ETH zürich

Macromolecular Engineering: Networks and Gels

Lecture 18: Design considerations of networks and gels

Prof. Dr. Mark W. Tibbitt, 28. April 2022

Some Recent Engineering Applications of Rubber

Some Recent Engineering Applications of Rubber[1]

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THE wide variety of demands made upon rubber as a material of commerce seem paradoxical unless it is fully realized that the term "rubber" as used in industry connotes, not a single substance, but a vast range of compositions, each designed to meet the engineering requirements of some particular service, and each representing careful development on the part of the rubber technologist in order to secure the desired physical and chemical characteristics.

The rubber manufacturer has facilities for selecting and blending with the basic material a variety of materials other than rubber, for processing and vulcanizing rubber compounds to meet specific requirements, and for combining rubber in commercial articles with almost every other type of structural material. These facilities, together with the rapid strides being made continually in rubber technology through research, are resulting in new applications of rubber and rubber structures to the needs of industry. Engineers are constantly bringing more of their problems to the rubber technologist, recognizing in rubber an engineering material of fundamental importance, capable of being widely varied in useful physical and chemical properties.

The efforts of rubber technologists to meet the needs of various industries for materials and structures of unique characteristics have resulted in a continual expansion of the engineering applications of rubber. Some recent developments are described, with confidence that engineers will visualize and suggest other new ways in which rubber may be applied to the solution of industrial problems.

Rubber Bearings

The remarkable resistance to abrasion of soft, vulcanized rubber, its resilience, its low coefficient of friction when wet, its non-compressibility, and its ability to absorb shock are properties which render it of outstanding value as a bearing material in certain kinds of service. The success of rubber bearings depends, however, not only upon the properties of a unique engineering material, but also upon the Vulcalock process of bonding the rubber to a metal shell, and upon certain fundamental features of design. The fluted construction shown in Figure 1 and the spirally grooved construction used in vertical guide bearings (Figure 2) both provide waterways essential to continuous lubrication of the bearing and the washing away of abrasive material.

Years of continuous use have proved beyond all question that rubber is better fitted for certain types of installation than any other bearing material. Where lubrication by oil is difficult or impossible, and where other bearings cut out owing to sand or other abrasives, rubber bearings endure. There are cases on record where they have outworn other bearing materials, such as *lignum vitae* and babbitt, by as much as ten times.

The highest operating temperature ordinarily recommended for rubber bearings is 150° F. Special bearings have been designed, however, for use at higher temperatures, in places where loads are not excessive and where it is possible to work out a satisfactory holding device for the special type bearing required. Another limitation necessarily imposed is that rubber bearings are not serviceable in contact with oils.

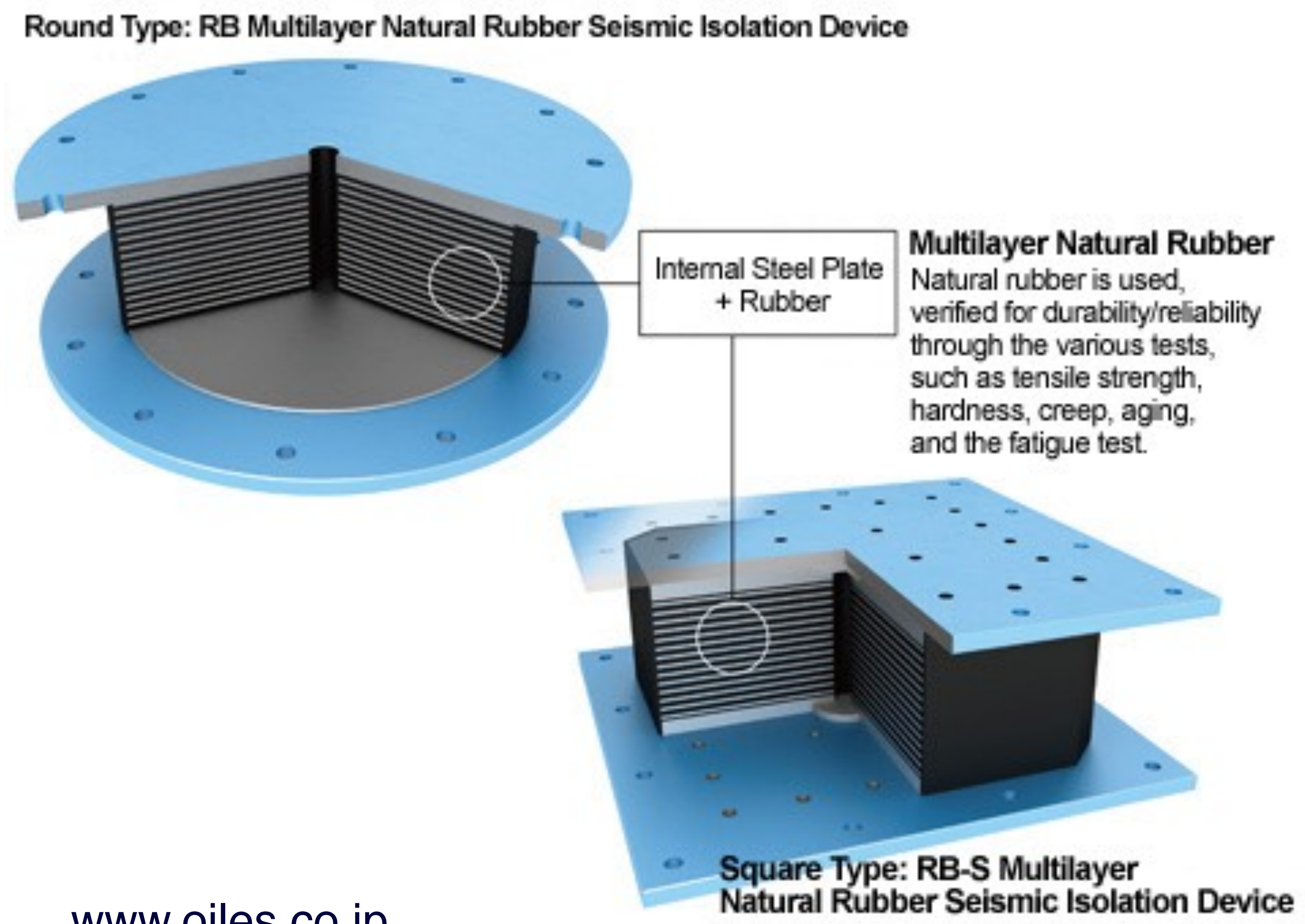
While water-lubricated soft-rubber bearings are most widely known for their outstanding performance in marine service, they have also been applied economically to industrial uses. The installation of rubber bearings, for example, provides the simplest and by far the most effective solution of three problems of deep-well turbine-pump operation—cutting of bearings and shaft by sand and grit, shaft vibration, and lubrication. In one case a deep-well turbine pump was required to handle water containing 25 per cent of sharp sand. After continuous operation for 144 hours at a speed of 1150 r. p. m., the shaft had worn only 0.004 inch and there was no trace whatsoever of wear on the rubber bearing.

