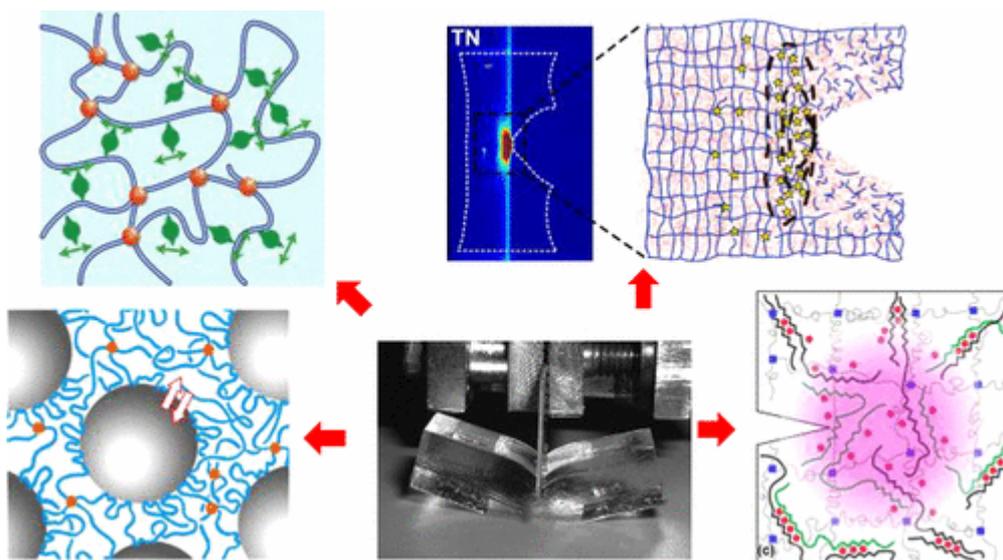


## 50<sup>th</sup> anniversary perspective: Networks and Gels: Soft but Dynamic and Tough

**Costantino Creton**<sup>1,2,3</sup>

1. *Laboratoire de Sciences et Ingénierie de la Matière Molle, CNRS, ESPCI Paris, PSL Research University, 10 Rue Vauquelin, 75005 Paris, France*
2. *Laboratoire Sciences et Ingénierie de la Matière Molle, Université Pierre et Marie Curie, Sorbonne-Universités, 10 rue Vauquelin, France*
3. *Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, Japan*



### Abstract

*Soft polymer networks have seen an explosion of recent developments motivated by new high tech applications in the biomedical field or in engineering. We present a candid and critical overview of the current understanding of the relation between the structure and molecular architecture of polymer networks and their mechanical properties, restricting ourselves to soft networks made of flexible polymers and displaying entropic elasticity. We specifically review and compare recent approaches to synthesize swollen hydrogels with enhanced toughness, resilient but tough unfilled elastomers and self-healing networks containing dynamic bonds. The purpose is less to draw a comprehensive catalogue of approaches than to identify and unify the underlying principles controlling toughening mechanisms and mechanical self-healing behaviour and to point out remaining challenges.*

# 1 Introduction

Polymer networks are generally defined as polymer chains connected by crosslinking points. These crosslinking points prevent flow at a scale larger than the mesh size and make the networks swell in good solvents but not dissolve. Depending on the glass transition temperature they can be either in the glassy state or in the rubbery or soft state. In the present review we will focus on recent advances in the area of soft networks which combine low elastic modulus (from a few kPa to a few MPa) and large extensibility. We will extend the definition of crosslinks from permanent covalent bonds to reversible and dynamic bonds but will focus on soft solids and not viscoelastic fluids.

Classical soft networks are of course elastomers, such as crosslinked natural rubber, styrene-butadiene rubber or silicone rubber<sup>1</sup>. Spurred by the discovery of vulcanization by Goodyear in 1840 these elastomers have found widespread engineering applications, the largest of which being vehicle tires and seals. Beyond elastomers, the other large family of soft networks are swollen gels, and in particular hydrogels, that are essentially polymer solutions that are prevented from flowing by the presence of crosslinking points. Their classical industrial applications involve the ability to absorb and retain large amounts of fluids such as the superabsorbents used in diapers.

In recent years, soft networks have found a much wider variety or more specialized applications both in engineering such as soft robotics<sup>2</sup> and wearable electronics<sup>3</sup>, or in the biomedical field such as tissue engineering<sup>4</sup>, soft prosthetics<sup>5</sup> and large strain actuators<sup>6</sup>. As new inventions and technologies such as elastomeric transducers<sup>6-7</sup>, stretchable conductive gels<sup>8</sup>, soft grippers<sup>2,9</sup> and of course 3D printing of soft materials and even hydrogels<sup>10</sup> are developed, there will be an increasing need to understand and optimize not only the chemistry of the product and its interactions with the environment but also its mechanical properties and range of use in terms of stress, strain and temperature.

Structure-mechanical properties relations in networks have been first studied in elastomers for a good reason: very stretchable and tough materials were developed relatively early for tire applications and it made sense to study in detail how mechanical properties such as elasticity, strength and toughness depended on molecular parameters accessible to the synthetic chemist or formulator, such as the effect of the average density of crosslinks or the effect of added filler on the experimental parameters such as the strain rate and temperature. The classic textbook of Treloar<sup>11</sup> contains a very detailed summary of the state of the art of soft network physics in the late 1950's and the excellent book edited by Alan Gent discusses mechanical properties of engineering elastomers<sup>1</sup>. This begs the question: why write a perspective paper on this topic now?

In recent years, stimulated by some innovative seminal papers, the field of polymer networks has seen a spectacular development of new approaches and materials often motivated by the desire to combine a set of mechanical or physical properties that are difficult to obtain in classical networks. For example, swollen networks are generally soft but relatively brittle due to the lack of internal dissipation mechanisms. Introducing such dissipation mechanisms through network design can lead to dramatic improvements in stiffness, stress at break and fracture energy while maintaining a large extensibility<sup>12-13</sup>. This effect has been particularly studied for water-swollen networks, also called hydrogels, whose relevance in the field of life sciences has been an additional motivation.

In elastomers, recyclability has been an important drive for innovation, since conventional elastomers are permanently and irreversibly crosslinked and cannot easily be reprocessed or welded once they are fully cured. The development of dynamic bonds that can break and reform has given rise to new soft materials that combine nearly reversible elasticity with the ability to self-heal within a reasonable time<sup>14-16</sup>. These spectacular results have been obtained through the introduction of polar groups into an

otherwise relatively non-polar material. Such polar groups will naturally tend to phase separate and form clusters<sup>17-18</sup> which are more or less long lived and most likely control the dynamics of self-healing as much as molecular diffusion does.

Another interesting combination of properties which is attractive in elastomer applications is the combination of stiffness and reversible elasticity at small strains (with minimal energy dissipation and creep), while maintaining high toughness. This combination of properties obtained with interpenetrating networks<sup>19-20</sup> inspired by the work on hydrogels, requires dissipation to be *strain* dependent rather than *strain rate* dependent as conventional elastomers are designed to be. Such a strategy opens possibilities to maintain elastomer toughness at high temperature and reduce energy dissipation in normal usage conditions.

The objective of this review is not to present a catalog of new materials but rather to rationalize strategies and mechanisms that have been developed to obtain new combinations of mechanical properties in soft polymer networks.

## 2 Simple Polymer Networks

Before we discuss molecular designs of networks it is important to briefly review the molecular origin of elasticity and dissipation at the molecular level and how this relates to the mechanical properties of soft materials. Although networks can be made with macroscopic fibers, nanotubules or semi-flexible polymers, this review will focus on networks made from flexible polymer chains, which are the most ubiquitous in our everyday life.

### 2.1 Basic elasticity

Small strain elasticity in flexible chains is directly related to the change in conformational entropy of the molecules. If the material is crosslinked, the much less mobile crosslink points provide a separator between strands and the shear elastic modulus  $\mu_x$  of a crosslinked network can be described by the sum of the free energy of the strands in the material, i.e.

$$\mu_x = \nu_x kT = \frac{\rho RT}{M_0 N_x} \quad 1$$

where  $\nu_x$  is the density of elastic strands<sup>21</sup>,  $\rho$  is the mass per unit volume of the polymer,  $M_0$  is the molecular weight of the monomer and  $N_x$  the number of monomers per elastic strands. Note that the prediction of the modulus from the chemistry, or in other words the prediction of  $\nu_x$  from the details of the chemical reactions involved in synthesizing the network remains a difficult problem and the recent very elegant work of Zhong et al.<sup>22</sup> quantifying short loops has shown a way to do it. It is important to note that equation 1 assumes that no interactions exist between chains (ideal gas approximation) so it essentially neglects the existence of crosslink points and entanglements and cannot be correct in large strain since it has no mechanism to limit deformation.

If the modulus is known and the material is incompressible, the large strain behavior can be approximated with a free energy function  $W$  based on the same physics and given by:

$$W = \frac{\nu_x k_B T}{2} (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad 2$$

where  $\lambda_1^2$ ,  $\lambda_2^2$  and  $\lambda_3^2$  are the principal stretches. Soft extensible materials are generally incompressible (e.g.  $\lambda_1 \lambda_2 \lambda_3 = 1$ ) so that, for the special case of uniaxial extension, equation 2 results in the following prediction for the nominal stress as a function of stretch::

$$\sigma_N = \nu_x k_B T \left( \lambda - \frac{1}{\lambda^2} \right) \quad 3$$

Where  $\lambda$  is the stretch in the tensile direction. This prediction for the stress-strain curve works well at small and moderate strains for unentangled crosslinked rubbers and hydrogels<sup>23</sup>. At large strains the main assumption of the affine network model, i.e. Gaussian elasticity of the polymer chains, does not hold anymore. In particular, the chains approach their finite extensibility limit and stiffen markedly. Several models have been used to account for that stiffening, but while the stiffening of an individual chain is well described by the Langevin function<sup>11</sup>, the stiffening of an elastic macroscopic material cannot be easily predicted simply from the density of crosslinks  $\nu_x$ . Hence, an additional finite extensibility parameter is used in empirical models. One of the simplest of such models was proposed by Gent in 1996<sup>24</sup>, where  $W$  and  $\sigma_N$  in uniaxial extension are written as:

$$W = -\frac{\nu_x k_B T}{2} J_m \ln \left( 1 - \frac{(I_1 - 3)}{J_m} \right) \quad 4$$

$$\sigma_N = \nu_x k_B T \left( \lambda - \frac{1}{\lambda^2} \right) / \left( 1 - \left( \frac{I_1 - 3}{J_m} \right) \right) \quad 5$$

where  $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$  is the sum of the square of the principal stretches also called the first invariant and  $J_m$  is the maximum allowable value of  $I_1 - 3$  and physically represents the square of the maximum extensibility in uniaxial tension.

In the presence of both entanglements and crosslinks, the large strain behavior should also include a softening mechanism that is well captured by molecularly based models combining the Doi-Edwards tube model and the affine network model. One of the most complete molecular models is the slip-link model proposed by Rubinstein and Panyukov in 2002<sup>25</sup>.

The prediction of the model in uniaxial extension is a slight softening both with positive stresses (in tension) and with negative stresses (in compression). The engineering stress  $\sigma_N$  is then given by:

$$\sigma_N = \nu_x k_B T \left( \lambda - \frac{1}{\lambda^2} \right) + \nu_e k_B T \left( \lambda - \frac{1}{\lambda^2} \right) / (0.74\lambda + 0.61\lambda^{-0.5} - 0.35) \quad 6$$

This model predicts well the non-linear behavior of networks at moderate strains in both tension and compression (which is not the case of many simple non-linear models) as long as the finite extensibility of the chains is not active<sup>25</sup>.

As discussed above, predicting how the finite extensibility of the network strands controls the strain hardening behavior and fracture of the material is a much more complex problem since interactions between strands now matter and mean field approaches are questionable. Nevertheless, more complex molecularly based models have been proposed to account for the combined effect of entanglements and finite extensibility<sup>26</sup> but all contain adjustable empirical parameters.

## 2.2 Limiting extensibility and failure

Experimentally, one should keep in mind that the measured strain and stress at break of a material corresponds to the point where a crack propagates through it. In the large majority of cases this property is characterized in a uniaxial tension test with a dogbone specimen or a strip specimen or in compression with a cylindrical sample. The point of break defines a nominal stress at break  $\sigma_{Nb}$  (force divided by the cross-section of the undeformed specimen) or a true stress at break  $\sigma_{Tb}$  (force divided

by the deformed cross-section). Because of this change in cross-section during deformation, for  $\lambda \gg 1$  and  $\lambda \ll 1$  the value of true stress is much larger (in tension) or much smaller (in compression) than the nominal stress and one should be careful in direct comparisons between tension and compression results.

Because the values of stress and strain at break are often not reproducible from sample to sample, the solid mechanics community prefers to use the fracture energy  $\Gamma$ , a quantity that stems from a fracture mechanics approach which assumes that failure occurs by the propagation of preexisting defects when the energy release rate at the crack tip  $\mathcal{G} > \Gamma$ <sup>27</sup>. In soft materials this approach has been successfully pioneered by Rivlin and Thomas<sup>28</sup> and the interested reader may consult some recent work on the specific issue of crack propagation in soft materials<sup>27, 29-31</sup>. The key result of the fracture mechanics approach in soft materials is a governing equation for the fracture energy (i.e. the energy per unit area to propagate a crack) that can be written as<sup>32</sup>:

$$\Gamma(v) = \Gamma_0(1 + \phi(a_T v)) \quad 7$$

where  $\phi(a_T v)$  is a velocity dependent dissipative factor and  $\Gamma_0$  is the threshold fracture energy for vanishing crack velocities. The idea behind this equation commonly used in both fracture and adhesion<sup>33</sup> is that the energy to break interfacial bonds is contained in  $\Gamma_0$  while the dissipative part is a bulk contribution. Lake and coworkers developed the first and still the most used<sup>34-36</sup> molecular theory for  $\Gamma_0$ . They proposed that when any of the main chain bonds breaks, the total bond energy of each bond of the stretched chain is irreversibly lost. Therefore the minimum energy necessary to break the chain is proportional to the length of that chain, i.e. to the number of C-C bonds comprising that chain  $N_x$ . If one assumes that only the strands crossing the fracture plane will break,  $\Gamma_0$  is then given by:

$$\Gamma_0 = N_x U_b \Sigma \quad 8$$

where  $\Sigma$  is the areal density of strands crossing the interface and  $U_b$  is the bond energy of a C-C bond (350 kJ/mol). For a homogeneously crosslinked network,  $\Sigma$  and  $N_x$  are not independent and one can write:

$$\Sigma \approx v_x a N_x^{1/2} \quad 9$$

where  $a$  is the size of the monomer. Substituting equation 9 into equation 8 and using equation 1,  $\Gamma_0$  can be rewritten as:

$$\Gamma_0 \approx N_x U_b v_x a N_x^{1/2} \propto U_b v_x a N_x^{3/2} \propto \frac{U_b a \rho}{M_0} N_x^{1/2} \quad 10$$

where  $\rho$  is the monomer density and  $M_0$  is the molar mass of the monomer. This equation is valid for both elastomers and swollen gels since the difference between the two cases is mainly contained in  $\rho$ , which for elastomers is a bulk unswollen density  $\rho_0$  of the order of  $10^3 \text{ kg/m}^3$  and for gels it is simply  $\rho = \rho_0 \phi_p$  where  $\phi_p$  is the polymer volume fraction. This prediction has been verified in gels and elastomers.

Combining equation 1 with Equation 10,  $\Gamma_0$  can be also rewritten as:

$$\Gamma_0 \approx U_b a \left(\frac{\rho}{M_0}\right)^{3/2} (k_B T)^{1/2} \mu_x^{-1/2} \quad 11$$

This is a key prediction that has been verified experimentally for simple networks in elastomers<sup>37</sup> and also applies to gels if corrections are made to account for the prestretching of strands in swollen gels<sup>38</sup>. This equation is the starting point of all efforts to improve mechanical properties of soft networks. Two important aspects are clear from equations 10 and 11:

- 1) In simple elastic networks, there is a trade-off between stiffness and toughness ( $\Gamma_0 \propto \mu_x^{-1/2}$ ) and
- 2) Elastic swollen gels with the same value of  $N_x$  are much more brittle than elastomers since  $\Gamma_0 \propto \rho_0 \phi_p$

Since many research studies do not focus on toughness but on extensibility, let's quickly examine how the Lake-Thomas model predicts the extensibility of the material.

If one assumes that all materials contain a crack precursor of the same initial length  $c$ , this precrack will propagate when the energy release rate exceeds the fracture energy  $\Gamma_0$ . In a single-edge notch sample typical of what is used in uniaxial tension<sup>39-40</sup> the energy release rate  $\mathcal{G}$  is approximately given by<sup>41</sup>:

$$\mathcal{G} = \frac{6cW(\lambda)}{\sqrt{\lambda}} \quad 12$$

where  $W(\lambda)$  is the strain energy density defined in equation 2. For  $\lambda \gg 1$ , in uniaxial tension  $W(\lambda)$  scales with  $\mu_x \lambda^2$ . So if we set  $\mathcal{G} = \Gamma_0$  at propagation and we use equation 11, we can write:

$$U_b a \left( \frac{\rho}{M_0} \right)^{3/2} (k_B T)^{1/2} \mu_x^{-1/2} = \frac{6c \mu_x \lambda_b^2}{\sqrt{\lambda_b}} \quad 13$$

Therefore, the extensibility  $\lambda_b$  at which the crack propagates and the sample fails, scales with  $\mu_x^{-1}$ . However, at the molecular scale, the maximum extensibility of a strand should be proportional to the square root of its number of monomers, i.e. to  $\mu_x^{-1/2}$ . In other words, if the only dissipative mechanism is the fracture of polymer strands, one expects the extensibility of the macroscopic *material* to decrease much faster with increasing crosslinking than the extensibility of the molecular *strand* and this is observed experimentally. In addition randomly crosslinked networks are often very heterogeneous and contain or easily create relatively large defects that further reduce  $\lambda_b$ .

