ as a function of applied stretch rate. The fracture energy of the chemical gel remains almost constant with stretch rate, except for the slightly higher value (about 10 J/m^2 difference) at $\dot{\lambda} = 0.3 \text{ s}^{-1}$. For the Ni^{2+} gels, at all three Ni^{2+} concentrations, Γ increases very significantly with $\dot{\lambda}$ and $[\text{Ni}^{2+}]$. Comparing gels identical concentration of Ni^{2+} and Zn^{2+} , the Ni^{2+} gel has a slightly higher Γ than Zn^{2+} gel in the whole $\dot{\lambda}$ range tested.

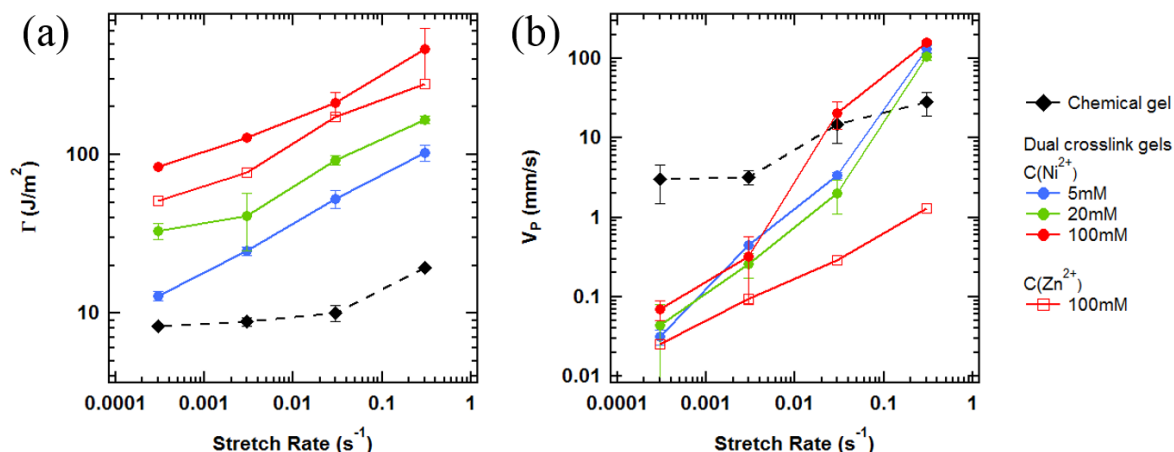


Figure 19. Plot of fracture energy (a) and crack propagation velocity (b) as a function of stretch rate, for chemical gel and dual crosslink gels.

To complete our fracture study, it is very important to study the crack propagation velocity. As shown in **Figure 19b**, the crack propagation velocity V_P of the chemical gel increases slightly with stretch rate probably due to its imperfect crosslinking structure. While for dual crosslink gels with Ni²⁺, the V_P increases nearly linearly with increasing stretch rate, with an exponent of 1.26, 1.36 and 1.41 for [Ni²⁺] = 5, 20 and 100 mM. For the Zn²⁺ gel, the exponent is 0.56, and the V_P is lower than the Ni²⁺ gel regardless of the stretch rate: the difference is large at high stretch rate (over 100 times), and smaller at low stretch rate (3 times).

If the fracture energy Γ is plotted as a function of the crack propagation velocity V_P (**Figure 20**) for both metal ion systems, the fracture energy always increases significantly with the increasing crack propagation velocity, the exponent is 0.22, 0.20, 0.24 and 0.42 for gel with [Ni²⁺] = 5, 20, 100 mM and for [Zn²⁺] = 100 mM, respectively, the fracture energy of the chemical gel increases with an exponent of 0.37. As mentioned in the beginning of this Chapter (**Figure 4**), this is the a typical behavior of soft materials.² One should note however that the higher exponent measured for the [Zn²⁺] system suggests a more efficient viscoelastic dissipation during crack propagation which is surprising given the fact that the main relaxation

time is much faster than the inverse of the strain rate. In other words fast exchanging physical crosslinks are able to create significant viscoelastic dissipation in large strain.