Cutter head and ladder bearings on suction dredges (Figure 3), subject to rapid wear and heavy strains, have been replaced by rubber without increasing the bearing size. Vertical guide bearings of tremendous sizes are used in hydraulic turbines (Figure 2). Bearings 2 feet in diameter and 6 feet long are not unusual. Rubber bearings in this service have given years of continuous operation.

Babbitt and bronze bearings in the centrifugal sand pumps used by a large mining company required replacement after

[1] Received March 6, 1931.

Construction - seismic isolation rubber bearings

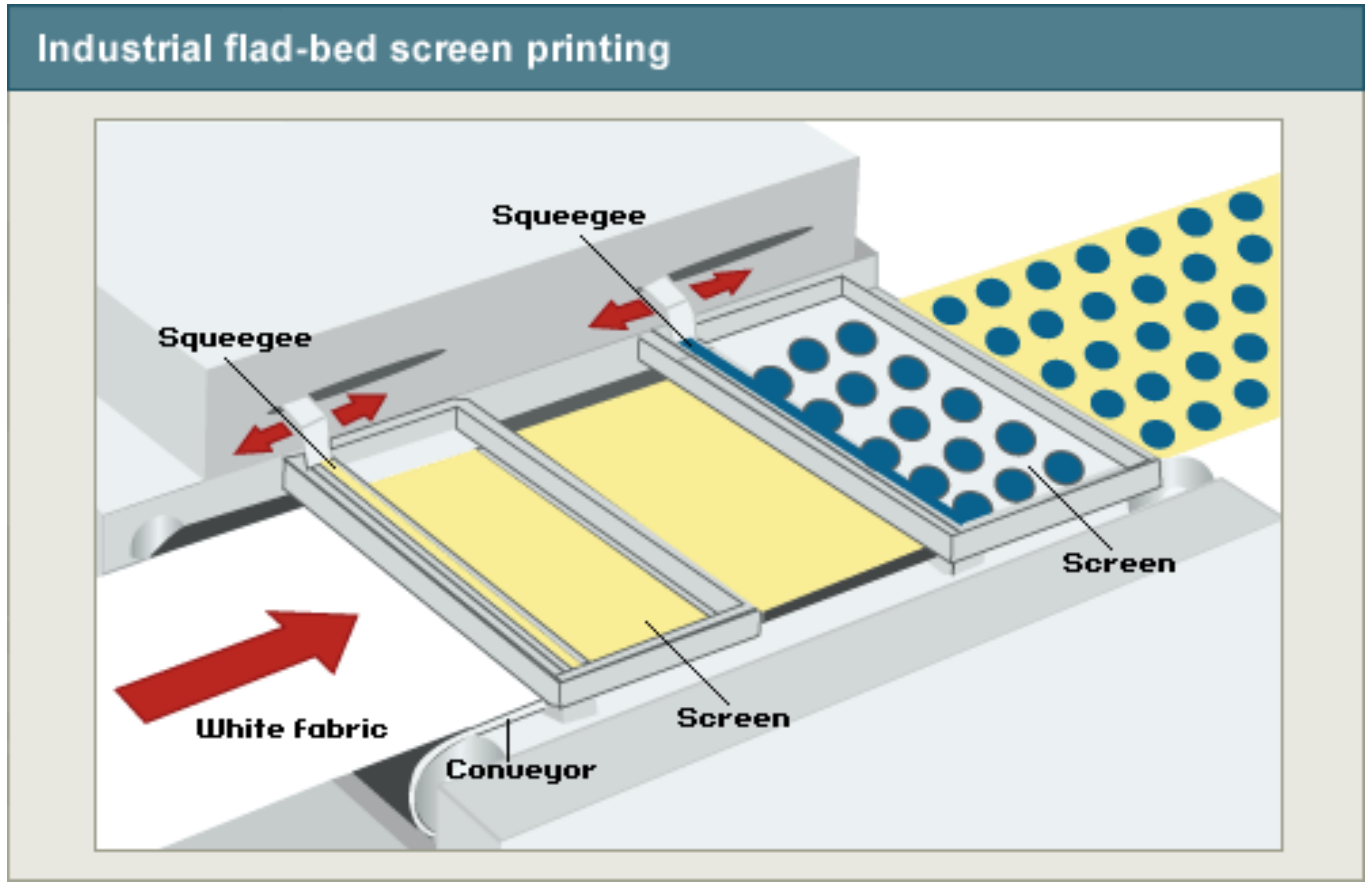


www.oiles.co.jp

wikipedia.org

Large rubber isolation bearings used to dampen seismic vibrations in structures susceptible to damage - durability