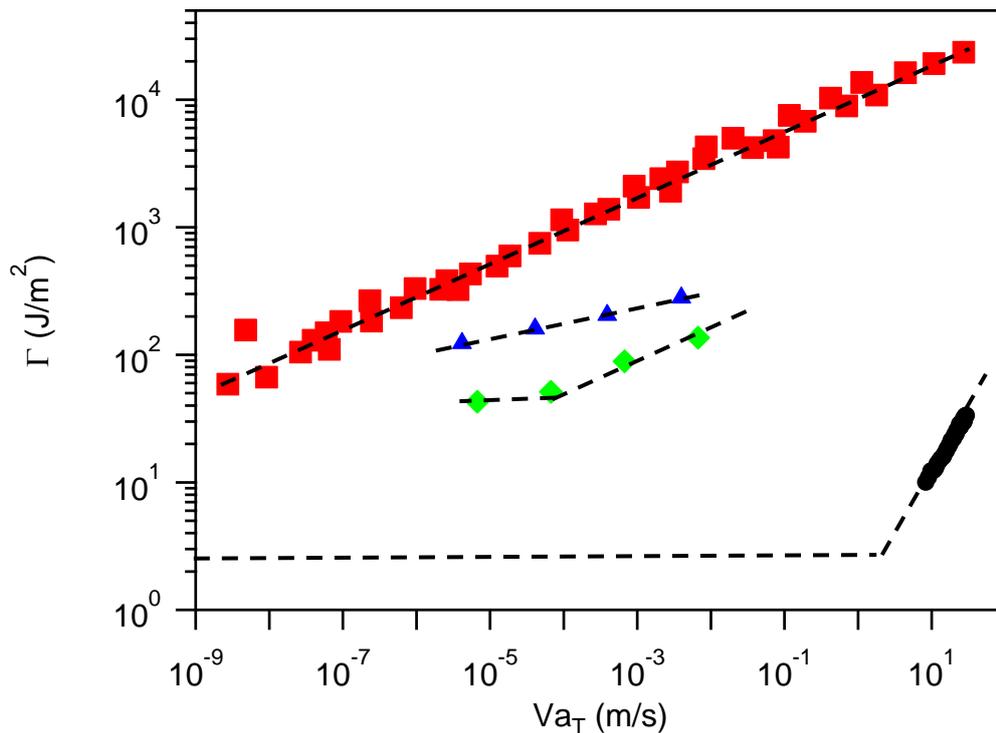
In summary, networks cannot extend more than the limiting extensibility of the connected polymer strands. However they generally break at extensibilities that are much less than this limiting extensibility because of local stress concentrations that facilitate the propagation of cracks. Any strategy to increase the toughness of the material has to keep the following two points in mind:

- The average limiting extensibility of the polymer strands is a hard limit so a low crosslink density (long strands) is essential.
- To reduce the forces applied on the polymer strands at the crack tip, the material has to be able to relax high stresses or alternatively to dissipate energy between the loading point (far from the crack) and the crack tip<sup>30</sup>. This is the realm of solid mechanics and it is important to focus now on larger length scales than the molecular scale.

In elastomers, the most important bulk energy dissipation mechanism is molecular friction, which is controlled by the monomer friction coefficient. A measurement of the linear viscoelastic properties of a soft material generally reveals an elastic and viscous component of the complex shear modulus  $\mu^*(\omega)$  which varies with frequency. For crosslinked networks, the low frequency limit of this quantity is  $\mu_x$ . However, at high frequency  $\mu'(\omega)$  typically increases and so does  $\mu''(\omega)$ . Conversely, several examples of measurements of  $\Gamma$  for typical soft materials show that the fracture energy generally increases very significantly with crack propagation velocity<sup>42-43</sup>. The functional form of  $\Gamma(v)$  is similar to that found for adhesion, i.e. a threshold value  $\Gamma_0$  and a power-law dependence at higher crack velocities, i.e.  $\phi(a_T v) \sim v^n$ . The value of the exponent  $n$  has been reported to vary between 0.1 and 1 depending on the material as reported in Figure 1 for two rubbers and two crosslinked gels<sup>40, 42, 44-45</sup>. An interesting result shown in Figure 1 is the possibility to construct a master curve from fracture data measured at different temperatures by using velocity shifts of the horizontal axis. This result was interpreted early on as proof of the viscoelastic nature of the dissipative processes involved at the

crack tip<sup>44, 46-49</sup>. Based on this insight many researchers in physics and mechanics have sought to account quantitatively for the dissipation of energy during fracture by using linear viscoelastic properties of the materials and a good recent review is provided by Persson<sup>50-51</sup>. If the materials is viscoelastic at the typical strain rates at which it is deformed during the fracture experiments, molecular friction can make a very significant contribution and toughen a network.

In other words *any simple network will become tougher as the testing temperature approaches its glass transition and molecular friction is active*. However, a typical well crosslinked rubber is used about 40-50°C above its glass transition temperature mainly to avoid viscoelastic losses and heating during normal use. At that temperature, the ratio of the dissipative vs. storage component ( $\tan \delta$ ) of the 1 Hz modulus is well below 0.1 and viscoelastic losses due to monomer friction do not make a large contribution. This is also true for gels swollen with low viscosity solvents and in particular hydrogels.



**Figure 1:** a) Fracture energy  $\Gamma$  as a function of propagation velocity or reduced propagation velocity for different materials. ■ ) Master curve at 25°C for a styrene-butadiene rubber ( $T_g = -25^\circ\text{C}$ ) tested with the trouser tear geometry. Data from<sup>44</sup>. ◆ ) Polyurethane rubber ( $T_g = -55^\circ\text{C}$ ) at 25°C tested with the single edge notch geometry. Data from<sup>40</sup>. ▲ ) Double network hydrogel at 25°C. Data from<sup>45</sup>. ● ) Gelatin gel (5 wt% polymer) at room temperature in the pure shear geometry. Data from<sup>42</sup>. Horizontal lines are values of  $\Gamma_0$  when reported.

In summary two dissipation mechanisms controlling crack propagation have been clearly identified in simple networks, a covalent bond breakage mechanism, which occurs very locally at the crack tip and sets a threshold value, and a molecular friction mechanism which is clearly strain rate dependent and is responsible for the increase of the fracture energy with crack propagation rate.

While this combination of mechanisms is a good framework to think about dissipation in fracture of soft materials, it does not explain all experimental results. For example, hydrogels do not have an internal molecular friction mechanism and can be quite tough, networks can become tougher or more brittle as the strain rate is increased. Filled systems are significantly tougher than unfilled ones while they are not significantly more dissipative in linear viscoelasticity.

We will now discuss other types of dissipation mechanisms at the molecular scale able to delay crack propagation and toughen soft materials.

### 3 Toughening soft elastic networks through network design

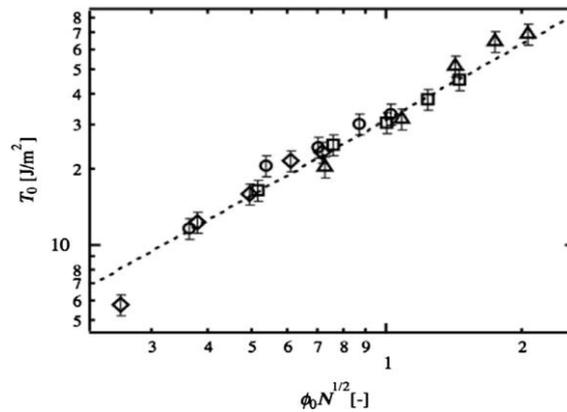
In recent years there has been a push towards developing new soft materials, in particular hydrogels, combining a high extensibility, i.e. a large stretch at break  $\lambda_b$ , with a large stress at break  $\sigma_{Nb}$  or, if crack propagation experiments were carried out, a large value of  $\Gamma$ .

Classical polymer soft networks are synthesized either by crosslinking existing high molecular weight polymers, or by simultaneously polymerizing and crosslinking low molecular weight precursors. These two methods create generally randomly crosslinked networks which are elastic but contain many molecular heterogeneities<sup>52</sup> and are relatively brittle in the absence of viscoelastic dissipation as discussed above. Therefore one strategy used to increase  $\sigma_b$  and  $\lambda_b$  simultaneously was to synthesize networks with a very homogeneous structure in order to avoid potential sites of nucleation of fracture and for elastomers to avoid trapping entanglements<sup>53</sup>.

#### 3.1 Designing homogeneous networks

This was first done with silicone chemistry, with many studies focusing on reducing the heterogeneities inherent in a random crosslinking process by starting with precursors of known and uniform molecular weight. The objective was to test rubber elasticity theories<sup>54-56</sup> but some of the studies focused on mechanical strength as well<sup>57</sup>. This strategy was supposed indeed to give rise to more homogeneous networks and hence reduces the intrinsic defects present in the material, delaying the nucleation of crack precursors and, therefore, increasing  $\lambda_b$  for unnotched samples. However neutron scattering experiments showed that for end-linked PDMS chains the networks were in general far from perfect and homogeneous<sup>58-59</sup> and these materials remain quite brittle.

A better recent example are the hydrogels made from two types of tetra-polyethylene glycol chains<sup>60</sup>. Such networks are very homogeneous, from neutron scattering experiments<sup>61</sup>, and show a large reversible extensibility. However, since they have no built-in energy dissipation mechanisms, the artificial introduction of a defect such as a notch will cause propagation and the fracture energy  $\Gamma$  measured with a fracture mechanics test remains relatively low<sup>38</sup>. An example of the fracture energy of these materials as a function of strand length in the network is shown in Figure 2 and confirms very convincingly the Lake and Thomas theory (see equation 10) but values of  $\Gamma_0$  are only in the range of 10-70 J/m<sup>2</sup>.



**Figure 2:** Threshold fracture energy  $T_0$  (original symbol  $T_0$ ) of a series of model hydrogels based on the tetra-PEG segments.  $\phi_0$  is the monomer concentration in the gel and  $N$  is the number of monomers in each chain. Reprinted from <sup>62</sup>

Another example of an original and more homogeneous structure is the so called slide-ring gel made with polyrotaxane<sup>63</sup>. Because crosslink points can slide along the chain and redistribute forces, local heterogeneities are minimized during deformation and the materials show the very remarkable property of having the same modulus (controlled by the density of elastic chains) and very different extensibilities because the length of the chain between non sliding crosslinks varies<sup>64</sup>. However, in the absence of other dissipative mechanisms the fracture energy of these organogels in notched samples remains relatively low. Yet the strategy of sliding crosslinks can be combined with another dissipative mechanism and result in quite tough materials suitable for applications<sup>65</sup>.

While making the material homogeneous can delay fracture by avoiding the presence of large defects, the best way to slow the propagation of a crack is to introduce energy dissipation mechanisms that reduce local stress concentrations in front of a propagating crack and reduce the elastic energy transferred to the crack tip.

### 3.2 Dissipation mechanisms in soft tough materials.

As discussed above the principle of creating tough networks relies on creating dissipation mechanisms. Although hydrogels and elastomers are very similar in structure, there are some key differences that I would like to discuss first. Hydrogels do not have an equivalent to the glass transition temperature of elastomers and therefore no intrinsic molecular friction mechanism. However, because water typically dissolves well polar molecules that can interact strongly with each other, it is much easier to introduce randomly dispersed dynamic molecular interactions in hydrogels than in non-polar elastomers where many polar molecules are generally insoluble and form clusters. A classic example of the latter are ionomers<sup>18, 66</sup>.

Three general methods have been used to toughen hydrogels while retaining the reversible elasticity, all relying on breaking internal bonds, also called sacrificial bonds, and dissipating energy to delay crack propagation. However the strategies used were very different.

The first strategy involves creating sacrificial bonds that break because they are *overloaded* relative to the main bonds. This is the situation of the double network gels developed by the Gong group at U. Hokkaido<sup>67</sup>. These gels are synthesized in two steps of polymerization and as a result, contain two

populations of strands, a minority population close to its maximum extensibility and the rest of the strands nearly unstretched<sup>68-69</sup>.

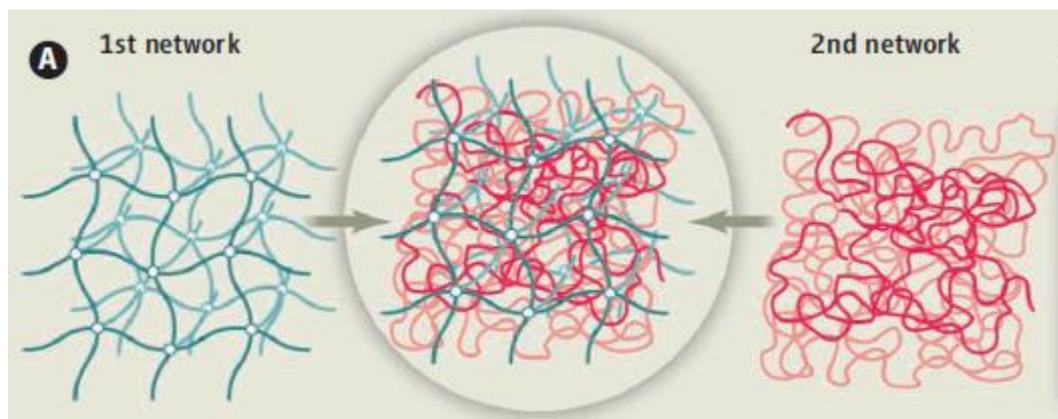
A second strategy involves introducing *plasticity* in the gel by incorporating stiffer domains that can only be deformed above a certain stress level<sup>13, 29, 70-75, 76-77</sup>. This creates a large damage zone in front of a crack but also permanent deformation. This method, which introduces an internal friction inside the material by creating strong but breakable interactions can be very effective in stopping crack propagation in a prenotched sample by blunting it.

Finally it is possible to introduce very dynamic bonds in the gel that can break and reform at a different position<sup>39, 78-81</sup>. This type of dual crosslink gel has a very strong strain rate dependence but can become very tough in a strain rate regime where the dynamic bonds do not much change the stress-strain curve but delay the propagation of cracks. This last strategy only works for a majority of dynamic bonds relative to the permanent bonds.

It is important in all cases that the connectivity of the sparsely crosslinked covalent framework is maintained (to avoid creep of the gel).

### 3.3 Double network gels and elastomers containing prestretched chains

By far the strongest motivation pushing the development of novel networks has been the need to mechanically reinforce swollen hydrogels to approach the properties of their natural counter parts such as cartilage<sup>82</sup>. Synthetic hydrogels had been mainly studied for their ability to swell reversibly in water<sup>83-84</sup> and as model systems to study network elasticity in the absence of viscoelastic dissipation<sup>85-86</sup>. Everything changed in 2003 when the group of Jian Ping Gong published a seminal paper reporting exceptional resistance to fracture from a gel composed of 90% of water<sup>67</sup>. This gel, named “double network (DN)” was synthesized in a sequential way with a well crosslinked network synthesized first and subsequently swollen with a solution of monomer that was then polymerized in presence of a very small amount of crosslinker. These gels, very elastic (non dissipative)<sup>68</sup> in small strain, were found not only capable of a high strain and stress at break in compression but also to be tear resistant, strongly suggesting the existence of an internal dissipation mechanism slowing or delaying crack propagation<sup>45, 68, 87</sup>. It is interesting to note that in 2003 the idea of interpenetrated networks (IPN) was by itself not new and an interesting review of synthesis and applications envisioned earlier will provide information to the curious reader<sup>88</sup>. However, the IPN architecture had never really been explored for its effect on toughness. These novel gels made by the Gong group were very asymmetric, i.e. one network highly swollen by the other resulting in a minority network of almost fully stretched strands interpenetrated by a majority network of Gaussian chains, (see Figure 3). When such a material is deformed it displays the modulus of the stiff network until chemical bonds of the stiff network progressively randomly break and the stress is transferred to the majority extensible network<sup>69, 89</sup>. When the first network is too damaged to sustain the load, a macroscopic softening occurs and necking is observed in uniaxial tension<sup>89-90</sup>. In a subsequent study where tetra-PEG networks were used as first network, Matsuda et al. showed that the stress level at which this necking occurs was proportional to the areal density of first network strands crossing a plane normal to the tensile direction<sup>89</sup>, but that the necking stress was a factor of 20-25 lower than what would be expected if the yield stress was the product of the force to break a covalent bond times the areal density  $\Sigma$  of the strands crossing the interface<sup>89</sup>. This result strongly suggests that the bond breakage in the first network (the blue network in Figure 3) is not random but that some stress concentration mechanism exists within the first network itself.



**Figure 3:** Schematic of the fabrication of a double network gel. The first network is initially synthesized in its Gaussian configuration. Then it is swollen in the second monomer. At this stage the first network is swollen isotropically, but the material is not tough. The second monomer is then polymerized and the interpenetrated networks are formed. Note that the second network chains are Gaussian. Reprinted from <sup>12</sup>.

The important question is why no macroscopic crack forms in the material while the stiff network breaks more and more extensively to the point of forming a necked region? This is true only if the areal density of stretched chains is very much smaller than the areal density of unstretched chains suggesting that there must be also a stress balance between the two networks at the necking point<sup>91</sup> to create strain hardening at large strain and stable necking.