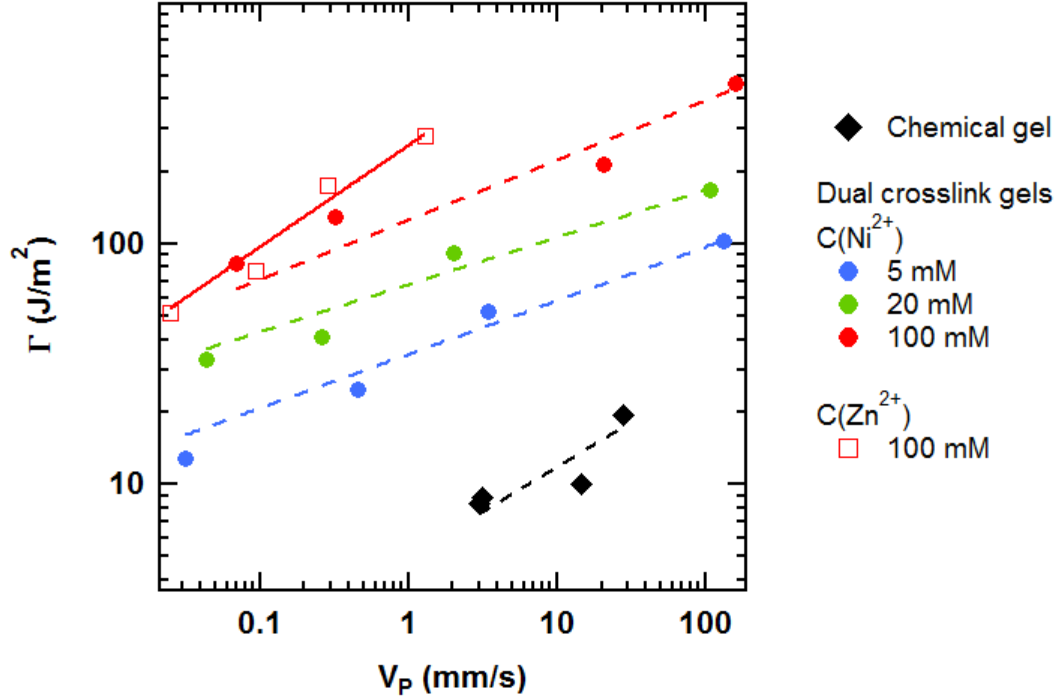


Figure 20. Plot of fracture energy as a function of crack propagation velocity.

5.2.1.6 Local fracture energy Γ_{local}

It should be noted that, as discussed for the PVA-borax system this measured fracture energy Γ includes the dissipated elastic energy during loading and the local fracture energy Γ_{local} can be estimated by accounting for the dissipated energy with a model of unloading curves. In order to calculate the amount of energy available for fracture, it is necessary to estimate the area under the unloading curve. The unloading rate $\dot{\lambda}_U$ can be written as⁸:

$$\dot{\lambda}_U = \frac{\lambda_C - 1}{\delta t} = \frac{\lambda_C - 1}{\omega - c} V_P \quad (9)$$

where, ω is the width of the sample, and c is the length of the crack. For this AAm-VIm- M^{2+} system, the unloading rate $\dot{\lambda}_U$ is close to the loading rate, and since a detailed material model

has not been developed, the Γ_{local} can still be roughly estimated based on the loading unloading cycles at different strain rates (**Chapter 2, Figure 22**). By calculating the area under the unloading curves, the Γ_{local} can be estimated, and plotted as a function of the stretch rate (**Figure 21**). Interestingly the Γ_{local} for these two dual crosslink gels have very similar value and increasing tendency.