Textile industry - rubber rollers for fabric printing



BBC

oecotextiles.wordpress.com

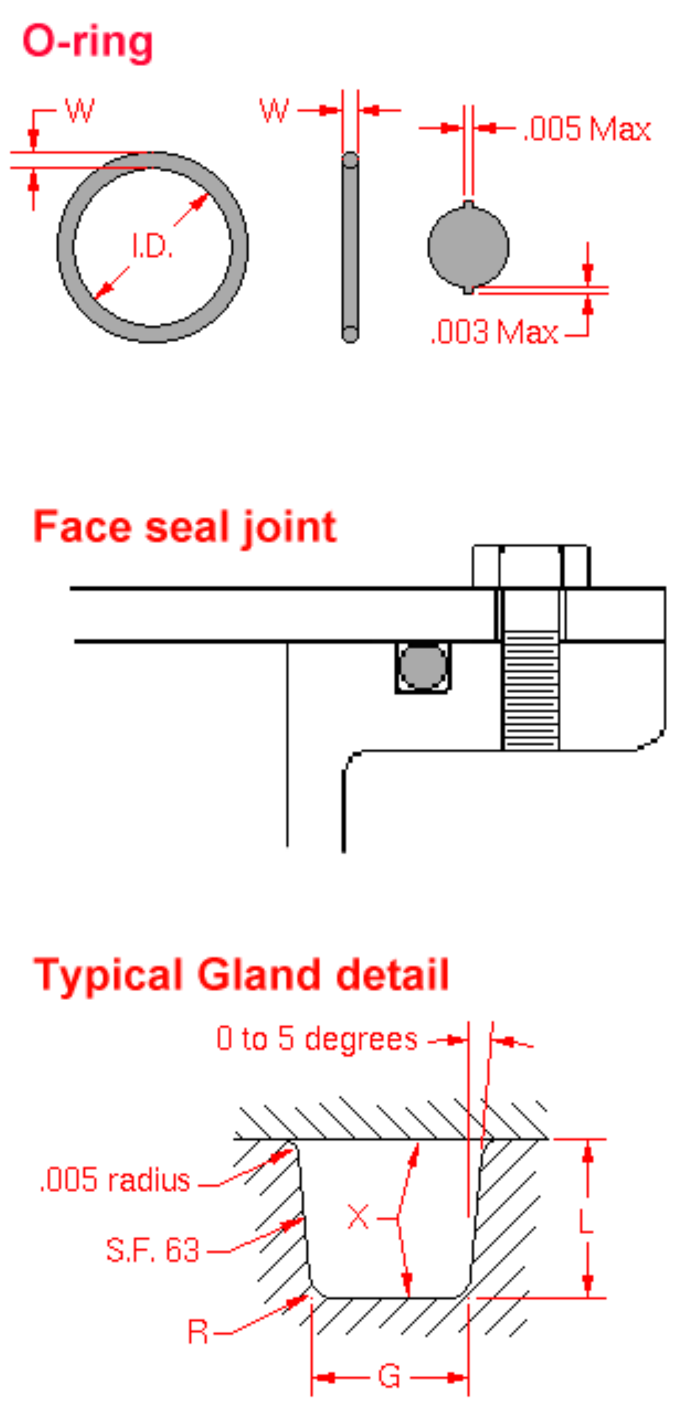
Rolling rubber stamps for printing applications commonly used for textile printing - solvent compatibility

Electronics - lithium-ion polymer batteries

wikipedia.org

Polymer gels and solid state polymers for ion transport in batteries - diffusion

Sealing gaskets - O rings and the *Challenger* disaster



wikipedia.org

Use of rubber rings to provide seals in piping and for high vacuum applications - elasticity

"For a successful technology, reality must take precedence over public relations, for nature cannot be fooled."

https://www.youtube.com/watch?v=raMmRKGkGD4

Macromolecules

Perspective

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50th Anniversary Perspective: Networks and Gels: Soft but Dynamic and Tough

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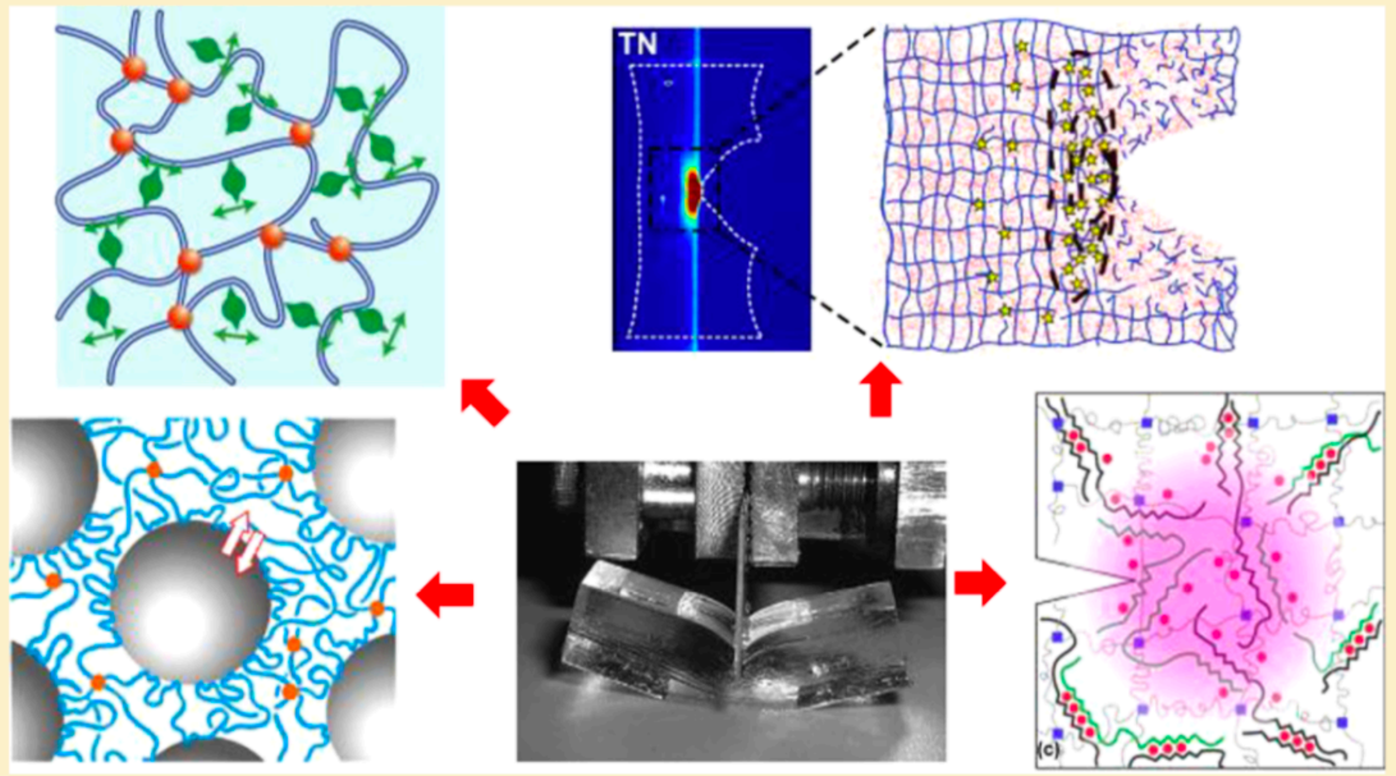
ABSTRACT: Soft polymer networks have seen an explosion of recent developments motivated by new high tech applications in the biomedical field or in engineering. We present a candid and critical overview of the current understanding of the relation between the structure and molecular architecture of polymer 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 behavior and to point out remaining challenges.