Some more specific molecular mechanisms have been proposed, in particular by Brown<sup>92</sup>, that imagine that the first network breaks by forming microcracks stabilized by bridging chains of the second network. Many questions remain on how these microcracks propagate and on the criterion for the propagation of a macroscopic crack in this damaged zone. Furthermore, the details of the large strain behavior depend also on the details of the connectivity between the two networks<sup>93-95</sup>.

Nevertheless this class of DN hydrogels possess some very specific general properties that sets them apart:

- 1) The nature of the dissipation mechanism due to covalent bond breakage does not entail any rate dependent process making the fracture energy of such materials nearly independent of strain rate<sup>87</sup>.
- 2) The strands of the network synthesized first are stretched *out of equilibrium* and exert a compressive pressure on the other network.
- 3) Once the first network has been damaged, the material is extremely elastic with negligible energy dissipation as long as the stretch ratio remains below that of the first cycle.

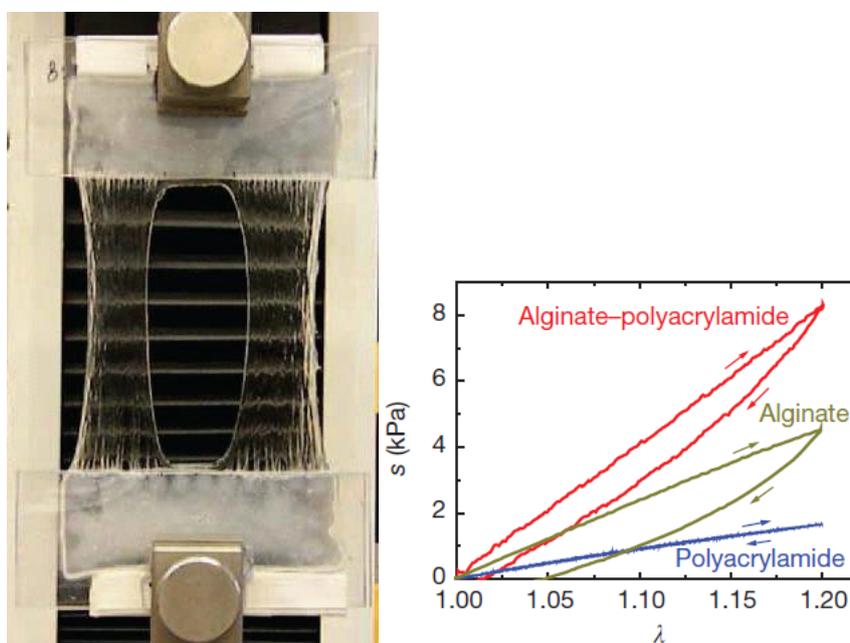
Because of the inherent generality of this toughening principle, several other analogous hydrogel systems have been synthesized such as polyacrylamide-polyethylene glycol<sup>96</sup>, polyacrylamide-polydimethyl acrylamide or polyvinyl alcohol-polyacrylamide<sup>97</sup>. This synthesis strategy was even extended to polymethyl acrylate and polyethyl acrylate elastomers by Ducrot et al.<sup>19-20, 98</sup> who convincingly demonstrated with chemoluminescence experiments that the toughening mechanism was due to the scission of sacrificial bonds over a large volume ahead of the crack during propagation<sup>19</sup>.

### 3.4 Hydrogels with internal molecular friction mechanisms

Because the synthesis of double or multiple network gels or elastomers containing prestretched chains needs to be carried out in two or more steps and requires a swelling stage, other strategies were developed to make tough gels in a *single* synthesis step. Although all of these studies claim to be

inspired by the DN gels of Gong, the reinforcing mechanism principle is fundamentally different and causes very different properties particularly as a function of strain, strain rate and in repeated cycling. This category of hydrogels has a built-in energy dissipation mechanism through the breakup and partial reformation of nanoclusters, nanocrystals or generally a stiffer dispersed phase, which is immiscible with the main stretchy network. This dispersed phase is not out of thermodynamic equilibrium and can in principle return to its original state after a deformation cycle.

The best known example of this class of gels is the alginate/polyacrylamide gel developed by Suo and coworkers<sup>13</sup> that uses alginate chains crosslinked by  $\text{Ca}^{++}$  ions. These clusters of breakable ionic bonds provide internal plasticity in an extensible polyacrylamide matrix, which provides the restoring force. These gels are extremely tough to break even with a notch due to their capability to blunt the crack (see Figure 4a) but rely on coulombic interactions that weaken significantly in the presence of salt and presumably cannot have stable properties *in vivo*. In pure water, their mechanical properties are somewhat different from those of the DN hydrogels. As shown in Figure 4b they show some hysteresis even at low strain<sup>13</sup> while DN gels are fully elastic up to 40-50% deformation<sup>68</sup> and DN elastomers can be elastic up to 100% strain<sup>19</sup>. On the other hand, the hysteresis is partially recoverable and the second cycle hysteresis is relatively elastic<sup>99</sup>.

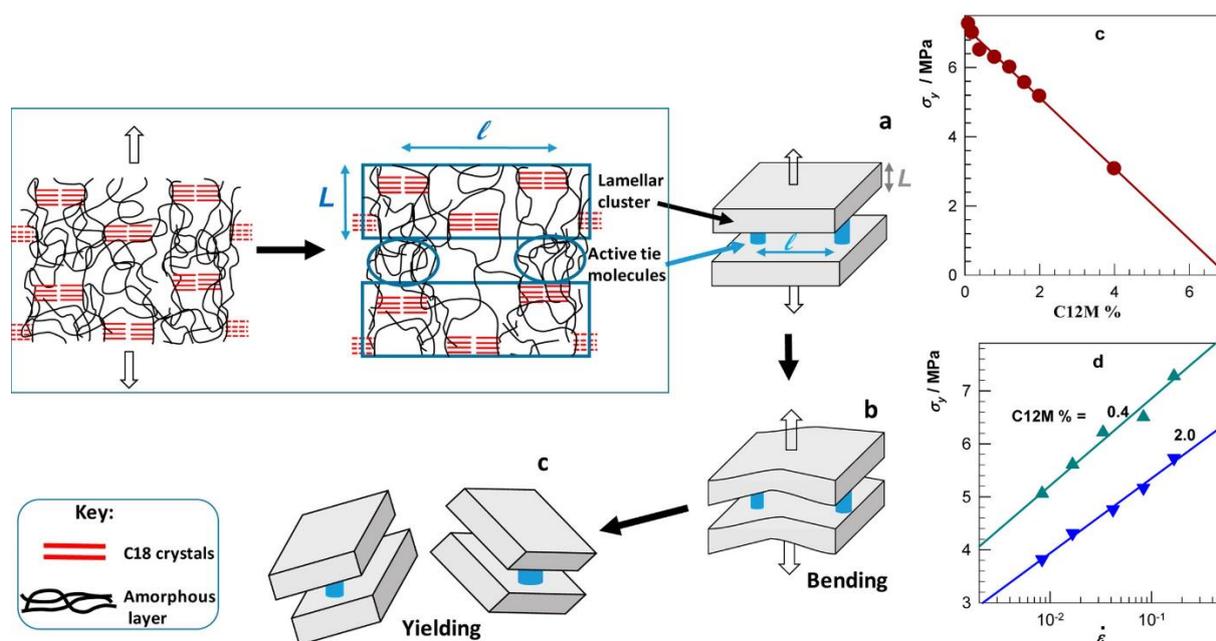


**Figure 4:** a) Blunted crack in an alginate-polyacrylamide hydrogel stretched to  $\lambda = 17$ . b) Loading-unloading curves of different gels : The polyacrylamide gel (blue) shows a perfectly elastic and reversible behavior, while the alginate alone is dissipative and shows significant residual deformation. Finally the alginate-polyacrylamide gel shows some hysteresis even at such low strain.

An alternative way to combine two types of crosslinks to increase dissipation and toughness is the introduction of ionic crosslinks in the hydrophilic phase of a swollen A-B-A triblock with a charged long B midblock and short A glassy hydrophobic blocks<sup>74</sup>. In this specific case, the center PMAA block is used at a pH where it is in its salt form and various divalent cations are introduced in the solution. The physical but long-lived ionic crosslinks introduce stiffening, mechanical hysteresis and plasticity in the gel that increase significantly the stress at break without losing much extensibility. However the reversibility of the deformation depends on the strength of the interaction and on the concentration of divalent cations, and there is a trade-off between strength and reversibility.

A third interesting example of this toughening strategy has been proposed by Li et al.<sup>75</sup> using small crystals of PVOH to obtain plasticity in a stretchy matrix. In their study, they first prepared a finely

crystallized polyvinyl alcohol by heating the dry polymer above its glass transition to cause crystallization, and subsequently swelled it in an acrylamide solution which is then polymerized to create the stretchable interpenetrated framework. Multiple cycling was not investigated for these materials but it is very likely that this type of gels would show significant dissipation not only during the first cycle but at every cycle, making it unsuited for fatigue experiments. These gels do not rely on electrostatic interactions for the plasticity mechanism but their properties probably depend on the details of the process used to obtain crystals and will probably be quite temperature sensitive.



**Figure 5:** On the left side: cartoon presenting two lamellar clusters interconnected by two active tie molecules and showing the deformation by bending and breakup of the lamellar clusters under force. at the yield point. On the right side: value of the yield stress as a function of  $C_{12}$  molar fraction and as a function of strain rate. Figure reprinted from<sup>71</sup>.

A relatively obvious way to introduce breakable clusters in a hydrogel is to graft hydrophobic side chains to a hydrophilic backbone to create hydrophobic nanoclusters in the material<sup>100</sup>. This strategy depends highly on the nature and the length of the side chain. For  $C_{12}$  side chains, it led to significant hysteresis at normal loading-unloading strain rates<sup>101</sup> but to almost no toughening in fracture experiments with notched samples. On the other hand, a very similar type of gel containing  $C_{18}$  and  $C_{12}$  side chains (scheme in **Figure 5**) led to the formation of hydrophobic nanocrystals in the gel which then significantly toughened the material by a plasticity mechanism<sup>71</sup> creating a yield stress in the material, very similar to that provided by the PVOH nanocrystals in the work of Li et al<sup>75</sup>. As shown on the right side of **Figure 5**, these “semi-crystalline” hydrogels have a very strain rate dependent behavior and their properties can be tuned (presumably by weakening the crystals) by mixing  $C_{12}$  side chains with the  $C_{18}$ .

Finally an interesting reversible toughening method triggered by phase separation has been recently reported<sup>102</sup>. The idea is to synthesize a gel containing two different polymer sequences (grafts, block copolymers), a fully hydrophilic sequence and a thermosensitive sequence that becomes insoluble at a given temperature. In the study of Guo et al.<sup>102</sup> the backbone is made of poly-n-isopropyl acrylamide and the side chains are poly-dimethyl acrylamide. At  $T \sim 35^\circ\text{C}$  the backbone becomes progressively insoluble and a phase separation occurs in isochoric conditions, creating a minority percolating domain (the backbone) where the polymer concentration is high and the material is highly dissipative due to molecular friction, and a majority domain (the side chains) where the polymer is now dilute and

much less dissipative. The resulting nanocomposite material is very tough at  $T > 40^\circ\text{C}$  and is able to deflect a crack<sup>102</sup> in an analogous way to what is observed in natural rubber<sup>103-104</sup>.

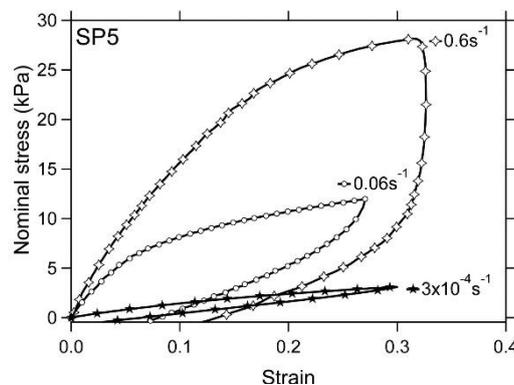
In general such internal plastic deformation mechanisms cause also a change in structure with increasing deformation (reorganization of the crystals or nanoclusters that reform elsewhere, etc..) which is analogous to what is observed in some thermoplastic polyurethanes elastomers or polyester thermoplastic elastomers. This change in structure is mostly dependent on the attained level of strain but can be also dependent on strain rate. Unlike the double covalent networks, it is often partially recoverable, albeit after long times (minutes or hours) and with the help of an increase in temperature. An important question for the use of this class of materials in practical applications is the steady-state behavior in cyclic loading at the same strain and this will be discussed in the perspectives.

### 3.5 Dual crosslink networks

A third type of complex network is the so-called dual crosslink network that combines, in the same network, permanent covalent crosslinks and dynamic crosslinks that can break and reform as a function of time in an analogous way as polymer melts of chains carrying<sup>105-106</sup> sticker groups. This type of soft network does not usually lead to permanent deformation or irreversible changes in structure but the mechanical behavior depends very strongly on the applied strain rate since bonds break and reform at rates that are commensurable with the applied strain rates.

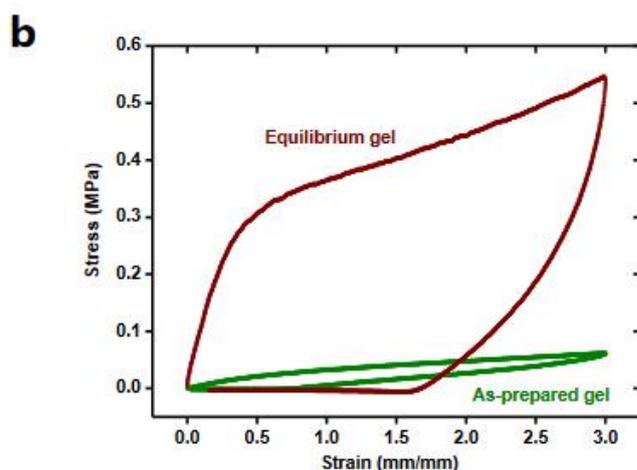
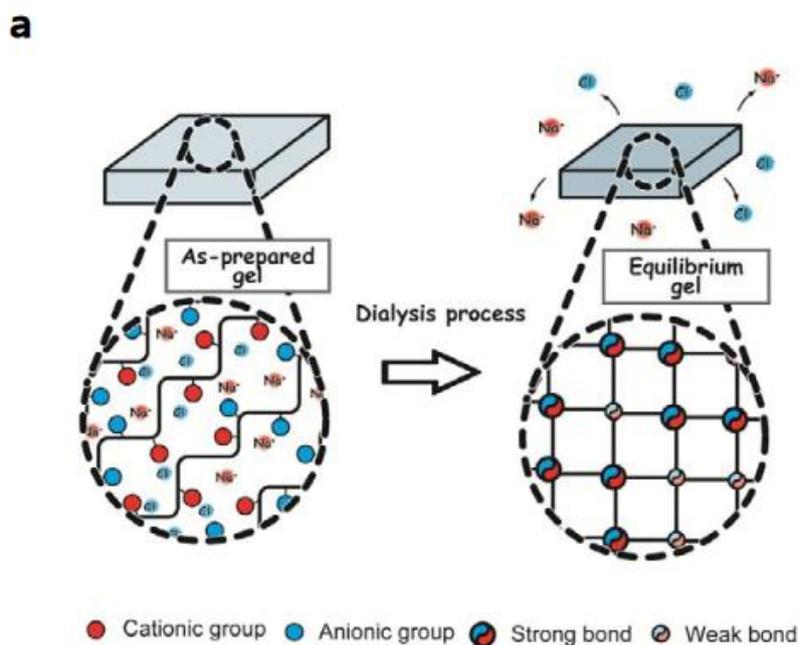
A good first example are nanocomposite hydrogels<sup>39, 80, 107-108</sup>. These materials are in essence complex viscoelastic materials and have intrinsic time dependent dissipative mechanisms. Unlike the previous examples, the linear viscoelastic properties are no longer those of an elastic material, but show a high value of  $\tan \delta(\omega)$ <sup>80</sup> and a mechanical behavior that is very dependent on strain rate<sup>80</sup>, in stark contrast with the covalent double networks discussed in section 3.3. The time-dependent toughening mechanism that increases both extensibility, stiffness and toughness has been attributed to the desorption and readsorption of polymer chains from the fillers and the most interesting results are clearly obtained with a loosely chemically crosslinked network and a relatively high fraction of nanoparticles, in order to form a percolating but temporary network between nanoparticles<sup>39, 107</sup>.

It is interesting to see in Figure 6 that for silica filled hydrogels of poly(dimethylacrylamide), the amount of dissipated energy during a loading-unloading cycle depends greatly on the strain rate applied. When the strain rate imposed on the materials is much lower than the dynamics of the bonds, there is no longer a hysteresis in the loading/unloading curve and the effect on stiffness is lost.



**Figure 6:** Strain rate effect of a nanocomposite hydrogel: loading–unloading cycles for varied strain rates (from  $3 \times 10^{-4} \text{ s}^{-1}$  to  $0.6 \text{ s}^{-1}$ ). Data from <sup>80</sup>.

A different example of very viscoelastic and tough gels containing crosslinks with different dynamics, are the hydrogels made from oppositely charged polyelectrolytes<sup>109</sup> or with a charge-balanced random copolymer synthesized from oppositely charged monomers<sup>110</sup>. In both cases, the polymerization is carried out in the presence of salt and after polymerization the salt is dialyzed out so that strong interactions form between oppositely charged monomers. The optimized properties of the resulting gel (in pure water) are those of a very viscoelastic tough gel similar to some elastomeric materials used for energy adsorption such as polyvinyl butyral in glass laminates<sup>111</sup>. The interactions between oppositely charged monomers introduce essentially a monomer friction coefficient, the magnitude of which decreases with increasing water content and salt content. In both cases the best mechanical properties are obtained in the absence of salt (when electrostatic interactions are strongest) and at relatively low water concentration of the order of 50 wt%. An example of the difference between the mechanical properties of these ionic gels in pure water and in salt solution (0.5 M) is shown in **Figure 7**.