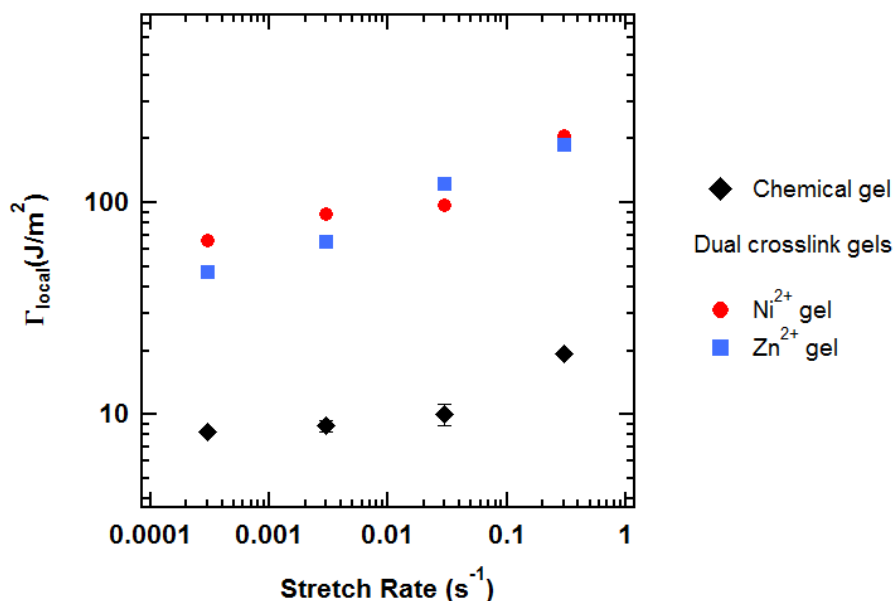


Figure 21. The Γ_{local} as a function of the stretch rate.

5.2.2 Comparison between the AAm-VIm-M²⁺ and the PVA-borax systems

As shown above, the AAm-VIm-M²⁺ dual crosslink gels show stretch rate dependent fracture properties. Here we compare the fracture properties of the AAm-VIm-M²⁺ system with those of the PVA-borax system. The difference between the PVA-borax ($C_{borax} = 1$ mM) gel, AAm-VIm-Ni²⁺ [Ni^{2+}] = 100 mM) gel, and AAm-VIm-Zn²⁺ ($[Zn^{2+}] = 100$ mM) gel is qualitatively discussed. In order for the comparison of these three systems having a very different relaxation time to be also as quantitative as possible, the stretch rate is normalized by the relaxation time

as previously done in Chapter 4. At 25 °C, the relaxation time τ_R of these three gels is 1.58 s, 0.022 s and 0.000045 s, respectively. **Figure 22(a)** shows the fracture energy Γ as a function of $\dot{\lambda}\tau_R$. Due to the very different toughness of these gels, the value of the fracture energy is also very different, the AAm-VIm- M^{2+} gels have a higher fracture energy than the PVA-borax gel at most of the stretch rates. Still we can qualitatively see a global tendency: with increasing $\dot{\lambda}\tau_R$ up to $\dot{\lambda}\tau_R, \sim 10^{-2}$, the fracture energy increases, then it decreases ($\dot{\lambda}\tau_R, > 10^{-1}$). This result suggests that at very slow stretch rates such as $\dot{\lambda}\tau_R, < 10^{-4}$, which is not easily tested for the PVA-borax system (very slow traction thus very long experimental duration is required), the fracture energy decreases and presumably approaches that of the chemical gel.

In **Figure 22(b)** crack propagation velocity V_P as plotted as a function of $\dot{\lambda}\tau_R$. A change in the behavior at $\dot{\lambda}\tau_R, \sim 10^{-2}$ is observed. At high stretch rates ($\dot{\lambda}\tau_R, > 10^{-1}$), the value of V_P is high and independent of the stretch rate. It decreases with decrease in $\dot{\lambda}\tau_R$.

This indicates that, despites all the differences of these two systems (different polymer, preparation methods, physical crosslinking...), the same basic dual crosslink structure results in similar tendency of the fracture properties. Each system shows part of the puzzle, which gives us a chance to look at the mechanical properties through very wide (over 8 decades) time range.