Tradeoff between modulus and toughness in soft materials

Network modulus

$$\mu_x = \nu_x kT = \frac{\rho RT}{M_0 N_x}$$
$$\mu_x = \text{modulus} = G'$$
$$M_0 = \text{monomer mass}$$
$$N_x = \text{monomers per strand}$$

Network toughness

$$\Gamma(v) = \Gamma_0(1 + \phi(a_T v))$$
$$\Gamma_0 = \text{fracture energy at limiting velocity}$$
$$\phi(a_T v) = \text{velocity dependent dissipation}$$
$$\Gamma_0 = N_x U_b \sum$$
$$U_b = \text{bond energy} \sim 350\text{kJ/mol}$$
$$\sum \approx \nu_x a N_x^{1/2} = \text{areal density of strands}$$
$$\Gamma_0 \approx U_b \nu_x a N_x^{3/2} \approx \frac{U_b a \rho}{M_0} N_x^{1/2}$$
$$\Gamma_0 \approx U_b a \left(\frac{\rho}{M_0}\right)^{3/2} (kT)^{1/2} \mu_x^{-1/2}$$

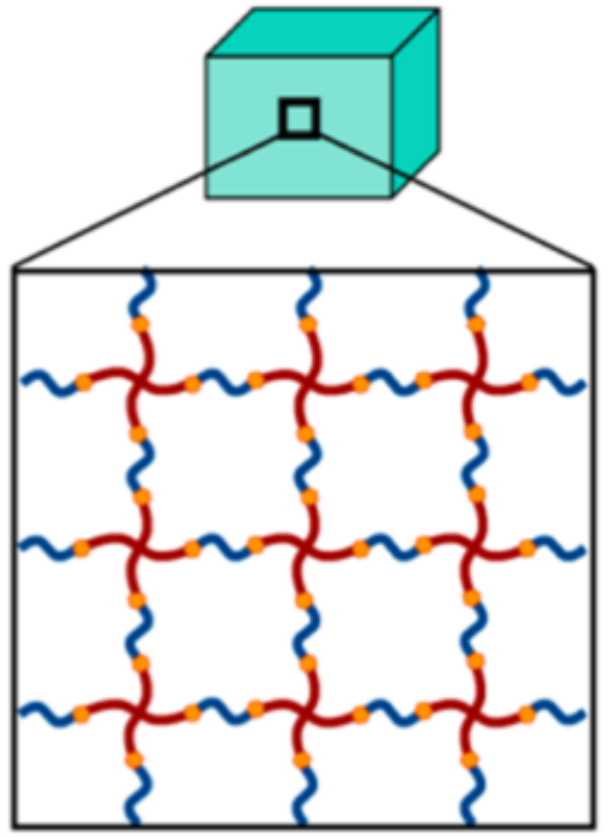
This implies a tradeoff between network modulus (elasticity) and fracture energy (toughness). Further, swollen gels with a similar value of Nx are more brittle than pure elastomers.

$$\Gamma_0 \propto \mu_x^{-1/2} \qquad \Gamma_0 \propto \rho_0 \phi_p$$

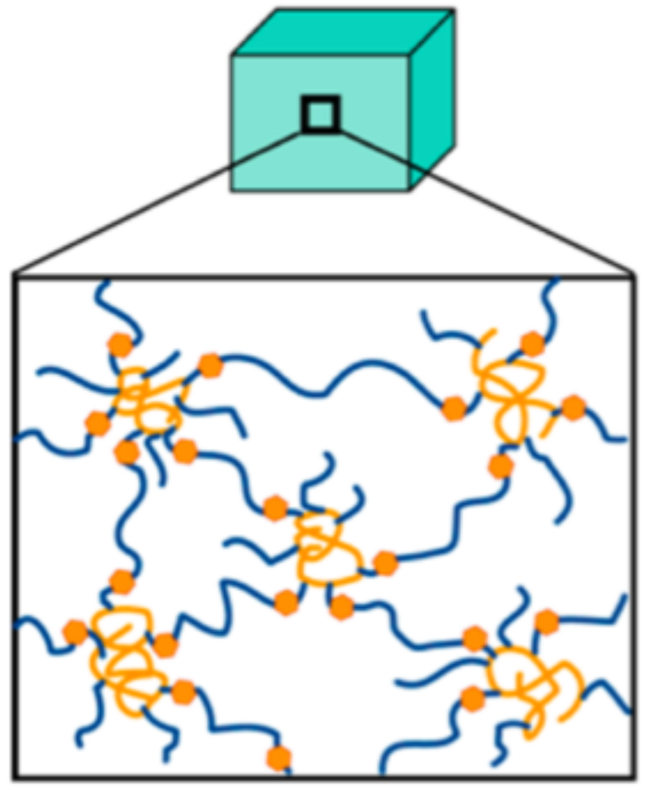
Creton *Macromolecules* **2017**, *50*, 8297.