**Figure 7:** Schematics of polyampholyte hydrogel in the as-prepared state (in the presence of excess salt) and equilibrium state (in pure water). a) Illustration of the structure in the as-prepared state (with excess free ions) and the equilibrium state in pure water. b) cyclic stress-strain curves of the as-prepared and water-equilibrated gel. The equilibrium state of the gel is measured in water, while the as-prepared state of the gel is measured in air. Figure reprinted from the supplementary information of<sup>110</sup>.

The gels in pure water have reported values of  $\Gamma$  in pure shear experiments of a few  $\text{kJ/m}^2$ , comparable with those of alginate/polyacrylamide gels mentioned earlier. However like the gels described in section 3.4 the recovery of the original properties after a loading/unloading cycle can take hours and would make the use in cyclic applications problematic.

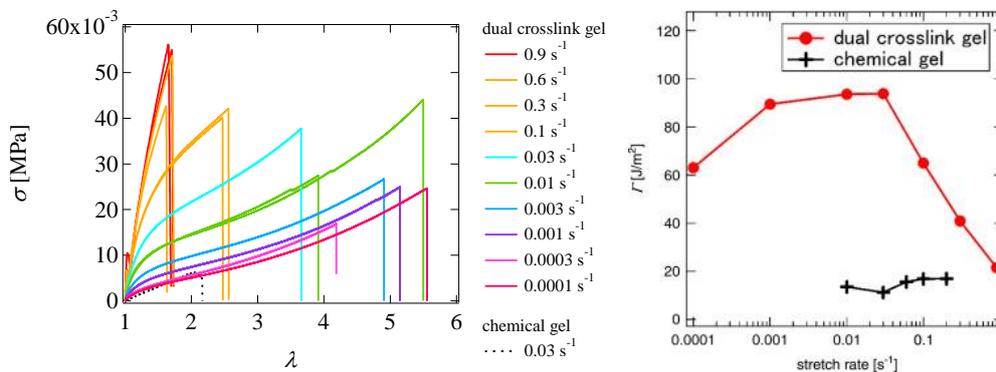
Interestingly the large strain properties of the polyampholyte gels show some strain hardening<sup>112</sup> suggesting a dual population of crosslinks with different dynamics, a slow dynamics and a fast one. The stress-strain curves of materials combining a strain softening at intermediate strain and a strain hardening at higher strains can be fitted well with an empirical model developed for soft viscoelastic adhesives that combines the strain hardening model of Gent (equation 5) and a non-linear viscoelastic model<sup>113</sup>. Since there is no specific reason to have two types of crosslinks from the schematic of **Figure 7a**, one may surmise that the structure is more complex and more heterogeneous than shown in the cartoon of **Figure 7** and probably depends on how the dialysis was performed.

While the two previous categories of gels have slow or very slowly exchanging bonds, some interesting properties can be obtained also with much faster exchanging bonds. Mayumi et al.<sup>79</sup> explored the strain rate dependence of the tensile stress-strain properties of a model dual crosslink polyvinyl alcohol gel containing a minority of permanent covalent crosslinks and a majority of very dynamic crosslinks due to the reversible reaction of borax with the OH groups of the PVOH<sup>114-115</sup>. They showed that in uniaxial tensile tests carried out over 4 decades of strain rates, the stress could be described to a first approximation by the product of a strain dependent component (in their case neo-Hookean elasticity) and a time dependent component due to the bond dynamics which could be written as:

$$\sigma(\lambda, t) = (\lambda - \lambda^{-2})f(t) \quad 14$$

where  $f(t)$  is the small strain relaxation modulus of the gel due to the opening and closing of the dynamic bonds<sup>79</sup>.

The interesting aspect of this study combining linear rheology and uniaxial extension in large strain is that at low strain rates, the presence of these dynamic bonds does not influence the elastic modulus but greatly increases the extensibility relative to the purely chemical gel as shown in Figure 8a, suggesting a dissipative effect delaying crack propagation. A similar result has been reported by Kean et al.<sup>116</sup> on organogels. A subsequent study on the same experimental system focused specifically on crack propagation in notched samples<sup>78</sup> and found that the presence of these dynamic crosslinks was able to increase the fracture energy  $\Gamma$  by a factor of 4 relative to the pure chemical gel as shown in figure 8b.



**Figure 8:** a) Stress–strain curves for the dual cross-link gels at various initial strain rates. For the comparison, the curve for the chemical gels at an initial strain rate of  $0.03 \text{ s}^{-1}$  (dashed line) is also shown. b) Plot of the fracture energy as a function of stretch rate for the dual crosslink gel and for the chemical gel.

However, interestingly, this maximum improvement in  $\Gamma$  occurred at imposed stretch rates  $d\lambda/dt$  100 to 1000 times slower than the inverse of the characteristic relaxation time of the gel measured in linear rheology by a peak in  $\tan \delta(\omega)$ . Furthermore the measured  $\Gamma$ , characteristic of crack initiation, decreased markedly with increasing stretch rate in stark contrast with what is generally observed in elastomers<sup>43</sup>. Mayumi et al. argued that the dissipative mechanism active in these gels is very different than simple molecular friction and proposed a mechanism that is discussed in section 4 of this review.

### 3.6 Tough elastomers

Because tough elastomers have existed for a long time and their structure resembles that of gels, it is important to discuss briefly and for the sake of comparison which structural features make traditional commercial elastomers tough, so that we can put into perspective the new elastomeric materials that are now being developed and make some analogies with gels.

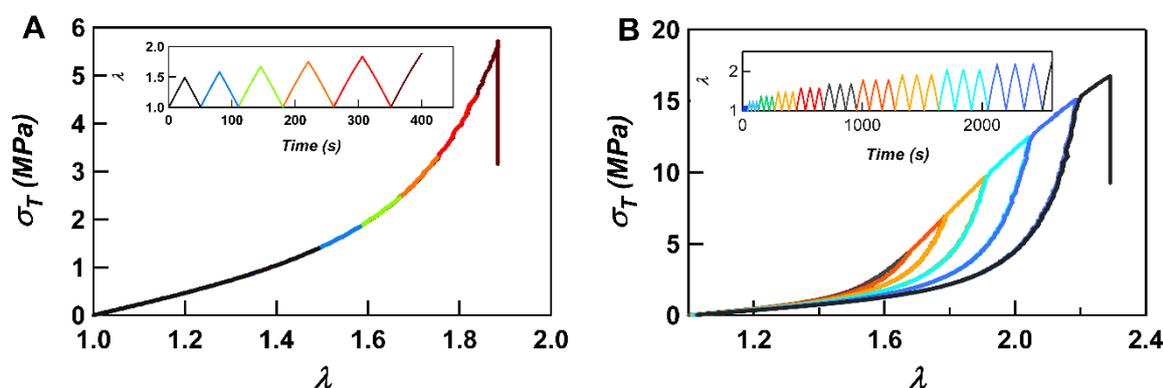
Traditional elastomers have been made tough with a combination of a well-chosen glass transition temperature, which sets the temperature range where viscous dissipative mechanisms are active (see equation 7), and the use of selected nanofillers (carbon black and silica mainly) that introduce strain dependent damage mechanisms and increase the stiffness of the material at the same time<sup>1</sup>. Monomer friction introduces viscoelastic dissipation as a crack propagates and since the extent of dissipation increases with strain rate (i.e. crack velocity) this mechanism is always effective in slowing down a crack or avoiding a propagation altogether<sup>50</sup>. The second mechanism introduces a softening damage in the material that is generally called Mullins effect<sup>117-118</sup> and has striking similarities with the observed first cycle hysteresis of double networks gels<sup>68</sup> and multiple network elastomers<sup>19-20</sup>. Both in filled elastomers and multiple network elastomers this damage hysteresis has a marked dependence on the magnitude of the applied strain and involves chemical bond breakage among other dissipative mechanisms, as recently demonstrated with chemoluminescent crosslinkers in a commercial silicone elastomer<sup>19, 119</sup>. In filled elastomers, the extent of dissipation obtained from the presence of the filler depends markedly on its nature (geometry), volume fraction and matrix/filler interaction. Although there is no model that predicts strength or toughness from the structure and type of dispersion of the filler, some trends can be inferred from experimental results. The most effective fillers form complex nanoclusters with a large specific surface and form a percolating network. This requires a homogeneous but random dispersion<sup>120</sup>. Typically very regular dispersions of nanofillers showing long range order do not provide an effective reinforcement.

In natural rubber (poly cis1,4 isoprene), and unfortunately nearly only in natural rubber, strain-induced crystallization at high strain provides an additional strain-dependent stiffening mechanism which locally dramatically increases the average stress needed to break covalent bonds in the amorphous regions and as a result slows or stops crack propagation in monotonous tearing<sup>103</sup> and in dynamic and fatigue conditions<sup>121</sup>. If generalized, such a mechanism would be ideal to create a self-toughening of the soft material only active in large strain. However, to be effective the polymer needs to readily crystallize under strain at much higher temperatures than its quiescent melting point, an uncommon feature. The interested reader is referred to recent work focusing more specifically on this fascinating mechanism in natural rubber<sup>122-125</sup>.

Finally the family of thermoplastic elastomers which are generally made from block copolymers (triblocks and diblocks or multiblocks) are crosslinked by glassy, semi-crystalline or strongly hydrogen bonded domains. At high temperature these block copolymers are not phase-separated and can be readily processed (hence the name thermoplastic elastomers) and at low temperature the phase separation creates physical crosslinking points. If the soft block is the majority phase, the materials possess elastomeric properties and generally have a less reversible elasticity than conventionally

crosslinked elastomers but a very high strength and toughness even in the unfilled state as for example the family of polyurethanes and polyurethane ureas<sup>126-127</sup>. The necessary dissipative mechanisms can be again due to viscoelastic dissipation but in addition come from the strain-dependent damage in the hard phase of the material that fulfills the same function that the fillers do in conventional elastomers. The excellent review paper of Thor Smith<sup>128</sup> gives a concise but rather complete overview of the tensile stress-strain properties of commercial elastomers and thermoplastic elastomers in the 1970's.

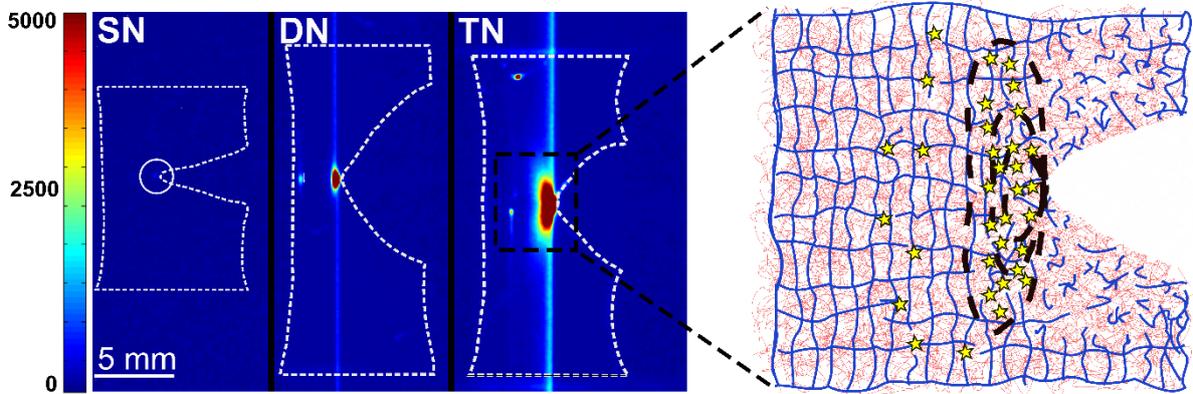
In addition to these conventional elastomers, which have been commercially sold for decades, some new types of elastomers have been developed in the laboratories in order to overcome some limitations of conventional ones. One such limitation is the necessary incorporation of fillers that introduces processing constraints and often loss of transparency. Inspired by the work of Gong, Ducrot et al. developed multiple network elastomeric networks by using acrylate chemistry and multiple steps of swelling and polymerizations<sup>19-20</sup>. The materials obtained contain a minority network of chains prestretched out of equilibrium and a majority of chains that are not stretched. The initial modulus is controlled by both networks but as the material is stretched the stress is carried increasingly by the minority network. They showed that it was possible to combine a very elastic response with a significant increase in toughness obtaining values of  $\Gamma$  typical of filled elastomers. While none of the materials underwent necking in uniaxial tension like the double network gels, they demonstrated that depending on the degree of prestretching of the chains of the network, the response could be either purely elastic until crack propagation occurs (Figure 9a), or display internal damage by sacrificial bond breaking before failure. As shown in Figure 9b these materials only dissipate energy in the first cycle and then subsequent cycles are very elastic, in contrast with conventional elastomers that always display some viscoelastic dissipation in steady-state cycles.



**Figure 9:** A) stress-strain curve of a single sample of double network elastomer submitted to a step-cycle loading. The inset represents the applied stretch as a function of time. All curves follow the same path on the stress-strain curve for this elastomer. B) The same graph for a single sample of triple network. In this case each  $N^{\text{th}}$  cycle follows a different path when the value of  $\lambda$  of the  $N^{\text{th}}$  cycle exceeds the maximum value of  $\lambda$  of the  $(N-1)^{\text{th}}$  cycle. Note that despite the damage in large strain, the initial modulus is nearly the same for all cycles. Reprinted from<sup>19</sup>.

The incorporation of mechanoluminescent probes in the prestretched sacrificial network demonstrated conclusively that for simple networks with no prestretched chains and containing luminescent crosslinkers (SN in Figure 10) almost no light was emitted during crack propagation. This shows that bond scission is indeed, very localized near the crack tip, as predicted by the Lake-Thomas model. For the system with intermediate chain prestretching (DN in Figure 10), there is significant light emission near the crack tip and for the materials containing highly prestretched chains (TN in Figure 10), the light emission due to sacrificial bond breakage is significant and occurring over several  $\text{mm}^2$ . Such combination of elasticity in a steady-state cycle and strain-dependent damage with nearly no viscoelastic dissipation is unprecedented in elastomers. While the multiple steps involved in the

synthesis are not practical for bulk samples, they may be useful for thin films. Furthermore the near absence of time dependence dissipative mechanism makes it an interesting and tunable model system to study how molecular damage can be harnessed to provide toughness in soft materials.



**Figure 10:** Intensity colorized images of propagating cracks on notched samples containing a luminescent crosslinker in the prestretched network showing the light emission due to the breakage of sacrificial bonds; the size and geometry of the sample are shown with a white dashed line. Vertical lines in the DN and TN image are due to detector artifacts; in DN and TN, spots far from the crack tip are due to reflection of the light on surface inhomogeneities and do not correspond to a local light emission. On the right: schematic of the sacrificial bond breaking mechanism in front of the crack tip for the DN and TN; the 1<sup>st</sup> network is represented in blue, second (and third) networks in red and the stars represent breaking events in the blue network. Reprinted from<sup>19</sup>.

## 4 Modeling of tough soft materials

We will briefly discuss the specific challenges in modeling the mechanical behavior of such tough and soft materials while also pointing out some recent advances.

Soft materials are by definition extensible and require large strain modeling. As was discussed in the beginning of this review, modelling is well established as long as the material is elastic. What is more challenging is the incorporation of time dependent behavior and strain-dependent damage into this large strain formalism (which includes finite extensibility and fracture).

Let us start with the combination of time-dependent behavior and large strain. In a series of papers<sup>129-131</sup> Long et al. proposed a full 3-D model to describe the large strain behavior of the dual crosslink gels described in section 3.5. Their model is based on the physical idea of nonlinear springs representing polymer strands that can attach and detach as a function of time to the network and carry the stress. By assuming that chains are stretched (without any relaxation) when they are attached at both ends and are instantly fully relaxed when they are detached (viscous friction is neglected) this relatively simple model is able to capture quantitatively loading/unloading curves at different strain rates with only 4 adjustable physically based parameters. Although the formalism is fully adapted to 3D simulations we focus for clarity on the uniaxial extension solution that can be expressed analytically. The normalized stress is given by:

$$\frac{\sigma}{\mu} = [\rho + n(t)] \left[ \lambda(t) - \frac{1}{\lambda^2(t)} \right] + \bar{\gamma}_{\infty} \int_0^t \phi_B \left( \frac{t-\tau}{t_B} \right) \left[ \frac{\lambda(t)}{\lambda^2(t)} - \frac{\lambda(\tau)}{\lambda^2(\tau)} \right] d\tau \quad 15$$

with

$$\bar{\gamma}_\infty = \frac{1 - \rho}{t_H + \frac{t_B}{2 - \alpha_B}} \quad 16$$

and

$$n(t) = \bar{\gamma}_\infty \frac{t_B}{2 - \alpha_B} \left( 1 + (\alpha_B - 1) \frac{t}{t_B} \right)^{\frac{2 - \alpha_B}{1 - \alpha_B}} \quad 17$$

where  $\bar{\gamma}_\infty$  is the steady state reformation rate of physical bonds and  $n(t)$  is the fraction of strands attached at both ends by physical bonds at  $t = 0$  and still attached at  $t$ . The four adjustable parameters of the model are:  $\mu\rho$ , the fraction of the shear modulus due to permanent crosslinks,  $\mu\bar{\gamma}_\infty$  which is rate at which the modulus recovers due to reattachment of physical bonds,  $t_B$ , the characteristic time for bond breakage and  $\alpha_B$  the width of the distribution. Note that the characteristic healing time  $t_H$  is obtained from the three other parameters. While lacking direct molecular insight, such a model is a good framework to combine non-linear elasticity<sup>131</sup> with time dependent behaviour and is fully adapted to model soft solids in 3D. In the case of hydrogels it captures well the fact that viscous friction is very low and relaxation in water, in the absence of strong bonds, is very fast. Note that the same four parameters determined in large strain experiments can fit the steady-state behavior in classical linear rheology<sup>130</sup>.