Figure 23 shows the local fracture energy Γ_{local} as a function of crack propagation velocity V_P , for AAm-VIm- M^{2+} gel with $[Ni^{2+}] = 100$ mM, $[Zn^{2+}] = 100$ mM, and the PVA-borax dual crosslink gels. The PVA-borax gel has a higher Γ_{local} (around 50 J/m²) at low V_P , (< 10 mm/s), and a low value (around 20 J/m²) at high V_P , which is very close to the value of the pure chemical gel while for both the AAm-VIm- Ni^{2+} gel, and the Zn^{2+} gel Γ_{local} increases with V_P as classically observed for viscoelastic materials.

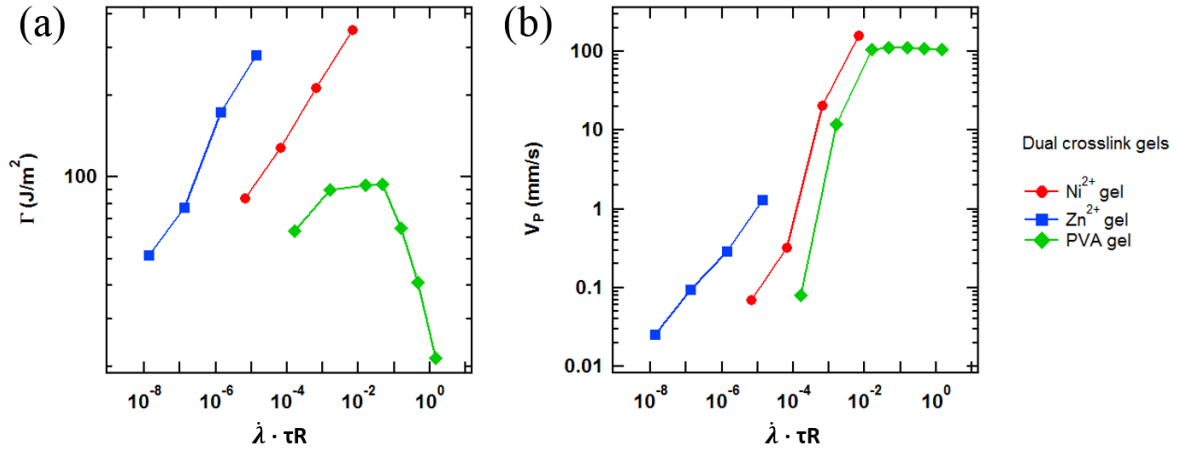


Figure 22. Fracture energy Γ (a) and crack propagation velocity V_P (b) as a function of $\lambda \tau_R$, for Ni²⁺ (red), Zn²⁺ (blue), and PVA-borax dual crosslink gels.