Designing for extensibility and toughness

Ideal network



'Real' network



Tibbitt et al. *Macromolecules* **2013**, *46*, 2785.

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 that 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 cross-link 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.[30] This is the realm of solid mechanics, and it is important to focus now on larger length scales than the molecular scale.

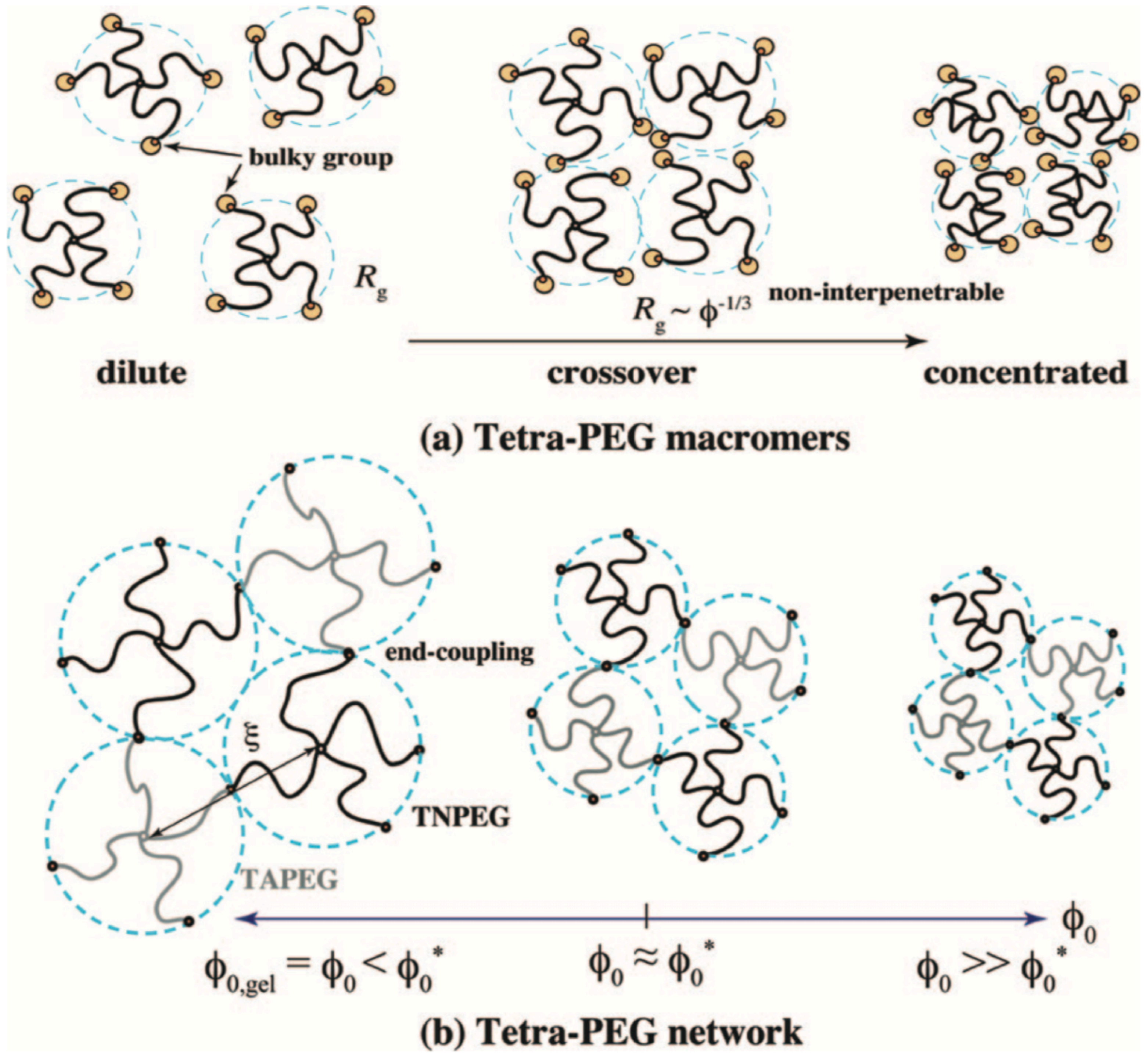


Figure 14. Schematic models showing the concentration-dependence of (a) macromer solutions and (b) Tetra-PEG gels. Due to the presence of bulky/hydrophobic groups at the end of arm chains, macromers are noninterpenetrable even at $\phi_0 > \phi_0$*. By end-coupling of the end-groups exclusively between TAPEG and TNPEG, a regularly arranged Tetra-PEG gel is formed with a diamond-like architecture.