Another relatively simple but insightful model to address viscoelasticity and finite extensibility has been proposed by Deplace et al.<sup>113</sup> to model soft pressure-sensitive-adhesives (PSA). PSA are made from high molecular weight polymers with a low entanglement density and an even lower crosslink density. This type of viscoelastic network combines the highly dissipative character of entangled networks with a finite extensibility due to the low level of permanent crosslinking. Deplace et al.<sup>113</sup> propose to model them with a hybrid constitutive model combining an upper convected Maxwell model<sup>132</sup> for the fluid part and the Gent model<sup>24</sup> described in equations 5 and 6 for the strain hardening part. In uniaxial extension this type of model fits very well a rate dependent softening process combined with a mostly rate independent strain hardening stage at very large strain. Since this model is a hybrid it would need adaptation to be incorporated in a finite element code.

The second ingredient that need to be incorporated in models is damage. Filled elastomers undergo significant damage during their first cycle deformation and given the technological relevance of these materials, modeling such a damage has been the focus of many studies. Damage models typically consider that the material softens and/or becomes more extensible due to chemical bond breakage or any other structural rearrangement during deformation. An interesting early paper worth pointing out for its physical insight is that of Bueche<sup>133</sup> who imagined that the shortest chains in the heterogeneous network will break first, hence increasing its maximum extensibility. This idea inspired the solid mechanics community that developed several 3-D versions<sup>134-135</sup> called network alteration models and adapted to finite element codes. A later version of this class of phenomenological models also incorporated the anisotropy of the damage observed experimentally<sup>136</sup>. However, it should be noted that in filled elastomers the first direct evidence of bond scission has only been obtained recently with luminescent crosslinkers that emit light upon breaking<sup>119</sup>. Many other mechanisms due to filler/matrix interactions can be responsible for the observed softening<sup>118</sup>.

Double network gels and multiple network elastomers are in many ways a cleaner model system than filled elastomers since the damage observed in first cycle extension and compression is uniquely due to bond scission<sup>19, 68</sup>. As a result more refined damage models have been developed<sup>137-139</sup> focusing on the molecular interpretation of the damage and in particular of the necking phenomenon observed for

certain gels. The existence of a transition to an extended damage zone above a certain level of stress (a yield or necking stress) has been observed for a series of DN gels<sup>89-90, 140-141</sup> and has important implications for the fracture process.

Tanaka<sup>142</sup> and Brown<sup>92</sup> developed simultaneously two models to account for the exceptional toughness of DN gels, and both assumed the existence of a damage zone in front of the crack tip. Both models assume that energy is dissipated to *form* the damage zone and the fracture of the damaged zone is then controlled by the strain energy stored in that zone. However, Brown's model is a molecular model that makes some hypotheses and predictions on the change in toughness expected by changing the molecular structure which still need to be confirmed experimentally. A good comparison and a detailed discussion of these models, which differ in the hypotheses made to estimate the strain energy, has been recently published in a recent review by Long and Hui<sup>30</sup>.

Based on the existence of a damage zone at the crack tip, Zhang et al.<sup>31</sup> also proposed a finite element model to predict the fracture energy of such gels based on the coupling between a cohesive zone for the fracture plane and an energy dissipated in the bulk due to damage. In their model, the bulk damage amplifies the interfacial energy dissipated which they call  $\Gamma_0$ . To fit the experimental data they obtained on a polyacrylamide/alginate hydrogel, they use the bulk hysteresis (measured in uniaxial extension) and measure the intrinsic value of fracture energy  $\Gamma_0$  on a prestretched sample which has only little visible hysteresis in uniaxial tension. The numerical prediction of the fracture energy of a virgin sample falls very close to the experimental value. The value of  $\Gamma_0$  used (300 J/m<sup>2</sup>) is numerically too high to be an intrinsic value of the fracture of bonds in the plane of fracture and would most likely be dependent on the maximum strain applied during the prestretching. Yet the approach is insightful and is the first to include explicitly damage for crack propagation in soft materials. It is interesting to note that the existence of such a damaged zone was proposed also by Mzabi et al.<sup>143</sup> from digital image correlation measurements of the strain field near the tip of a crack in a carbon-black filled styrene-butadiene crosslinked rubber. It is very likely that such localized damage close to the crack tip is coupled with viscoelastic dissipation in many tough soft materials.

## 5 Dynamic and reconfigurable networks

In recent years there has been a renewed interest in the design of materials that combine the reversible entropic elasticity of a traditional elastomer with the ability to reconfigure the network. Relative to what has been discussed in sections 3 and 4, the bonds are here much less dynamic with detachment/reattachment times that can be hours or days. Such a combination of properties is attractive because traditional chemically crosslinked elastomers do not adhere to each other without a surface treatment and a glue and cannot be easily recycled. However the introduction of dynamic bonds in an elastomer poses some important questions:

- 1) Does thermodynamics distribute these dynamic crosslinks in a homogeneous way? Most functional groups used for dynamic bonds are polar groups and are poorly soluble in a non-polar elastomer and, therefore, form clusters or even crystalline domains. The formation of these clusters that are typically much longer lived than single bonds changes the dynamics and imparts considerable viscoelasticity as for example ionomers<sup>18, 66</sup> or long-lived multiple hydrogen bonds<sup>144</sup>.
- 2) Dynamic bonds can cause an increase in creep under fixed load particularly at higher temperatures when the bonds are the most dynamic. As a result, there is generally a trade-off between reprocessability and temperature resistance.
- 3) Polar components tend to absorb water so that this type of material has properties that generally depend markedly on the degree of humidity.

Most studies published nowadays conveniently avoid discussing creep and moisture resistance and focus on the positive aspects of self-healing. Yet creep resistance and durability are important properties in the applications of traditional elastomers.

The area of networks made from dynamic bonds has been first boosted in the academic field by the seminal work of Sijbesma et al. on the incorporation of the ureidopyrimidone (UPy) functionality in a low  $T_g$  polymer, initially to prepare high molecular weight entangled polymers with reversible chain extenders<sup>145</sup>. The UPy function is able to associate with itself by a quadruple hydrogen bond and forms then a rather long-lived bond that typically does not associate in clusters. A further evolution along this direction was the work of Feldman et al. that used random copolymers of n-butyl acrylate and UPy to form transient networks<sup>144</sup>. However in both these examples the dynamic bonds slow down the dynamics but not enough to really form an elastomer at low frequency or display the large strain behavior of a conventional elastomer with reversible elasticity up to large strain. The first success in this endeavor was obtained by the Leibler group at the ESPCI that succeeded in combining a relaxation time of the order of weeks at 50°C with full self-healing capacity in a few hours<sup>16</sup>. The near absence of hysteresis in loading/unloading cycles and of significant residual deformation after relaxation of stress is typical of chemically crosslinked elastomers while the self-healing capacity is not. These fully soluble supramolecular materials are made from oligomers of fatty acids functionalized with hydrogen-bonding moieties and form fully amorphous structures that however contain some order at the few nm scale. Interestingly the self-healing capacity continuously decreases over time and is only maintained for a few hours<sup>146</sup> suggesting the existence of slow forming clusters of hydrogen bonds that break when the material breaks and slowly reform. Such slow self-organization process is fairly typical of supramolecular materials<sup>147</sup>. In the following years this topic became immensely popular and many long lived dynamic chemistries have been reported. The materials have the reversible extensibility of rubbers but maintain a self-healing ability. Since recent reviews are available on these topics<sup>148-149</sup> I will only mention some interesting examples such as multiple hydrogen bonds<sup>144, 150-151</sup> or host-guest molecules<sup>152</sup>. In all of these cases the introduction of reversible bonds also introduces some hysteresis between loading and unloading and sometimes some residual deformation.

If a better resistance to creep and more elasticity is desirable at room temperature and a self-healing capability is only needed at high temperature, a better alternative are the networks crosslinked with dynamic covalent chemistry, pioneered by the seminal contribution of Montarnal et al.<sup>14</sup> and named vitrimers for their rheological similarities with inorganic glasses. In this case the bonds are no longer weak bonds but reversible covalent bonds that can exchange at high temperature giving the material the opportunity to relax stresses or to heal, while at low temperature all properties of a covalent network are recovered. Exchangeable bonds such as those present in vitrimers act in a fundamentally different way from the polar clusters due to hydrogen bonds or ionic clusters that are present in TPU or in ionomers. While the equilibrium concentration and size of the polar clusters will reduce with increasing temperature, leading to a sharp softening point and to a structure changing with temperature, the majority of the exchangeable bonds of the vitrimers is always closed, and it is only the dynamics of exchanging that speeds up with temperature and not the structure that changes. This gives a much slower decrease of the viscosity with increasing temperature analogously to inorganic glasses (hence the name vitrimer). In other words the resistance to creep should be much better for vitrimers for the same self-healing capability and while the original work was done on glassy epoxies, several studies on soft networks have appeared since<sup>15, 153-156</sup>. The potential of this type of chemistry in engineering materials has only been very recently explored<sup>157</sup> and does in my opinion bear real promise in terms of applications.

## 6 General comments and future directions

After this overview of the state of the art of the mechanics of soft polymer networks it is time to discuss some perspectives. First of all it is clear that this field has exploded in the last ten years, pushed by new scientific discoveries and inventions as discussed in the introduction. As new inventions and technologies are developed there will be an increasing need to optimize not only the chemistry of the product and its interactions with the environment but also its mechanical properties and range of use in terms of stress, strain and temperature to be able to guide designers. This need for optimization offers great opportunities for the curious scientist not only to create new materials but also to understand better how they work. I am going to focus now on some open questions that provide opportunities.

### 6.1 Tough gels and unfilled elastomers

In the area of tough gels and elastomers, while we understand in general how to toughen a soft material, the compromise between elasticity and resilience, i.e. stable shape, no residual deformation, little or no creep and little or no hysteresis, and toughness remains difficult to achieve. In other words, we are able to make tough viscoelastic or viscoplastic materials but have a harder time with very elastic and resilient ones. In this area the opportunities are in the careful engineering of *high strain or high strain rate* dissipation mechanisms such as the strain-induced crystallization of natural rubber<sup>158</sup>, the high strain damage in double network gels<sup>89</sup> or elastomers<sup>19-20</sup> or the fast exchanging bonds in gels<sup>116</sup> while maintaining an industrially viable manufacturing process for the material. There are also opportunities for the polymer physicists since while it is clear that introducing a stiffer and breakable phase into a soft material provides toughness<sup>92, 159</sup>, there is no tested micromechanical and molecular model that can predict fracture or crack growth or even macroscopic yielding of the breakable phase. Current existing models of tough materials provide opportunities to carry out and analyze systematic experiments. Furthermore, almost all fracture theories rely on the existence of preexisting cracks or flaws, and yet the size of flaws where this ceases to be true, is relatively large for soft materials<sup>29</sup> suggesting that there are mechanisms of nucleation and growth of flaws occurring in soft materials that are fundamentally different from those of sharp cracks and are yet to be discovered.

### 6.2 Durability and fatigue behavior

Because this is a seldom discussed topic it is worthwhile to say a few words about durability and fatigue. Engineering materials and in particular rubbers are subjected to many cycles in their typical lifetimes. A truck tire can function for 150 million cycles and a car tire 20-40 m cycles. A typical knee or hip will experience about 100 million cycles during a lifetime as everyone can now check on their own cellphones. That is significant and requires specific wear resistant properties. For engineering applications these durability tests are well developed and focus on the propagation under cyclic load of a preexisting crack<sup>121, 143</sup>. Even for those well investigated cases of filled rubbers, understanding what makes a soft elastomer resistant to crack propagation in fatigue is only qualitatively understood. Yet the new tough soft elastomers that have been developed provide in some cases much simpler model systems to test some ideas.

Hydrogels are still far from real applications but functions such as ionic conductivity are really promising<sup>8</sup>. Two aspects need to be considered for applications: the first one is stability in time. In air water evaporates and the gels will dry. Adding Lithium salt to make them hygroscopic helps but

precludes using charged systems for toughness since the presence of large salt concentrations will screen the ionic interactions used to obtain dissipative mechanisms. Fatigue testing of hydrogels has just started and shows that some gels that display exceptional toughness in a single continuous loading experiment perform quite poorly in fatigue<sup>160</sup>. For example the alginate/polyacrylamide gel showed a value of  $\Gamma$  of the order of 10 kJ/m<sup>2</sup> when notched samples are stretched to failure, a value comparable to that of a tough filled rubber<sup>13</sup>. However the same gels show crack propagation velocities of the order of several microns/s at applied energy release rates that would only grow a crack at a few nm/s in a filled rubber<sup>143, 160</sup>. This difference would result in 3 orders of magnitude differences in lifetime for the same applied  $G$  and needs to be addressed.

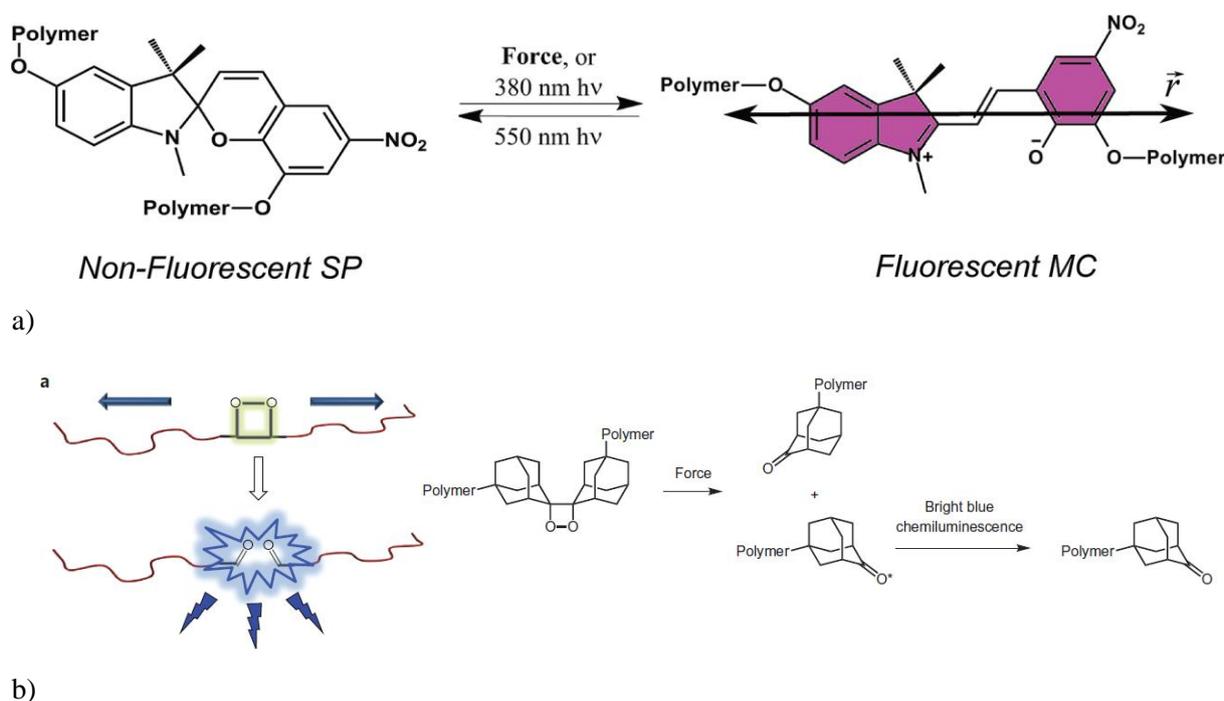
Although the field is still in its infancy, it is worthwhile to make some remarks. Contrary to popular belief, permanent damage of the material during the first cycle does not preclude a good resistance to fatigue. Actually all filled elastomers for engineering applications display some amount of permanent damage during the first cycle, the so-called Mullins effect<sup>118</sup>. More important for fatigue is the evolution of the material in the subsequent cycles which are usually at lower deformations. Properties needed for cyclic deformation are somewhat different than what is needed for a high fracture toughness in a continuous loading experiment. In particular energy dissipation during every cycle (a loading-unloading hysteresis) causes damage in the bulk material, temperature increases and increased usage costs. What is much preferable is either a dissipation mechanism that acts at a higher frequency or only at higher strains preventing crack growth by blunting it.