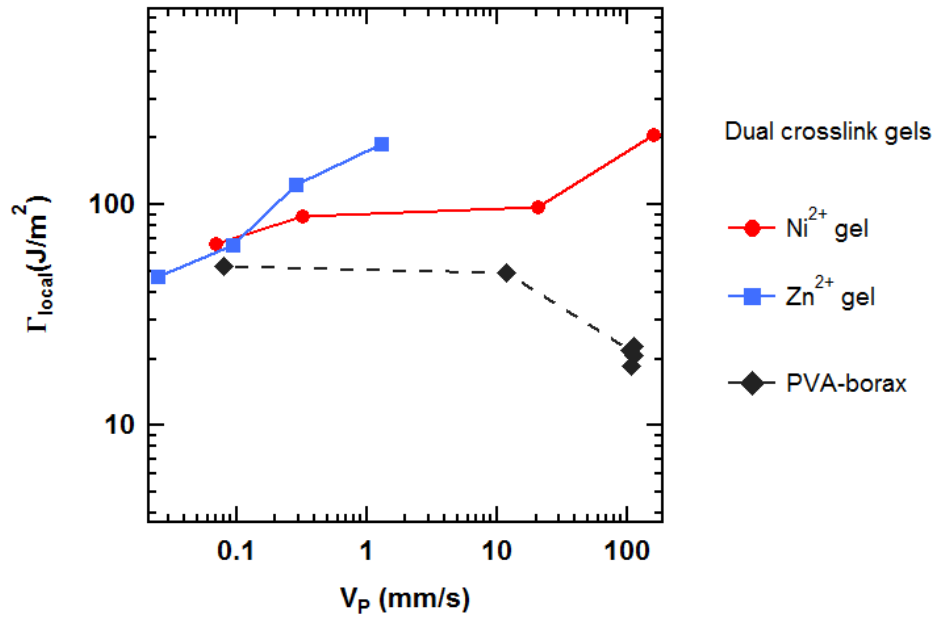


Figure 23. Γ_{local} as a function of crack propagation velocity V_P for Ni²⁺ (red), Zn²⁺ (blue), and PVA-borax dual crosslink gels.

5.3 Conclusion

A series of systematic fracture experiments in a single edge notch geometry have been carried out, over a range of stretch rates on AAm-VIm- M^{2+} dual crosslink gels, with different physical crosslinking density, as well as different metal ions (Ni^{2+} and Zn^{2+}). The Fracture energy and crack propagation velocity were studied and analyzed, the comparison between dual crosslink gels and chemical gel of two systems were made. Our main conclusions are following:

(1) Effect of physical crosslinking density:

There's a small effect of the stretch rate on the stiffness and the strain at break for the chemical gels, while a significant effect for the dual crosslink gels due to the breaking and healing of the physical crosslinks. Higher physical crosslinking density results in a higher critical extension ratio and higher fracture energy, all dual crosslink gels have strong stretch rate dependency.

(2) Effect of different metal ions:

Both gels have stretch rate dependent behavior, λ_C of the un-notched samples are much higher than that of the notched samples regardless of stretch rate (2 – 4 times). Compare to the Zn^{2+} gel, the Ni^{2+} gel has a higher initial modulus, fracture energy, and higher crack propagation velocity regardless of the stretch rate. However, the higher exponent measured from the V_P as a function of stretch rate for the $[Zn^{2+}]$ system suggests a more efficient viscoelastic dissipation during crack propagation, which indicates that fast exchanging physical crosslinks are able to create significant viscoelastic dissipation in large strain.

(3) Comparison with the PVA-borax dual crosslink gels:

The AAm-VIm- M^{2+} gels had a higher fracture energy than the PVA-borax gel at most of the stretch rate, the stretch rate was normalized by the relaxation time to see the global tendency: with increasing $\dot{\lambda}\tau_R$ up to $\dot{\lambda}\tau_R, \sim 10^{-2}$, the fracture energy increases, then it decreases ($\dot{\lambda}\tau_R, > 10^{-1}$), each system showed part of this tendency.

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General conclusion

The PVA-borax dual crosslink gel^{1,2} developed by Mayumi *et al.*, based on the introduction of transient crosslinks led to interesting improvements in strength and toughness compared to the chemical gel, in particular at low strain rates. The effect of the dynamics of chain association/dissociation on the mechanics were investigated thoroughly on a system with a low chemical crosslink density. However, the coupled effect of chemical and physical crosslinking for variable relative densities was not clear, and more experiment and theoretical analysis were needed with different compositions of gels. Additionally, the complexity and limitations of the physical chemistry of the PVA-Borax system at the molecular level, motivated us to develop and study a new dual crosslink gel (AAm-VIm-M²⁺ system). In particular the PVA-borax system gave no access to low physical crosslinking density, the dynamics was slow and difficult to tune, and the physical crosslinking ratio difficult to determine.

In this work, systematic studies have been conducted on the PVA-borax and the AAm-VIm-M²⁺ dual crosslink gels, in order to investigate the effect of the interplay between chemical and physical crosslinks on the small strain rheology, large strain extension and failure properties.