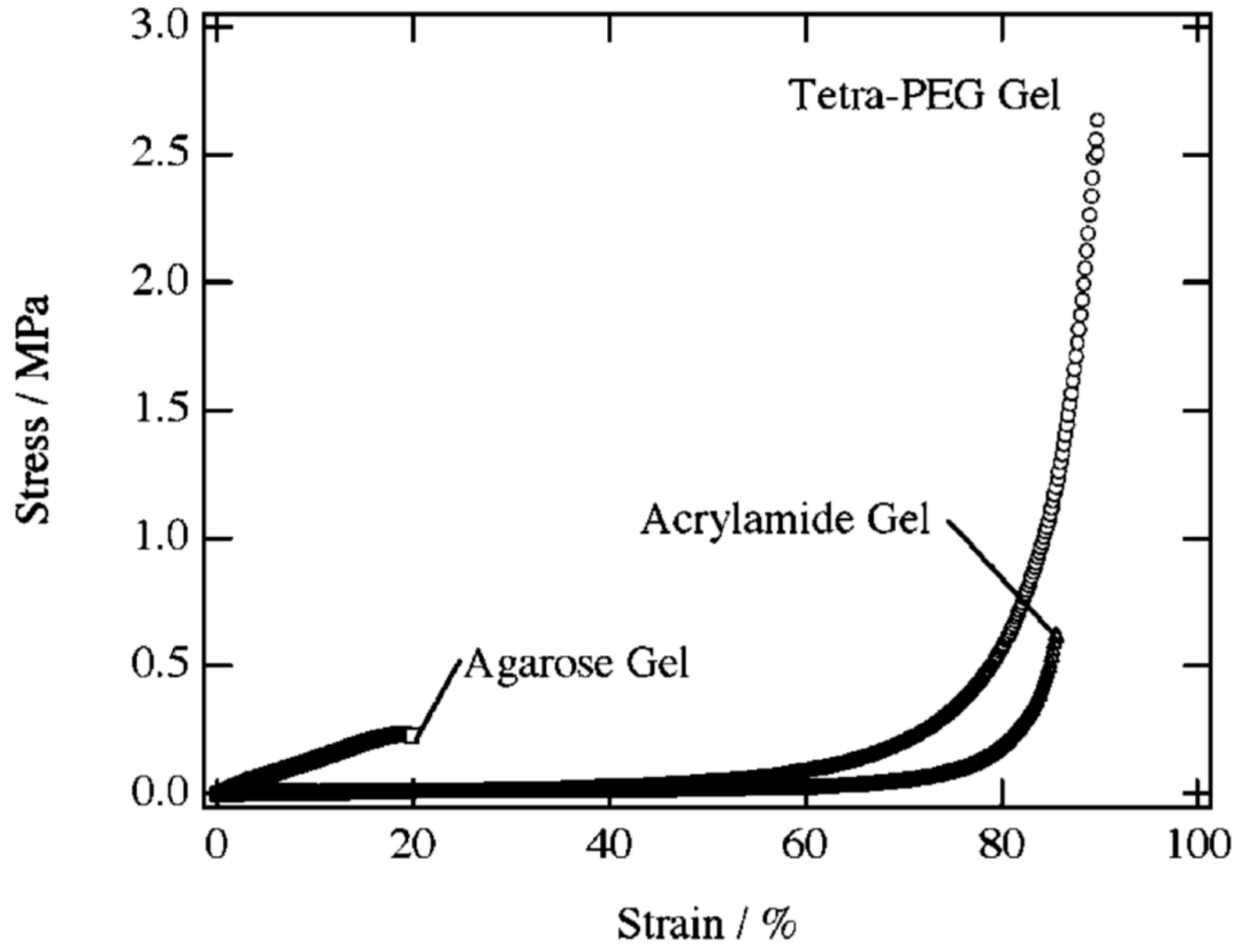


Figure 2. Stress−strain curves of agarose gel (square), acrylamide gel (triangle), and tetra-PEG gel (circle).

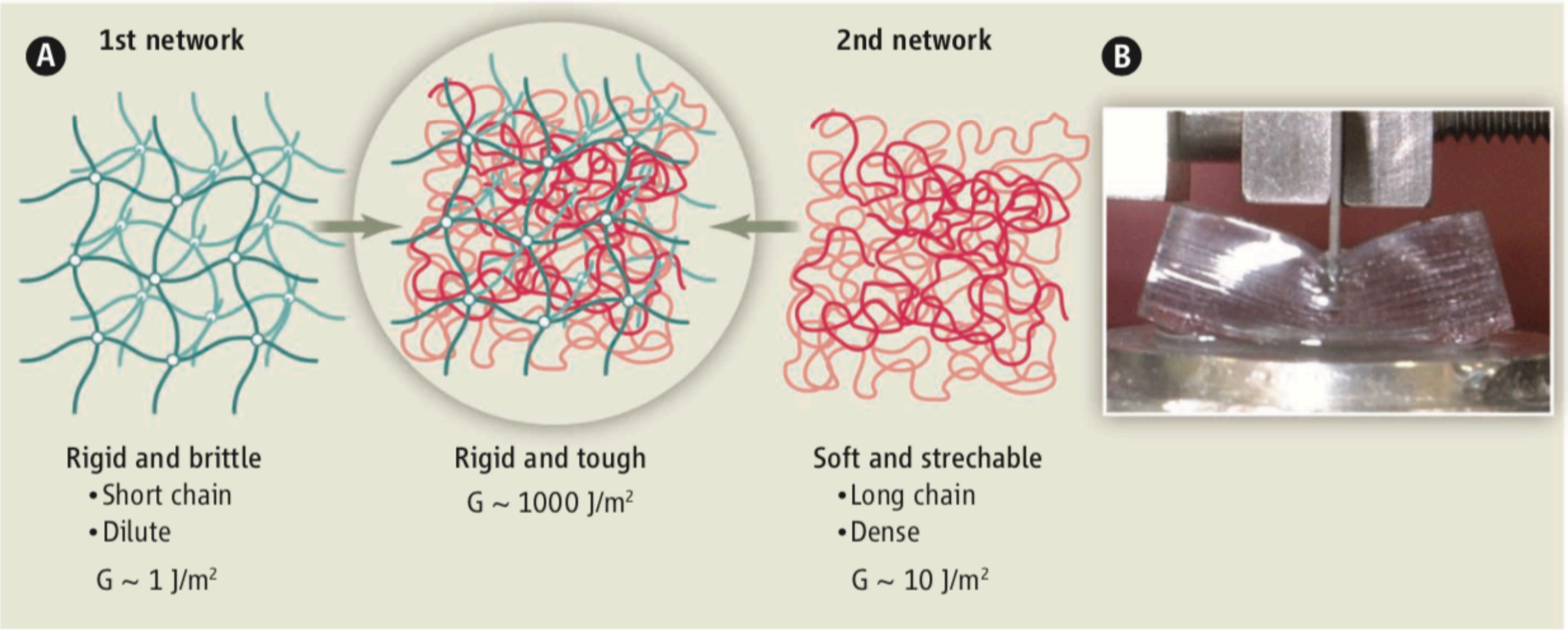
Table 1 Physical measurements for PEG-based hydrogels