### 6.3 Dynamic networks: bond strength, dynamics and solubility

In the area of dynamic networks an important scientific question that has been insufficiently addressed is that of the balance between crosslinking chemistry and solubility. As reviewed above, in recent years many new chemistries have been used in soft materials to provide crosslinks ranging from relatively dynamic single hydrogen bonds, widely used in soft adhesives<sup>161-162</sup>, to more long-lived multiple hydrogen bonds<sup>144, 163-164</sup> or ionic bonds in water<sup>13, 74, 110</sup> and finally reversible covalent chemistry<sup>165</sup> that provide very long-lived bonds that can exchange over much longer time. In all cases the spatial distribution of these bonds is controlled by the solubility of the functional group providing the dynamic bond in the soft matrix material. This solubility may of course be different for a very non-polar elastomer, where clusters will form easily or a more polar one where the dynamic bonds may disperse more easily<sup>17, 147, 166-167</sup>. If the functional group providing the physical crosslinking is not fully soluble, this causes the formation of clusters that can then work both as multifunctional crosslinks and as fillers, generally reducing the reversibility of the deformation and introducing additional strain dependent dissipation mechanisms. A classic example of insoluble polar groups are the so-called ionomers that form quite strong clusters providing strength and toughness at the expense of reversible deformation<sup>66</sup>. On the other hand a very soluble crosslinking chemistry will be more randomly distributed and provide a structure more similar to that of covalently crosslinked networks which displays a better resilience. Furthermore the existence or not of longer-lived clusters may have an effect on processes such as molecular diffusion that control self-healing at interfaces so that systematic studies investigating not only rheological properties but structure will be important in the future. A related question suggested by one of the reviewers of this paper, is the question of the role played by the type of clusters involved. While the general toughening mechanisms may be similar the properties of thermoplastic polyurethanes, using hydrogen bonded clusters, and those of polybutylene terephthalate based thermoplastic polyester elastomers, using crystalline clusters are quite different and the reasons for these differences are unknown.

## 6.4 New experimental techniques

In general progress in developing molecular models connecting structure and properties has to rely on better experimental data and better defined model systems. This is particularly true for the mechanical properties of soft materials since structure generally changes, reversibly or not, upon deformation. One of the recent experimental developments that will help in this endeavor is mechanochemistry<sup>168</sup> used as a reporting tool of damage or of local stress in soft materials during deformation or macroscopic crack propagation<sup>169</sup>. The idea is simple in principle: certain suitably designed molecules are able to change their light absorption spectrum, become fluorescent or emit light when a mechanical stimulus is applied. In other words molecules can be used as either force sensors<sup>170-171</sup> or detectors of bond breakage<sup>172-173</sup>. The first such example which is by far the most studied is the spiropyran molecule<sup>174</sup> (Figure 11a) that can transform into merocyanine when a force higher than  $\sim 240$  pN (at an AFM pulling rate  $\sim 300$  nm/s) is applied to one of the chemical bonds<sup>170</sup>. Another well publicized example is bis-adamantane dioxetane<sup>172</sup> (Figure 11b) which emits light when the dioxetane cycle breaks thermally<sup>175</sup> or mechanically<sup>172, 176</sup>. If these molecules are incorporated into transparent materials they can act as detectors of bond breakage or simply of a high force on the molecule. The quantitative exploitation of this information is still in its infancy<sup>19, 119, 169, 171</sup> but development of new molecules and new understanding of the relationship between bond energy and scission force<sup>168</sup> will certainly permit spectacular advances in the understanding of the mechanisms of macroscopic material fracture in different conditions.



**Figure 11:** a) Spiropyran molecule (left) and its force-activated fluorescent counterpart merocyanine. Reprinted from<sup>177</sup>. b) Left: schematic representation of the mechanically induced decomposition of a polymeric bis(adamantyl) dioxetane that results in chemiluminescence when the ketone product relaxes from its excited state to the ground state. Right: molecular basis of the mechanically induced chemiluminescence. Reprinted from<sup>172</sup>

Soft materials deform significantly and when organized structures exist inside the material, they may markedly change upon deformation often in a non-affine way. The best example of which being solid fillers<sup>178</sup>. Neutron scattering has been used with much success to probe the structure of networks and gels, and in particular their level of network heterogeneity<sup>179</sup>, but cannot be used at high acquisition

rates or for small samples or localized measurements that require a highly focused beam. X-ray scattering with Synchrotron radiation on the other hand makes it now possible to study structure with extremely fast acquisition rates or with very focused beams (20  $\mu\text{m}$  or even less if fast acquisition rate is not required) that make it possible to study either fast changing structures in real time in uniaxial tension such as strain-induced crystallization<sup>124, 180</sup> or to map localized changes in structure (at the crack tip for example)<sup>181-183</sup>. Some interesting recent studies using new tools have revealed new phenomena in filled elastomers such as nanocavitation by using the scattering invariant in small-angle X-ray scattering<sup>184</sup> or local heating at the crack tip with infrared thermography<sup>185</sup> or details of the filler structure by nanotomography<sup>186</sup>. Such tools have not yet been used extensively on gels but could of course be adapted if a proper scattering contrast is used.

Another field that develops very fast is the measurement of strain fields through digital image correlation or particle tracking. Materials chemists usually test the properties of the materials they make with relatively simple tests, such as dynamic mechanical analysis or uniaxial tensile or compressive tests, where the strain is uniformly applied. However a central question in understanding the strength of materials is their response to strain and stress gradients. Highly localized stresses, called stress concentrations in solid mechanics, increase the probability of chemical bond scission even at relatively low values of average stress. In the last ten years, the solid mechanics community has developed techniques to map the displacement field on a surface by analyzing the correlation between images containing a random pattern<sup>187</sup> or discrete particles<sup>188</sup>. These techniques called digital image correlation or particle tracking can be used to reconstruct the strain fields at the tip of a crack and be compared with simulations or gain some insight on the non-linear behavior of the material<sup>143</sup>. Although this approach requires familiarity with data treatment, software is now available to use for the material scientist and can be used to detect for example localized damage in a material or precursors of cracks.

## 7 Concluding remarks

Soft networks made from flexible chains such as elastomers and hydrogels have seen spectacular new developments in recent years both in terms of new materials and in terms of new understanding. I have focused in this perspective on two important advances: how to make a network stiff and tough without using fillers or monomer friction and how do dynamic crosslinks affect properties.

Toughening is dependent on introducing dissipative mechanisms into a covalent (or long-lived) extensible network. These dissipative mechanisms can depend on *strain*, on *strain rate* or on both. The strain dependent dissipation mechanisms kicking in only at high strain are well adapted to toughness in repeated cycles while a maximum toughness can be obtained with strain and strain rate dependent mechanisms that are active at the strain rate where the material is deformed. To go from new laboratory developments to applications the behavior in fatigue or aging conditions has not yet been much explored.

On the molecular front we have seen that sacrificial bonds can be overloaded covalent bonds (sections 3.3 and 3.6), nanoclusters of bonds introducing plasticity (section 3.4) or dynamic bonds (section 3.5). All provide toughness in simple extension of notched samples but the effectiveness and range of strain and strain rate where toughening is observed vary as does the strain rate dependence of the mechanical properties and the recoverability of the properties after unloading. While many new materials have been discovered and general guidelines for toughening are now clear, predictive molecular models of toughening still lack and will be useful for knowledge based optimization.

Dynamic reconfigurable networks for recycling and self-adhesion are based on much less dynamic bonds to be able to behave as much as possible as covalent networks at high strain rates and low temperatures while being more dynamic at long times or higher temperatures. Successes will

undoubtedly be based on the fine tuning of the dynamics and structure but important challenges are to decouple individual molecular mobility (needed for self-healing and recyclability) from macroscopic viscosity (controlling creep).

Finally I am convinced that progress in understanding the behavior of these new exciting materials in a more quantitative and predictive way will come from applying new experimental techniques such as mechanochemistry, digital image correlation, X-ray tomography or small and wide angle X-ray scattering with microfocused beams, that can be used to have a multi-scale characterization of the material. A true multidisciplinary and collaborative approach will be needed to combine the synthetic toolbox of the polymer chemist that creates new materials with the analytical toolbox of the physicist and mechanician.

## 8 Acknowledgment:

The author is indebted to Hugh Brown for particularly enlightening discussions on molecular toughening mechanisms. He has also benefitted from discussions with Jian Ping Gong, Stephen Craig, Ralph Colby, Michael Rubinstein, Zhigang Suo, Herbert Hui, Rong Long, Ludwik Leibler, Markus Bulters, Meredith Wiseman, and with his colleagues at the SIMM lab of the ESPCI, Tetsuharu Narita, Alba Marcellan and Matteo Ciccotti. *This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Advanced Grant CHEMECH, N° 695351).*

## 9 References

1. Gent, A. N., *Engineering with Rubber*. Hanser: Munich, 2001; Vol. 1, p 365.
2. Martinez, R. V.; Glavan, A. C.; Keplinger, C.; Oyetibo, A. I.; Whitesides, G. M., Soft Actuators and Robots that Are Resistant to Mechanical Damage. *Adv Funct Mater* **2014**, *24* (20), 3003-3010.
3. Rogers, J. A.; Someya, T.; Huang, Y., Materials and Mechanics for Stretchable Electronics. *Science* **2010**, *327* (5973), 1603-1607.
4. Lee, K. Y.; Mooney, D. J., Hydrogels for tissue engineering. *Chem Rev* **2001**, *101* (7), 1869-1879.
5. Minev, I. R.; Musienko, P.; Hirsch, A.; Barraud, Q.; Wenger, N.; Moraud, E. M.; Gandar, J.; Capogrosso, M.; Milekovic, T.; Asboth, L.; Torres, R. F.; Vachicouras, N.; Liu, Q.; Pavlova, N.; Duis, S.; Larmagnac, A.; Vörös, J.; Micera, S.; Suo, Z.; Courtine, G.; Lacour, S. P., Electronic dura mater for long-term multimodal neural interfaces. *Science* **2015**, *347* (6218), 159-163.
6. Federico, C.; Iain, A.; Siegfried, B.; Gabriele, F.; Giuseppe, G.; Massimiliano, G.; Christian, G.; Claire, J.-M.; William, K.; Guggi, K.; Matthias, K.; Roy, K.; Benny, L.; Marc, M.; Silvain, M.; Stephan, N.; Benjamin, O. B.; Qibing, P.; Ron, P.; Björn, R.; Samuel, R.; Herbert, S., Standards for dielectric elastomer transducers. *Smart Materials and Structures* **2015**, *24* (10), 105025.
7. Brochu, P.; Pei, Q., Advances in Dielectric Elastomers for Actuators and Artificial Muscles. *Macromol. Rapid Commun.* **2010**, *31* (1), 10-36.
8. Keplinger, C.; Sun, J.-Y.; Foo, C. C.; Rothmund, P.; Whitesides, G. M.; Suo, Z., Stretchable, Transparent, Ionic Conductors. *Science* **2013**, *341* (6149), 984-987.
9. Gossweiler, G. R.; Brown, C. L.; Hewage, G. B.; Sapiro-Gheiler, E.; Trautman, W. J.; Welshofer, G. W.; Craig, S. L., Mechanochemically Active Soft Robots. *Acs Appl Mater Interfaces* **2015**, *7* (40), 22431-22435.

10. Hong, S.; Sycks, D.; Chan, H. F.; Lin, S.; Lopez, G. P.; Guilak, F.; Leong, K. W.; Zhao, X., 3D Printing of Highly Stretchable and Tough Hydrogels into Complex, Cellularized Structures. *Adv Mater* **2015**, *27* (27), 4035-4040.
11. Treloar, L. R. G., *The physics of rubber elasticity* 2nd edition ed.; Oxford University Press: London, 1958; p 338.
12. Gong, J. P., Materials both Tough and Soft. *Science* **2014**, *344* (6180), 161-162.
13. Sun, J.-Y.; Zhao, X.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z., Highly stretchable and tough hydrogels. *Nature* **2012**, *489* (7414), 133-136.
14. Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L., Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011**, *334* (6058), 965-968.
15. Imbernon, L.; Oikonomou, E. K.; Norvez, S.; Leibler, L., Chemically crosslinked yet reprocessable epoxidized natural rubber via thermo-activated disulfide rearrangements. *Polymer Chemistry* **2015**, *6* (23), 4271-4278.
16. Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L., Self-healing and thermoreversible rubber from supramolecular assembly. *Nature* **2008**, *451* (7181), 977-980.
17. Callies, X.; Fonteneau, C.; Véchambre, C.; Pensec, S.; Chenal, J. M.; Chazeau, L.; Bouteiller, L.; Ducouret, G.; Creton, C., Linear Rheology of Supramolecular Center-functionalized Polymers: Strong Stickers. *Macromolecules* **2015**, *48* (19), 7320-7326.
18. Chen, Q.; Tudryn, G. J.; Colby, R. H., Ionomer dynamics and the sticky Rouse model. *J Rheol* **2013**, *57* (5), 1441-1462.
19. Ducrot, E.; Chen, Y.; Bulters, M.; Sijbesma, R. P.; Creton, C., Toughening Elastomers with Sacrificial Bonds and Watching them Break. *Science* **2014**, *344* (6180), 186-189.
20. Ducrot, E.; Creton, C., Characterizing Large Strain Elasticity of Brittle Elastomeric Networks by Embedding Them in a Soft Extensible Matrix. *Adv Funct Mater* **2016**, *26* (15), 2482-2492.
21. Rubinstein, M.; Colby, R. H., *Polymer Physics*. 1st ed.; Oxford University Press: Oxford, 2003.
22. Zhong, M.; Wang, R.; Kawamoto, K.; Olsen, B. D.; Johnson, J. A., Quantifying the impact of molecular defects on polymer network elasticity. *Science* **2016**, *353* (6305), 1264-1268.
23. Treloar, L. R. G., The elasticity and related properties of rubbers. *Rep Prog Phys* **1973**, *36* (7), 755-826.
24. Gent, A. N., A New constitutive relation for rubber. *Rubber Chemistry and Technology* **1996**, *69*, 59-61.
25. Rubinstein, M.; Panyukov, S., Elasticity of polymer networks. *Macromolecules* **2002**, *35*, 6670-6886.
26. Edwards, S. F.; Vilgis, T. A., The Tube Model-Theory of Rubber Elasticity. *Rep Prog Phys* **1988**, *51* (2), 243-297.
27. Creton, C.; Ciccotti, M., Fracture and Adhesion of Soft Materials. *Rep Prog Phys* **2016**, *79* (4), 046601.
28. Rivlin, R. S.; Thomas, A. G., Rupture of rubber. I. Characteristic energy for tearing. *Journal of Polymer Science* **1953**, *10* (3), 291-318.
29. Chen, C.; Wang, Z.; Suo, Z., Flaw sensitivity of highly stretchable materials. *Extreme Mechanics Letters* **2017**, *10*, 50-57.
30. Long, R.; Hui, C.-Y., Fracture toughness of hydrogels: measurement and interpretation. *Soft Matter* **2016**, *12* (39), 8069-8086.
31. Zhang, T.; Lin, S.; Yuk, H.; Zhao, X., Predicting fracture energies and crack-tip fields of soft tough materials. *Extreme Mechanics Letters* **2015**, *4*, 1-8.
32. Gent, A. N.; Schultz, J., Effect of Wetting Liquids on the strength of adhesion of viscoelastic materials. *Journal of Adhesion* **1972**, *3*, 281-294.
33. Maugis, D.; Barquins, M., Fracture Mechanics and the adherence of viscoelastic bodies. *Journal of Physics D: Applied Physics* **1978**, *11*, 1989-2023.
34. Lake, G. J.; Lindley, P. B., Cut growth and fatigue of rubbers. II. Experiments on a noncrystallizing rubber. *Journal of Applied Polymer Science* **1964**, *8* (2), 707-721.

35. Lake, G. J.; Lindley, P. B., The mechanical fatigue limit for rubber. *Journal of Applied Polymer Science* **1965**, *9*, 1233-1251.
36. Lake, G. J.; Thomas, A. G., The strength of highly elastic materials. *Proceedings of the Royal Society of London, series A: Mathematical and Physical Sciences* **1967**, *A300*, 108-119.
37. Bhowmick, A. K., Threshold fracture of elastomers. *Journal of Macromolecular Science. Reviews in macromolecular Chemistry and Physics* **1988**, *C28* (3-4), 339-370.
38. Akagi, Y.; Sakurai, H.; Gong, J. P.; Chung, U.-i.; Sakai, T., Fracture energy of polymer gels with controlled network structures. *The Journal of Chemical Physics* **2013**, *139* (14), 144905.
39. Lin, W. C.; Fan, W.; Marcellan, A.; Hourdet, D.; Creton, C., Large Strain and Fracture Properties of Poly (dimethyl acrylamide)/silica Hybrid Hydrogels. *Macromolecules* **2010**, *43*, 2554-2563.
40. Cristiano, A.; Marcellan, A.; Keestra, B. J.; Steeman, P.; Creton, C., Fracture of Model Polyurethane Elastomeric Networks. *J Polym Sci Polym Phys* **2011**, *49* (5), 355-367.
41. Greensmith, H. W., Rupture of rubber. X. The change in stored energy on making a small cut in a test piece held in simple extension. *Journal of Applied Polymer Science* **1963**, *7* (3), 993-1002.
42. Baumberger, T.; Caroli, C.; Martina, D., Fracture of a biopolymer gel as a viscoplastic disentanglement process. *Eur. Phys. J. E* **2006**, *21* (1), 81-89.
43. Gent, A. N., Adhesion and strength of viscoelastic solids. Is there a relationship between adhesion and bulk properties? *Langmuir* **1996**, *12*, 4492-4496.
44. Gent, A. N.; Lai, S. M.; Nah, C.; Wang, C., Viscoelastic Effects in Cutting and Tearing Rubber. *Rubber Chemistry and Technology* **1994**, *67* (4), 610-618.
45. Tanaka, Y.; Kuwabara, R.; Na, Y. H.; Kurokawa, T.; Gong, J. P.; Osada, Y., Determination of fracture energy of high strength double network hydrogels. *Journal of Physical Chemistry B* **2005**, *109* (23), 11559-11562.
46. Ahagon, A.; Gent, A. N., Threshold fracture energies for elastomers. *Journal of Polymer Science, Polymer Physics Edition* **1975**, *13*, 1903-1911.
47. Plazek, D. J.; Gu, G. F.; Stacer, R. G.; Su, L. J.; Vonmeerwall, E. D.; Kelley, F. N., Viscoelastic Dissipation and the Tear Energy of Urethane Cross-Linked Polybutadiene Elastomers. *Journal of Materials Science* **1988**, *23* (4), 1289-1300.
48. Plazek, D. J.; Choy, I. C.; Kelley, F. N.; Vonmeerwall, E.; Su, L. J., Viscoelasticity and Tearing Energy of Fluorinated Hydrocarbon Elastomers. *Rubber Chemistry and Technology* **1983**, *56* (4), 866-882.
49. Bhowmick, A. K., Tear Strength of Elastomers over a Range of Rates, Temperatures and Cross-linking Tearing Energy Spectra. *Journal of Materials Science* **1986**, *21* (11), 3927-3932.
50. Persson, B. N. J.; Albohr, O.; Heinrich, G.; Ueba, H., Crack propagation in rubber-like materials. *Journal of Physics-Condensed Matter* **2005**, *17* (44), R1071-R1142.
51. Persson, B. N. J.; Brener, E. A., Crack propagation in viscoelastic solids. *Phys Rev E* **2005**, *71* (3), 036123.
52. Bastide, J.; Leibler, L., Large-Scale Heterogeneities in Randomly Cross-Linked Networks. *Macromolecules* **1988**, *21* (8), 2647-2649.
53. Urayama, K.; Kawamura, T.; Kohjiya, S., Structure-mechanical property correlations of model siloxane elastomers with controlled network topology. *Polymer* **2009**, *50* (2), 347-356.
54. Kawamura, T.; Urayama, K.; Kohjiya, S., Multiaxial Deformations of End-Linked Poly(dimethylsiloxane) Networks. 1. Phenomenological Approach to Strain Energy Density Function. *Macromolecules* **2001**, *34* (23), 8252-8260.
55. Gottlieb, M.; Macosko, C. W.; Benjamin, G. S.; Meyers, K. O.; Merrill, E. W., Equilibrium modulus of model poly(dimethylsiloxane) networks. *Macromolecules* **1981**, *14* (4), 1039-1046.
56. Mark, J. E.; Sullivan, J. L., Model networks of end-linked polydimethylsiloxane chains. I. Comparisons between experimental and theoretical values of the elastic modulus and the equilibrium degree of swelling. *The Journal of Chemical Physics* **1977**, *66* (3), 1006-1011.