First, the effect of the crosslinking density of the PVA-borax dual crosslink gels was studied for three aspects: additivity, extensibility and separability. The independent and additive contributions of two types of crosslinks to the elastic and viscous moduli was confirmed for all hydrogels investigated, the relaxation time increases with decreasing physical crosslinking density, due to the concomitant increase in the Rouse time and decrease in the healing time. The extensibility of the dual crosslink gels was found higher than that of the corresponding chemical gels, but increasing the concentration of physical crosslinks decreased the extensibility. The strong strain rate-dependent behavior could be separated into a strain-dependent and time-dependent term, and a master curve of the reduced stress as a function of time was obtained.

These stress-strain behaviors and the effect of physical crosslinks could be modeled with a physically based constitutive model connecting the breaking and re-forming kinetics of the physical bonds to the large deformation behavior of the gel. Two sets of parameters were determined by fitting the experimental data of the tensile and the torsion relaxation test, respectively, and can describe well both tensile and torsion behaviors of the dual crosslink gels at various crosslinking ratio with only four parameters.

Following the study of the effect of varying relative crosslinking concentration on the PVA-borax dual crosslink gels, the AAm-VIm- M^{2+} system was developed. The rheological and tensile properties of this bio-inspired metal-ligand coordination dual crosslink hydrogel were investigated over a wide range of strains and strain rates with two different metal ligands and several ligand concentrations, in comparison with the corresponding chemical gel. The rheological modulus and tensile modulus as well as the extensibility of the AAm-VIm- Ni^{2+} dual crosslink gels were found to be much higher than those of the bare chemical gel. Regardless of the concentration of the ligand, the $G''(\omega)$ curve showed a well-defined relaxation peak, which shifted to lower frequency with increasing crosslinking density, while the tensile extensibility of un-notched samples decreased with increasing $[M^+]$. On the other hand the dissipated energy in loading/unloading cycles increased with $[M^+]$. The AAm-VIm- Zn^{2+} gel was confirmed to have a much faster association/dissociation dynamic than the Ni^{2+} gel, which resulted in a lower hysteresis. The large strain properties were found strongly strain-rate dependent, with a marked softening at small strain and strain hardening at large strain, the Mooney plot and the stress relaxation tests suggested the presence of a slower relaxation mode in addition to the fast relaxation mode seen in linear rheology.

Compared to the PVA-borax dual crosslink gels, the AAm-VIm- M^{2+} dual crosslink gels have a relatively short ($10^{-3} - 10^{-1}$ s) and tunable main relaxation time, an easy and quick synthesis

process, easy access to low physical crosslinking density, much higher modulus and extensibility, and a second slow relaxation time. Despite all these differences, due to the same general structure and reinforcement mechanism, a rough master curve of loss tangent $\tan \delta$ was found, indicating the consistency in rheological properties between these two systems.

The fracture properties of the AAm-VIm- M^{2+} dual crosslink gels were studied and compared with that of the PVA-borax dual crosslink gels. For the AAm-VIm- M^{2+} dual crosslink gels, a significant effect of stretch rate was found on the stiffness and the strain at break, due to the breaking and healing of the physical crosslinks. Compare to the Zn^{2+} gel, the Ni^{2+} gel has a higher initial modulus, fracture energy, and higher crack propagation velocity (V_p) regardless of the stretch rate. However, the higher exponent measured in the Γ vs. V_p curve for the $[Zn^{2+}]$ system suggests a more efficient viscoelastic dissipation during crack propagation, which indicates that the fast exchanging physical crosslinks of the $[Zn^{2+}]$ based system are able to create significant viscoelastic dissipation in large strain. The stretch rate was normalized by the relaxation time to see the global tendency of these two systems: with increasing $\dot{\lambda}\tau_R$ up to $\dot{\lambda}\tau_R \sim 10^{-2}$, the fracture energy increases, then it decreases ($\dot{\lambda}\tau_R > 10^{-1}$), each system showed part of this tendency.