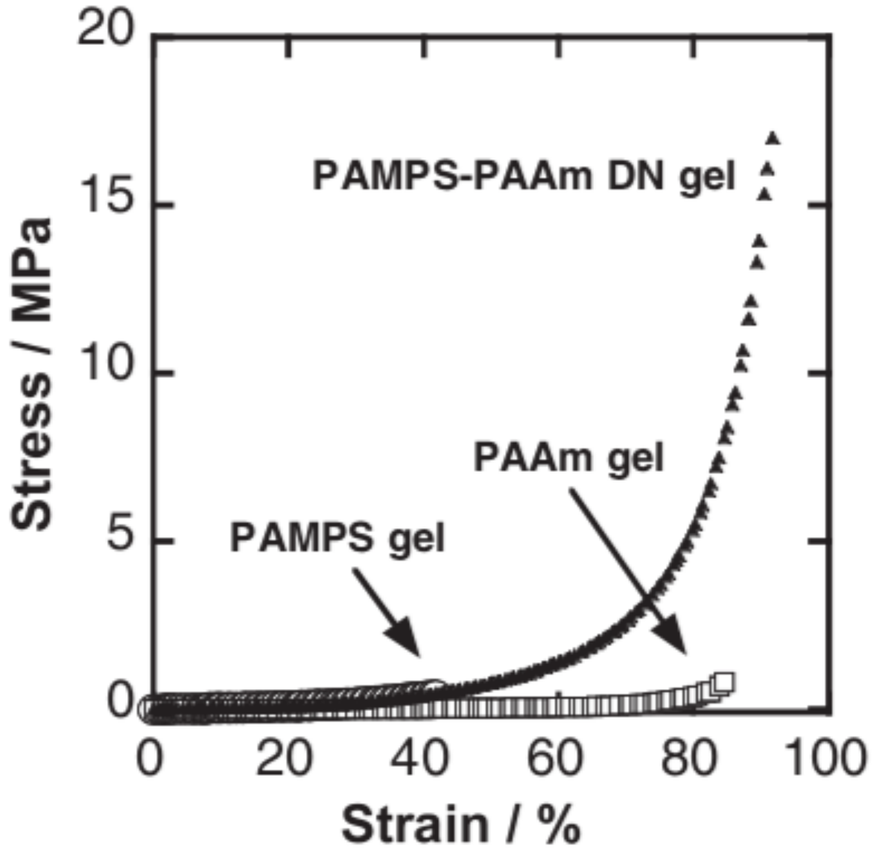
Gel	Method	PEG M_n (g/mol)	Gel fraction[a]	Swelling degree[b]	Max. true stress (kPa)	Extension to break
5a	Click	3400	0.89	800	680	400%
5b	Click	6000	0.930	1050	1380	1000%
5c	Click	8000	0.950	1050	1660	1250%
5d	Click	10000	0.965	1100	2390	1550%
6a	Photochemical	3400	0.91	600	160	50%
6b	Photochemical	14000	0.89	900	70	150%

[a] Gel fraction = (mass dried gel)/(mass polymer precursors). [b] Swelling degree = (mass swollen gel − mass dried gel)/(mass dried gel) × 100%.

Sakai et al. *Macromolecules* **2008**, *41*, 5379.
Matsunaga et al. *Macromolecules* **2009**, *42*, 1344.
Malkoch et al. *Chem. Comm.* **2006**, 2774.