57. Llorente, M. A.; Andradý, A. L.; Mark, J. E., Model networks of end-linked polydimethylsiloxane chains. XI. Use of very short network chains to improve ultimate properties. *Journal of Polymer Science: Polymer Physics Edition* **1981**, *19* (4), 621-630.
58. Seiffert, S., Scattering perspectives on nanostructural inhomogeneity in polymer network gels. *Prog. Polym. Sci.* **2017**, *66* (Supplement C), 1-21.
59. Mallam, S.; Horkay, F.; Hecht, A. M.; Rennie, A. R.; Geissler, E., Microscopic and macroscopic thermodynamic observations in swollen poly(dimethylsiloxane) networks. *Macromolecules* **1991**, *24* (2), 543-548.
60. Sakai, T.; Matsunaga, T.; Yamamoto, Y.; Ito, C.; Yoshida, R.; Suzuki, S.; Sasaki, N.; Shibayama, M.; Chung, U.-i., Design and Fabrication of a High-Strength Hydrogel with Ideally Homogeneous Network Structure from Tetrahedron-like Macromonomers. *Macromolecules* **2008**, *41* (14), 5379-5384.
61. Matsunaga, T.; Sakai, T.; Akagi, Y.; Chung, U.-i.; Shibayama, M., Structure Characterization of Tetra-PEG Gel by Small-Angle Neutron Scattering. *Macromolecules* **2009**, *42* (4), 1344-1351.
62. Sakai, T., Gelation mechanism and mechanical properties of Tetra-PEG gel. *Reactive and Functional Polymers* **2013**, *73* (7), 898-903.
63. Okumura, Y.; Ito, K., The Polyrotaxane Gel: A Topological Gel by Figure-of-Eight Cross-links. *Adv Mater* **2001**, *13* (7), 485-487.
64. Ohmori, K.; Abu Bin, I.; Seki, T.; Liu, C.; Mayumi, K.; Ito, K.; Takeoka, Y., Molecular weight dependency of polyrotaxane-cross-linked polymer gel extensibility. *Chemical Communications* **2016**, *52* (95), 13757-13759.
65. Noda, Y.; Hayashi, Y.; Ito, K., From topological gels to slide-ring materials. *Journal of Applied Polymer Science* **2014**, *131* (15), n/a-n/a.
66. Shabbir, A.; Huang, Q.; Chen, Q.; Colby, R. H.; Alvarez, N. J.; Hassager, O., Brittle fracture in associative polymers: the case of ionomer melts. *Soft Matter* **2016**.
67. Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y., Double-network hydrogels with extremely high mechanical strength. *Adv Mater* **2003**, *15* (14), 1155-1158.
68. Webber, R. E.; Creton, C.; Brown, H. R.; Gong, J. P., Large Strain Hysteresis and Mullins effect of tough Double-Network Hydrogels. *Macromolecules* **2007**, *40* (8), 2919-2927.
69. Nakajima, T.; Kurokawa, T.; Ahmed, S.; Wu, W.-I.; Gong, J. P., Characterization of internal fracture process of double network hydrogels under uniaxial elongation. *Soft Matter* **2013**, *9* (6), 1955-1966.
70. Tuncaboylu, D. C.; Sari, M.; Oppermann, W.; Okay, O., Tough and Self-Healing Hydrogels Formed via Hydrophobic Interactions. *Macromolecules* **2011**, *44* (12), 4997-5005.
71. Bilici, C.; Ide, S.; Okay, O., Yielding Behavior of Tough Semicrystalline Hydrogels. *Macromolecules* **2017**, *50* (9), 3647-3654.
72. Shull, K. R., Fracture and adhesion of elastomers and gels: Large strains at small length scales. *J Polym Sci Polym Phys* **2006**, *44* (24), 3436-3439.
73. Seitz, M. E.; Martina, D.; Baumberger, T.; Krishnan, V. R.; Hui, C.-Y.; Shull, K. R., Fracture and large strain behavior of self-assembled triblock copolymer gels. *Soft Matter* **2009**, *5* (2), 447-456.
74. Henderson, K. J.; Zhou, T. C.; Otim, K. J.; Shull, K. R., Ionically Cross-Linked Triblock Copolymer Hydrogels with High Strength. *Macromolecules* **2010**, *43* (14), 6193-6201.
75. Li, J.; Suo, Z.; Vlassak, J. J., Stiff, strong, and tough hydrogels with good chemical stability. *Journal of Materials Chemistry B* **2014**, *2* (39), 6708-6713.
76. Dankers, P. Y. W.; Hermans, T. M.; Baughman, T. W.; Kamikawa, Y.; Kieltyka, R. E.; Bastings, M. M. C.; Janssen, H. M.; Sommerdijk, N. A. J. M.; Larsen, A.; van Luyn, M. J. A.; Bosman, A. W.; Popa, E. R.; Fytas, G.; Meijer, E. W., Hierarchical Formation of Supramolecular Transient Networks in Water: A Modular Injectable Delivery System. *Adv Mater* **2012**, *24* (20), 2703-2709.
77. Guo, M.; Pitet, L. M.; Wyss, H. M.; Vos, M.; Dankers, P. Y. W.; Meijer, E. W., Tough Stimuli-Responsive Supramolecular Hydrogels with Hydrogen-Bonding Network Junctions. *Journal of the American Chemical Society* **2014**, *136* (19), 6969-6977.

78. Mayumi, K.; Guo, J.; Narita, T.; Hui, C. Y.; Creton, C., Fracture of dual crosslink gels with permanent and transient crosslinks. *Extreme Mechanics Letters* **2016**, *6*, 52-59.
79. Mayumi, K.; Marcellan, A.; Ducouret, G.; Creton, C.; Narita, T., Stress–Strain Relationship of Highly Stretchable Dual Cross-Link Gels: Separability of Strain and Time Effect. *ACS Macro Letters* **2013**, *2* (12), 1065-1068.
80. Rose, S.; Dizeux, A.; Narita, T.; Hourdet, D.; Marcellan, A., Time Dependence of Dissipative and Recovery Processes in Nanohybrid Hydrogels. *Macromolecules* **2013**, *46* (10), 4095-4104.
81. Dai, X.; Zhang, Y.; Gao, L.; Bai, T.; Wang, W.; Cui, Y.; Liu, W., A Mechanically Strong, Highly Stable, Thermoplastic, and Self-Healable Supramolecular Polymer Hydrogel. *Adv Mater* **2015**, *27* (23), 3566-3571.
82. Arakaki, K.; Kitamura, N.; Fujiki, H.; Kurokawa, T.; Iwamoto, M.; Ueno, M.; Kanaya, F.; Osada, Y.; Gong, J. P.; Yasuda, K., Artificial cartilage made from a novel double-network hydrogel: In vivo effects on the normal cartilage and ex vivo evaluation of the friction property. *J. Biomed. Mater. Res., Part A* **2010**, *93A*, 1160.
83. Gundogan, N.; Okay, O.; Oppermann, W., Swelling, elasticity and spatial inhomogeneity of poly(N,N-dimethylacrylamide) hydrogels formed at various polymer concentrations. *Macromolecular Chemistry and Physics* **2004**, *205* (6), 814-823.
84. Nisato, G.; Munch, J. P.; Candau, S. J., Swelling, structure, and elasticity of polyampholyte hydrogels. *Langmuir* **1999**, *15* (12), 4236-4244.
85. Sakai, T.; Kurakazu, M.; Akagi, Y.; Shibayama, M.; Chung, U.-i., Effect of swelling and deswelling on the elasticity of polymer networks in the dilute to semi-dilute region. *Soft Matter* **2012**, *8* (9), 2730-2736.
86. Urayama, K.; Kawamura, T.; Kohjiya, S., Elastic modulus and equilibrium swelling of networks crosslinked by end-linking oligodimethylsiloxane at solution state. *Journal of Chemical Physics* **1996**, *105* (11), 4833-4840.
87. Furukawa, H.; Kuwabara, R.; Tanaka, Y.; Kurokawa, T.; Na, Y.-H.; Osada, Y.; Gong, J. P., Tear Velocity Dependence of High-Strength Double Network Gels in Comparison with Fast and Slow Relaxation Modes Observed by Scanning Microscopic Light Scattering. *Macromolecules* **2008**, *41* (19), 7173-7178.
88. Sperling, L. H.; Mishra, V., The current status of interpenetrating polymer networks. *Polymers for Advanced Technologies* **1996**, *7* (4), 197-208.
89. Matsuda, T.; Nakajima, T.; Fukuda, Y.; Hong, W.; Sakai, T.; Kurokawa, T.; Chung, U.-i.; Gong, J. P., Yielding Criteria of Double Network Hydrogels. *Macromolecules* **2016**, *49* (5), 1865-1872.
90. Na, Y. H.; Tanaka, Y.; Kawachi, Y.; Furukawa, H.; Sumiyoshi, T.; Gong, J. P.; Osada, Y., Necking phenomenon of double-network gels. *Macromolecules* **2006**, *39* (14), 4641-4645.
91. Ahmed, S.; Nakajima, T.; Kurokawa, T.; Anamul Haque, M.; Gong, J. P., Brittle–ductile transition of double network hydrogels: Mechanical balance of two networks as the key factor. *Polymer* **2014**, *55* (3), 914-923.
92. Brown, H. R., A model of the fracture of double network gels. *Macromolecules* **2007**, *40* (10), 3815-3818.
93. Shams Es-haghi, S.; Leonov, A. I.; Weiss, R. A., Deconstructing the Double-Network Hydrogels: The Importance of Grafted Chains for Achieving Toughness. *Macromolecules* **2014**, *47* (14), 4769-4777.
94. Shams Es-haghi, S.; Weiss, R. A., Finite strain damage-elastoplasticity in double-network hydrogels. *Polymer* **2016**, *103*, 277-287.
95. Nakajima, T.; Furukawa, H.; Tanaka, Y.; Kurokawa, T.; Osada, Y.; Gong, J. P., True Chemical Structure of Double Network Hydrogels. *Macromolecules* **2009**, *42* (6), 2184-2189.
96. Myung, D.; Koh, W. U.; Ko, J. M.; Hu, Y.; Carrasco, M.; Noolandi, J.; Ta, C. N.; Frank, C. W., Biomimetic strain hardening in interpenetrating polymer network hydrogels. *Polymer* **2007**, *48* (18), 5376-5387.

97. Xin, H.; Brown, H. R.; Naficy, S.; Spinks, G. M., Mechanical recoverability and damage process of ionic-covalent PAAm-alginate hybrid hydrogels. *Journal of Polymer Science Part B: Polymer Physics* **2016**, *54* (1), 53-63.
98. Ducrot, E.; Montes, H.; Creton, C., Structure of tough multiple network elastomers by Small Angle Neutron Scattering. *Macromolecules* **2015**, *48* (21), 7945-7952.
99. Lin, S.; Zhou, Y.; Zhao, X., Designing extremely resilient and tough hydrogels via delayed dissipation. *Extreme Mechanics Letters* **2014**, *1*, 70-75.
100. Miquelard-Garnier, G.; Demoures, S.; Creton, C.; Hourdet, D., Synthesis and Rheological Behavior of New Hydrophobically Modified Hydrogels with Tunable Properties. *Macromolecules* **2006**, *39* (23), 8128-8139.
101. Miquelard-Garnier, G.; Hourdet, D.; Creton, C., Large strain behaviour of new hydrophobically modified hydrogels. *Polymer* **2009**, *50*, 481-490.
102. Guo, H.; Sanson, N.; Hourdet, D.; Marcellan, A., Thermo-responsive Toughening with Crack Bifurcation in Phase-Separated Hydrogels under Isochoric Conditions. *Adv Mater* **2016**, *28* (28), 5857-5864.
103. Sakulkaew, K.; Thomas, A. G.; Busfield, J. J. C., The effect of the rate of strain on tearing in rubber. *Polym Test* **2011**, *30* (2), 163-172.
104. Gent, A. N.; Pulford, C. T. R., Micromechanics of fracture in elastomers. *Journal of Materials Science* **1984**, *19* (11), 3612-3619.
105. Leibler, L.; Rubinstein, M.; Colby, R. H., Dynamics of Reversible Networks. *Macromolecules* **1991**, *24* (16), 4701-4707.
106. Rubinstein, M.; Semenov, A. N., Dynamics of entangled solutions of associating polymers. *Macromolecules* **2001**, *34*, 1058-1068.
107. Haraguchi, K.; Song, L., Microstructures Formed in Co-Cross-Linked Networks and Their Relationships to the Optical and Mechanical Properties of PNIPA/Clay Nanocomposite Gels. *Macromolecules* **2007**, *40* (15), 5526-5536.
108. Fukasawa, M.; Sakai, T.; Chung, U. I.; Haraguchi, K., Synthesis and Mechanical Properties of a Nanocomposite Gel Consisting of a Tetra-PEG/Clay Network. *Macromolecules* **2010**, *43* (9), 4370-4378.
109. Luo, F.; Sun, T. L.; Nakajima, T.; Kurokawa, T.; Zhao, Y.; Sato, K.; Ihsan, A. B.; Li, X.; Guo, H.; Gong, J. P., Oppositely Charged Polyelectrolytes Form Tough, Self-Healing, and Rebuildable Hydrogels. *Adv Mater* **2015**, *27* (17), 2722-2727.
110. Sun, T. L.; Kurokawa, T.; Kuroda, S.; Ihsan, A. B.; Akasaki, T.; Sato, K.; Haque, M. A.; Nakajima, T.; Gong, J. P., Physical hydrogels composed of polyampholytes demonstrate high toughness and viscoelasticity. *Nat Mater* **2013**, *12* (10), 932-937.
111. Elziere, P.; Dalle-Ferrier, C.; Creton, C.; Barthel, E.; Ciccotti, M., Large strain viscoelastic dissipation during interfacial rupture in laminated glass. *Soft Matter* **2017**, *13* (8), 1624-1633.
112. Sun, T. L.; Luo, F.; Kurokawa, T.; Karobi, S. N.; Nakajima, T.; Gong, J. P., Molecular structure of self-healing polyampholyte hydrogels analyzed from tensile behaviors. *Soft Matter* **2015**, *11* (48), 9355-9366.
113. Deplace, F.; Rabjohns, M. A.; Yamaguchi, T.; Foster, A. B.; Carelli, C.; Lei, C. H.; Ouzineb, K.; Keddie, J. L.; Lovell, P. A.; Creton, C., Bottom-up design of a soft-soft nanocomposite from polymer colloid particles. *Soft Matter* **2009**, *5*, 1440-1447.
114. Keita, G.; Ricard, A.; Audebert, R.; Pezron, E.; Leibler, L., The poly(vinyl alcohol)-borate system: influence of polyelectrolyte effects on phase diagrams. *Polymer* **1995**, *36* (1), 49-54.
115. Narita, T.; Mayumi, K.; Ducouret, G.; Hebraud, P., Viscoelastic Properties of Poly(vinyl alcohol) Hydrogels Having Permanent and Transient Cross-Links Studied by Microrheology, Classical Rheometry, and Dynamic Light Scattering. *Macromolecules* **2013**, *46* (10), 4174-4183.
116. Kean, Z. S.; Hawk, J. L.; Lin, S.; Zhao, X.; Sijbesma, R. P.; Craig, S. L., Increasing the Maximum Achievable Strain of a Covalent Polymer Gel Through the Addition of Mechanically Invisible Cross-Links. *Adv Mater* **2014**, *26*, 6013-6018.