This work shows that while it may be tempted to think that dual crosslink gels with similar linear rheology (dynamics) should have a general behavior, there are many differences in the details of the physical chemistry and the effect of relative concentration of chemical and physical crosslink as well as the details of the network architecture (chemical and physical), i.e. the relative position in space of the crosslink points may lead to very different large strain and in particular fracture behavior. This study has laid the groundwork on the one hand for the future development of a constitutive model of the AAm-VIm- M^{2+} dual crosslink gels

integrating the complexity of the large strain behavior and on the other hand to investigate the details of bond breakage at the crack tip with mechanochemistry tools.

Résumé

Des hydrogels résistants avec des points de réticulation permanents et temporaires ont été élaborés, et leur structure, leurs propriétés mécaniques et les mécanismes de renforcement ont été étudiés. L'origine de cet important renforcement mécanique vient de l'introduction de points de réticulation temporaires : la rupture de ces liaisons temporaires dissipe de l'énergie de déformation et redistribue les forces locales, qui protègent ainsi les liaisons permanentes qui à leur tour empêchent l'écoulement plastique du réseau. La rhéologie linéaire, les propriétés de traction non-linéaires et les propriétés de fracture de deux doubles réseaux ont été étudiées : un gel de poly(alcool vinylique) réticulé chimiquement par du glutaraldéhyde et réticulé physiquement par des ions borates (gel PVA-borax), et un gel de poly(acrylamide-co-1-vinylimidazole) réticulé chimiquement par du N,N'-Méthylènebisacrylamide et réticulé physiquement par des ions métalliques (gel AAm-VIm-M²⁺). Ces deux doubles réseaux ont des temps de relaxation très différents, ce qui a permis l'étude de la dynamique sur une grande plage de temps. Pour des taux de déformation optimaux, les deux gels présentent un important renforcement mécanique en termes de raideur, de déformation à la rupture et de capacité à résister à la propagation de fissure. Cependant, l'extensibilité et la résistance à la fracture du gel AAm-VIm-M²⁺ augmentent avec le taux de déformation et avec [M²⁺] tandis que la tendance inverse est observée pour le système Borax, ce qui suggère que, au-delà du temps de relaxation principal en petites déformations, les détails de l'architecture du réseau chimique et physique à l'équilibre sont importants pour le processus de fracture.

Clés

Hydrogel, renforcement mécanique, viscoélasticité, dissipation d'énergie, auto-cicatrisant, réticulation, fracture

Abstract

Tough hydrogels with permanent and transient crosslinks have been designed, and their structure, mechanical properties, and their reinforcement mechanisms have been investigated. The origin of this strong mechanical reinforcement comes from the introduction of the transient crosslinks, the breaking of these transient bonds dissipate strain energy and redistribute local forces, preventing the irreversible rupture of the permanent bonds, while the permanent bonds prevent the network from plastic flow. The linear rheology, nonlinear tensile and fracture properties of two different dual crosslink gels have been studied: a poly(vinyl alcohol) gel chemically crosslinked by glutaraldehyde and physically crosslinked with borate ion (PVA-borax gel), and a poly(acrylamide-co-1-vinylimidazole) gel chemically crosslinked by N,N'-Methylenebisacrylamide and physically crosslinked by metal ions (AAm-VIm-M²⁺ gel). These two dual crosslink gels have very different relaxation times, which made it possible to investigate the dynamics over a large time range. For optimized strain rates, both gel systems exhibited strong mechanical reinforcement in terms of stiffness, strain at failure, and the ability to resist crack propagation. However the extensibility and fracture toughness of the AAm-VIm-M²⁺ gel increased with strain rate and [M²⁺] while the opposite trend was observed for the Borax system, suggesting that, beyond the main relaxation time, the details of the chemical and equilibrium physical network architecture are important for the fracture process.

Keywords

Hydrogel, mechanical reinforcement, viscoelasticity, energy dissipation, self-healing, crosslinks, fracture