117. Mullins, L., Softening of Rubber by Deformation. *Rubber Chemistry and Technology* **1969**, *42* (1), 339-362.
118. Diani, J.; Fayolle, B.; Gilormini, P., A review on the Mullins effect. *Eur Polym J* **2009**, *45* (3), 601-612.
119. Clough, J. M.; Creton, C.; Craig, S. L.; Sijbesma, R. P., Covalent Bond Scission in the Mullins Effect of a Filled Elastomer: Real-Time Visualization with Mechanoluminescence. *Adv Funct Mater* **2016**, *26* (48), 9063-9074.
120. Heinrich, G.; Kluppel, M., Recent advances in the theory of filler networking in elastomers. *Adv Polym Sci* **2002**, *160*, 1-44.
121. Mars, W. V.; Fatemi, A., Factors that affect the fatigue life of rubber: A literature survey. *Rubber Chemistry and Technology* **2004**, *77* (3), 391-412.
122. Huneau, B., STRAIN-INDUCED CRYSTALLIZATION OF NATURAL RUBBER: A REVIEW OF X-RAY DIFFRACTION INVESTIGATIONS. *Rubber Chemistry and Technology* **2011**, *84* (3), 425-452.
123. Chenal, J. M.; Gauthier, C.; Chazeau, L.; Guy, L.; Bomal, Y., Parameters governing strain induced crystallization in filled natural rubber. *Polymer* **2007**, *48* (23), 6893-6901.
124. Candau, N.; Chazeau, L.; Chenal, J.-M.; Gauthier, C.; Ferreira, J.; Munch, E.; Rochas, C., Characteristic time of strain induced crystallization of crosslinked natural rubber. *Polymer* **2012**, *53* (13), 2540-2543.
125. Candau, N.; Chazeau, L.; Chenal, J.-M.; Gauthier, C.; Munch, E., A comparison of the abilities of natural rubber (NR) and synthetic polyisoprene cis-1,4 rubber (IR) to crystallize under strain at high strain rates. *Phys Chem Chem Phys* **2016**, *18* (5), 3472-3481.
126. Qi, H. J.; Boyce, M. C., Stress-strain behavior of thermoplastic polyurethanes. *Mechanics of Materials* **2005**, *37* (8), 817-839.
127. Yi, J.; Boyce, M. C.; Lee, G. F.; Balizer, E., Large deformation rate-dependent stress-strain behavior of polyurea and polyurethanes. *Polymer* **2006**, *47* (1), 319-329.
128. Smith, T. L., STRENGTH OF ELASTOMERS - PERSPECTIVE. *Polymer Engineering and Science* **1977**, *17* (3), 129-143.
129. Long, R.; Mayumi, K.; Creton, C.; Narita, T.; Hui, C.-Y., Time Dependent Behavior of a Dual Cross-Link Self-Healing Gel: Theory and Experiments. *Macromolecules* **2014**, *47* (20), 7243-7250.
130. Long, R.; Mayumi, K.; Creton, C.; Narita, T.; Hui, C.-Y., Rheology of a dual crosslink self-healing gel: Theory and measurement using parallel-plate torsional rheometry. *Journal of Rheology (1978-present)* **2015**, *59* (3), 643-665.
131. Guo, J.; Long, R.; Mayumi, K.; Hui, C.-Y., Mechanics of a Dual Cross-Link Gel with Dynamic Bonds: Steady State Kinetics and Large Deformation Effects. *Macromolecules* **2016**, *49* (9), 3497-3507.
132. Bird, R. B.; Armstrong, R. C.; Hassager, O., *Dynamics of Polymeric Liquids: Vol 1 Fluid Mechanics*. 2nd ed.; Wiley: New York, 1987; Vol. 1.
133. Bueche, F., Mullins effect and rubber-filler interaction. *Journal of Applied Polymer Science* **1961**, *5* (15), 271-281.
134. Marckmann, G.; Verron, E.; Gornet, L.; Chagnon, G.; Charrier, P.; Fort, P., A theory of network alteration for the Mullins effect. *J Mech Phys Solids* **2002**, *50* (9), 2011-2028.
135. Govindjee, S.; Simo, J., Transition from micro-mechanics to computationally efficient phenomenology: Carbon black filled rubbers incorporating mullins' effect. *J Mech Phys Solids* **1992**, *40* (1), 213-233.
136. Diani, J.; Brieu, M.; Vacherand, J. M., A damage directional constitutive model for Mullins effect with permanent set and induced anisotropy. *Eur J Mech A-solid* **2006**, *25* (3), 483-496.
137. Wang, X.; Hong, W., Pseudo-elasticity of a double network gel. *Soft Matter* **2011**, *7* (18), 8576-8581.
138. Zhao, X., A theory for large deformation and damage of interpenetrating polymer networks. *J Mech Phys Solids* **2012**, *60* (2), 319-332.
139. Lavoie, S. R.; Long, R.; Tang, T., A rate-dependent damage model for elastomers at large strain. *Extreme Mechanics Letters* **2016**, *8*, 114-124.

140. Tanaka, Y.; Kawauchi, Y.; Kurokawa, T.; Furukawa, H.; Okajima, T.; Gong, J. P., Localized Yielding Around Crack Tips of Double-Network Gels. *Macromol. Rapid Commun.* **2008**, *29* (18), 1514-1520.
141. Yu, Q. M.; Tanaka, Y.; Furukawa, H.; Kurokawa, T.; Gong, J. P., Direct Observation of Damage Zone around Crack Tips in Double-Network Gels. *Macromolecules* **2009**, *42* (12), 3852-3855.
142. Tanaka, Y., A local damage model for anomalous high toughness of double-network gels. *Europhys Lett* **2007**, *78* (5), 56005.
143. Mzabi, S.; Berghezan, D.; Roux, S.; Hild, F.; Creton, C., A critical local energy release rate criterion for fatigue fracture of elastomers. *Journal of Polymer Science: Polymer Physics* **2011**, *49*, 1518-1524.
144. Feldman, K. E.; Kade, M. J.; Meijer, E. W.; Hawker, C. J.; Kramer, E. J., Model Transient Networks from Strongly Hydrogen-Bonded Polymers. *Macromolecules* **2009**, *42* (22), 9072-9081.
145. Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W., Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding. *Science* **1997**, *278* (5343), 1601-1604.
146. Maes, F.; Montarnal, D.; Cantournet, S.; Tournilhac, F.; Corte, L.; Leibler, L., Activation and deactivation of self-healing in supramolecular rubbers. *Soft Matter* **2012**, *8* (5), 1681-1687.
147. Courtois, J.; Baroudi, I.; Nouvel, N.; Degrandi, E.; Pensec, S.; Ducouret, G.; Chanéac, C.; Bouteiller, L.; Creton, C., Supramolecular Soft Adhesive Materials. *Adv Funct Mater* **2010**, *20* (11), 1803-1811.
148. Enke, M.; Dohler, D.; Bode, S.; Binder, W. H.; Hager, M. D.; Schubert, U. S., Intrinsic Self-Healing Polymers Based on Supramolecular Interactions: State of the Art and Future Directions. In *Self-Healing Materials*, Hager, M. D.; VanDerZwaag, S.; Schubert, U. S., Eds. 2016; Vol. 273, pp 59-112.
149. de Espinosa, L. M.; Fiore, G. L.; Weder, C.; Johan Foster, E.; Simon, Y. C., Healable supramolecular polymer solids. *Prog. Polym. Sci.* **2015**, *49*, 60-78.
150. Faghihnejad, A.; Feldman, K. E.; Yu, J.; Tirrell, M. V.; Israelachvili, J. N.; Hawker, C. J.; Kramer, E. J.; Zeng, H., Adhesion and Surface Interactions of a Self-Healing Polymer with Multiple Hydrogen-Bonding Groups. *Adv Funct Mater* **2014**, *24* (16), 2322-2333.
151. Hentschel, J.; Kushner, A. M.; Ziller, J.; Guan, Z., Self-Healing Supramolecular Block Copolymers. *Angewandte Chemie International Edition* **2012**, *51* (42), 10561-10565.
152. Liu, J.; Tan, C. S. Y.; Yu, Z. Y.; Li, N.; Abell, C.; Scherman, O. A., Tough Supramolecular Polymer Networks with Extreme Stretchability and Fast Room-Temperature Self-Healing. *Adv Mater* **2017**, *29* (22).
153. Hernández, M.; Grande, A. M.; Dierkes, W.; Bijleveld, J.; van der Zwaag, S.; García, S. J., Turning Vulcanized Natural Rubber into a Self-Healing Polymer: Effect of the Disulfide/Polysulfide Ratio. *ACS Sustainable Chemistry & Engineering* **2016**, *4* (10), 5776-5784.
154. Amamoto, Y.; Otsuka, H.; Takahara, A.; Matyjaszewski, K., Self-Healing of Covalently Cross-Linked Polymers by Reshuffling Thiuram Disulfide Moieties in Air under Visible Light. *Adv Mater* **2012**, *24* (29), 3975-3980.
155. Canadell, J.; Goossens, H.; Klumperman, B., Self-Healing Materials Based on Disulfide Links. *Macromolecules* **2011**, *44* (8), 2536-2541.
156. Polgar, L. M.; Fortunato, G.; Araya-Hermosilla, R.; van Duin, M.; Pucci, A.; Picchioni, F., Cross-linking of rubber in the presence of multi-functional cross-linking aids via thermoreversible Diels-Alder chemistry. *Eur Polym J* **2016**, *82*, 208-219.
157. Röttger, M.; Domenech, T.; van der Weegen, R.; Breuillac, A.; Nicolaÿ, R.; Leibler, L., High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* **2017**, *356* (6333), 62-65.
158. Candau, N.; Laghmach, R.; Chazeau, L.; Chenal, J.-M.; Gauthier, C.; Biben, T.; Munch, E., Influence of strain rate and temperature on the onset of strain induced crystallization in natural rubber. *Eur Polym J* **2015**, *64* (0), 244-252.

159. Zhao, X., Multi-scale multi-mechanism design of tough hydrogels: building dissipation into stretchy networks. *Soft Matter* **2014**, *10* (5), 672-687.
160. Bai, R.; Yang, Q.; Tang, J.; Morelle, X. P.; Vlassak, J.; Suo, Z., Fatigue fracture of tough hydrogels. *Extreme Mechanics Letters* **2017**, *15*, 91-96.
161. Lakrout, H.; Creton, C.; Ahn, D.; Shull, K. R., Influence of molecular features on the tackiness of acrylic polymer melts. *Macromolecules* **2001**, *34*, 7448-7458.
162. Shabbir, A.; Goldansaz, H.; Hassager, O.; van Ruymbek, E.; Alvarez, N. J., Effect of Hydrogen Bonding on Linear and Nonlinear Rheology of Entangled Polymer Melts. *Macromolecules* **2015**, *48* (16), 5988-5996.
163. Liu, H.; Huang, G.; Zeng, J.; Xu, L.; Fu, X.; Wu, S.; Zheng, J.; Wu, J., Observing Nucleation Transition in Stretched Natural Rubber through Self-Seeding. *The Journal of Physical Chemistry B* **2015**, *119* (35), 11887-11892.
164. Luo, M.-C.; Zeng, J.; Fu, X.; Huang, G.; Wu, J., Toughening diene elastomers by strong hydrogen bond interactions. *Polymer* **2016**, *106*, 21-28.
165. Imbernon, L.; Norvez, S., From landfilling to vitrimer chemistry in rubber life cycle. *Eur Polym J* **2016**, *82*, 347-376.
166. Chen, S.; Binder, W. H., Dynamic Ordering and Phase Segregation in Hydrogen-Bonded Polymers. *Accounts Chem Res* **2016**, *49* (7), 1409-1420.
167. Callies, X.; Fonteneau, C.; Véchambre, C.; Pensec, S.; Chenal, J. M.; Chazeau, L.; Bouteiller, L.; Ducouret, G.; Creton, C., Linear Rheology of Bis-Urea Functionalized Supramolecular Poly(butylacrylate)s :

Part I – Weak Stickers. *Polymer* **2015**, *69*, 233-240.

168. Boulatov, R., The Challenges and Opportunities of Contemporary Polymer Mechanochemistry. *Chemphyschem* **2017**, *18* (11), 1419-1421.
169. Zhang, H.; Chen, Y. J.; Lin, Y. J.; Fang, X. L.; Xu, Y. Z.; Ruan, Y. H.; Weng, W. G., Spiropyran as a Mechanochromic Probe in Dual Cross-Linked Elastomers. *Macromolecules* **2014**, *47* (19), 6783-6790.
170. Gossweiler, G. R.; Kouznetsova, T. B.; Craig, S. L., Force-Rate Characterization of Two Spiropyran-Based Molecular Force Probes. *Journal of the American Chemical Society* **2015**, *137* (19), 6148-6151.
171. Lee, C. K.; Beiermann, B. A.; Silberstein, M. N.; Wang, J.; Moore, J. S.; Sottos, N. R.; Braun, P. V., Exploiting Force Sensitive Spiroyrans as Molecular Level Probes. *Macromolecules* **2013**, *46* (10), 3746-3752.
172. Chen, Y.; Spiering, A. J. H.; Karthikeyan, S.; Peters, G. W. M.; Meijer, E. W.; Sijbesma, R. P., Mechanically induced chemiluminescence from polymers incorporating a 1,2-dioxetane unit in the main chain. *Nature Chemistry* **2012**, *4* (7), 559-562.
173. Gostl, R.; Sijbesma, R. P., [small pi]-extended anthracenes as sensitive probes for mechanical stress. *Chemical Science* **2016**, *7* (1), 370-375.
174. Davis, D. A.; Hamilton, A.; Yang, J.; Cremer, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R., Force-induced activation of covalent bonds in mechanoresponsive polymeric materials. *Nature* **2009**, *459* (7243), 68-72.
175. Meijer, E. W.; Wynberg, H., The synthesis and chemiluminescence of stable 1,2-dioxetane: An organic chemistry laboratory experiment. *J Chem Edu* **1982**, *59* (12), 1071.
176. Clough, J. M.; van der Gucht, J.; Sijbesma, R. P., Mechanoluminescent Imaging of Osmotic Stress-Induced Damage in a Glassy Polymer Network. *Macromolecules* **2017**, *50* (5), 2043-2053.
177. Beiermann, B. A.; Kramer, S. L. B.; Moore, J. S.; White, S. R.; Sottos, N. R., Role of Mechanophore Orientation in Mechanochemical Reactions. *ACS Macro Letters* **2012**, *1* (1), 163-166.
178. Rharbi, Y.; Cabane, B.; Vacher, A.; Joanicot, M.; Boue, F., Modes of deformation in a soft hard nanocomposite: A SANS study. *Europhys Lett* **1999**, *46* (4), 472-478.
179. Shibayama, M., Universality and Specificity of Polymer Gels Viewed by Scattering Methods. *B Chem Soc Jpn* **2006**, *79* (12), 1799-1819.

180. Brüning, K.; Schneider, K.; Roth, S. V.; Heinrich, G., Kinetics of Strain-Induced Crystallization in Natural Rubber Studied by WAXD: Dynamic and Impact Tensile Experiments. *Macromolecules* **2012**, *45* (19), 7914-7919.
181. Brüning, K.; Schneider, K.; Roth, S. V.; Heinrich, G., Strain-induced crystallization around a crack tip in natural rubber under dynamic load. *Polymer* **2013**, *54* (22), 6200-6205.
182. Rublon, P.; Huneau, B.; Saintier, N.; Beurrot, S.; Leygue, A.; Verron, E.; Mocuta, C.; Thiaudière, D.; Berghezan, D., In situ synchrotron wide-angle X-ray diffraction investigation of fatigue cracks in natural rubber. *J Synchrotron Radiat* **2013**, *20* (1), 105-109.
183. Zhang, H.; Scholz, A. K.; de Crevoisier, J.; Berghezan, D.; Narayanan, T.; Kramer, E. J.; Creton, C., Nanocavitation around a crack tip in a soft nanocomposite: A scanning microbeam small angle X-ray scattering study. *Journal of Polymer Science Part B: Polymer Physics* **2015**, *53* (6), 422-429.
184. Zhang, H.; Scholz, A. K.; de Crevoisier, J.; Vion-Loisel, F.; Besnard, G.; Hexemer, A.; Brown, H. R.; Kramer, E. J.; Creton, C., Nanocavitation in Carbon Black Filled Styrene-Butadiene Rubber under Tension Detected by Real Time Small Angle X-ray Scattering. *Macromolecules* **2012**, *45* (3), 1529-1543.
185. Samaca Martinez, J. R.; Balandraud, X.; Toussaint, E.; Le Cam, J. B.; Berghezan, D., Thermomechanical analysis of the crack tip zone in stretched crystallizable natural rubber by using infrared thermography and digital image correlation. *Polymer* **2014**, *55* (24), 6345-6353.
186. Chen, L.; Zhou, W.; Lu, J.; Li, J.; Zhang, W.; Huang, N.; Wu, L.; Li, L., Unveiling Reinforcement and Toughening Mechanism of Filler Network in Natural Rubber with Synchrotron Radiation X-ray Nano-Computed Tomography. *Macromolecules* **2015**, *48* (21), 7923-7928.
187. Besnard, G.; Hild, F.; Roux, S., "Finite-Element" displacement fields analysis from digital images: Application to portevin-le chatelier bands. *Exp. Mech.* **2006**, *46* (6), 789-803.
188. Liu, W. R.; Long, R., Constructing Continuous Strain and Stress Fields From Spatially Discrete Displacement Data in Soft Materials. *J Appl Mech-t Asme* **2016**, *83*, 011006.