Combining elastic and dissipative hydrogels





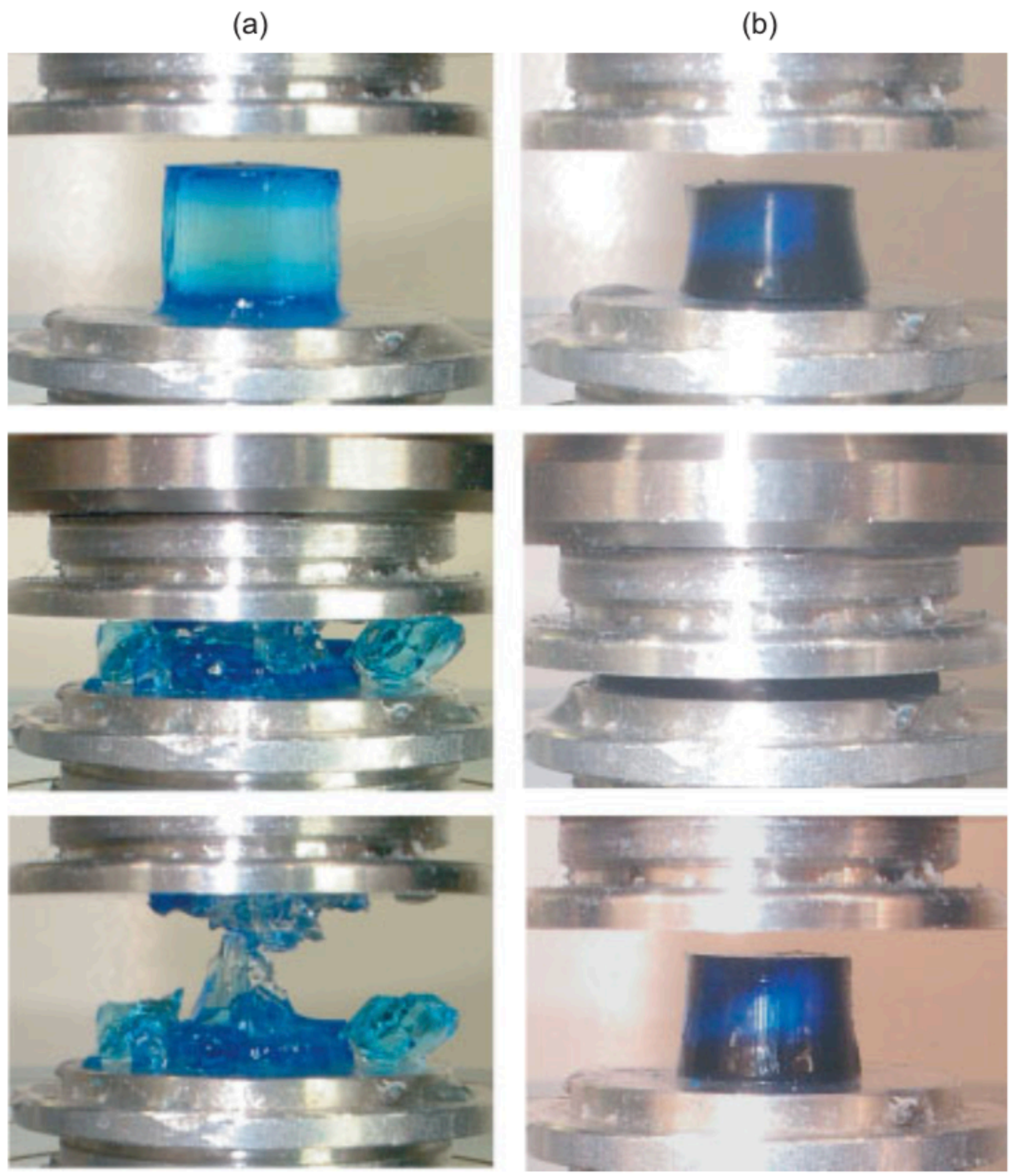
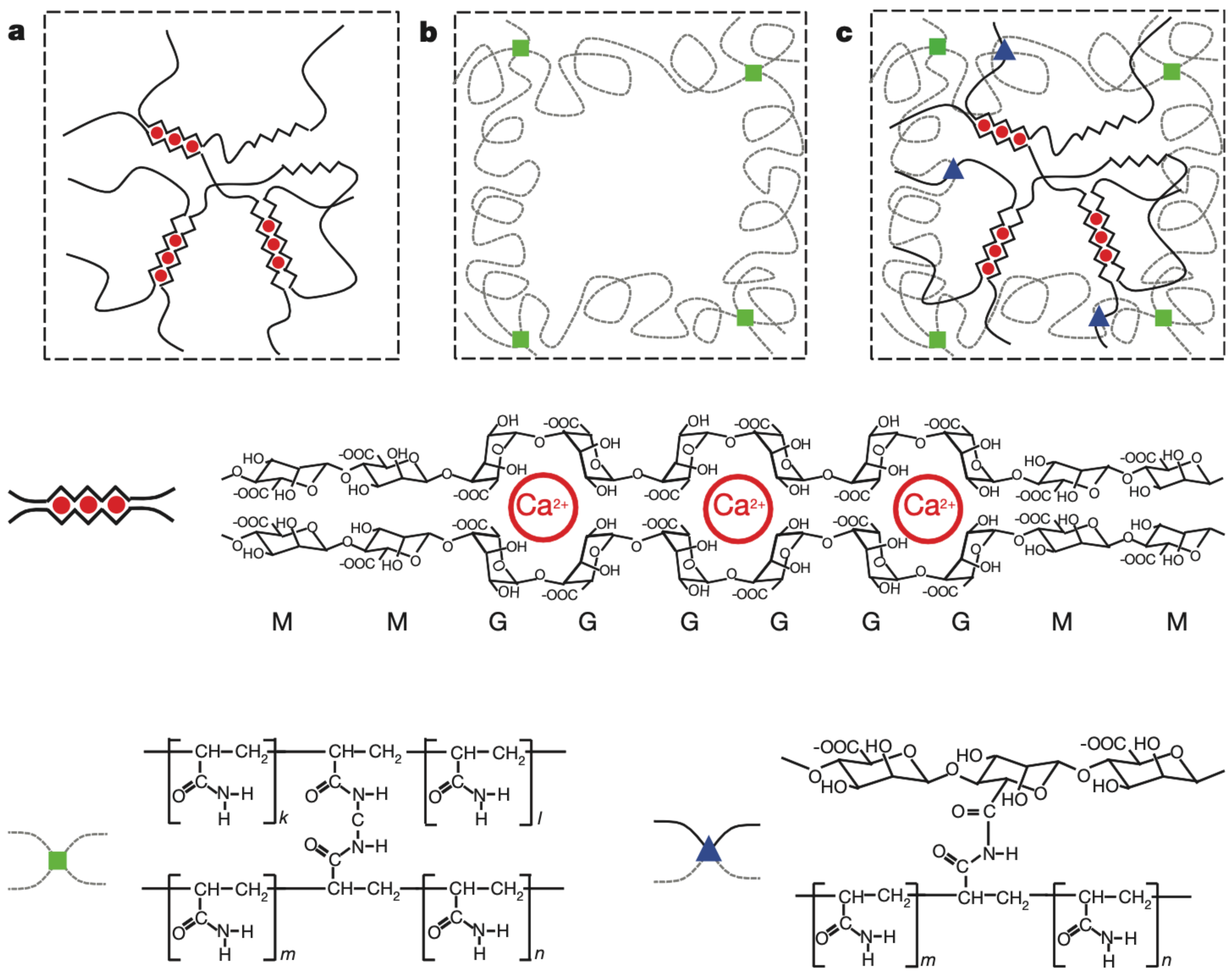


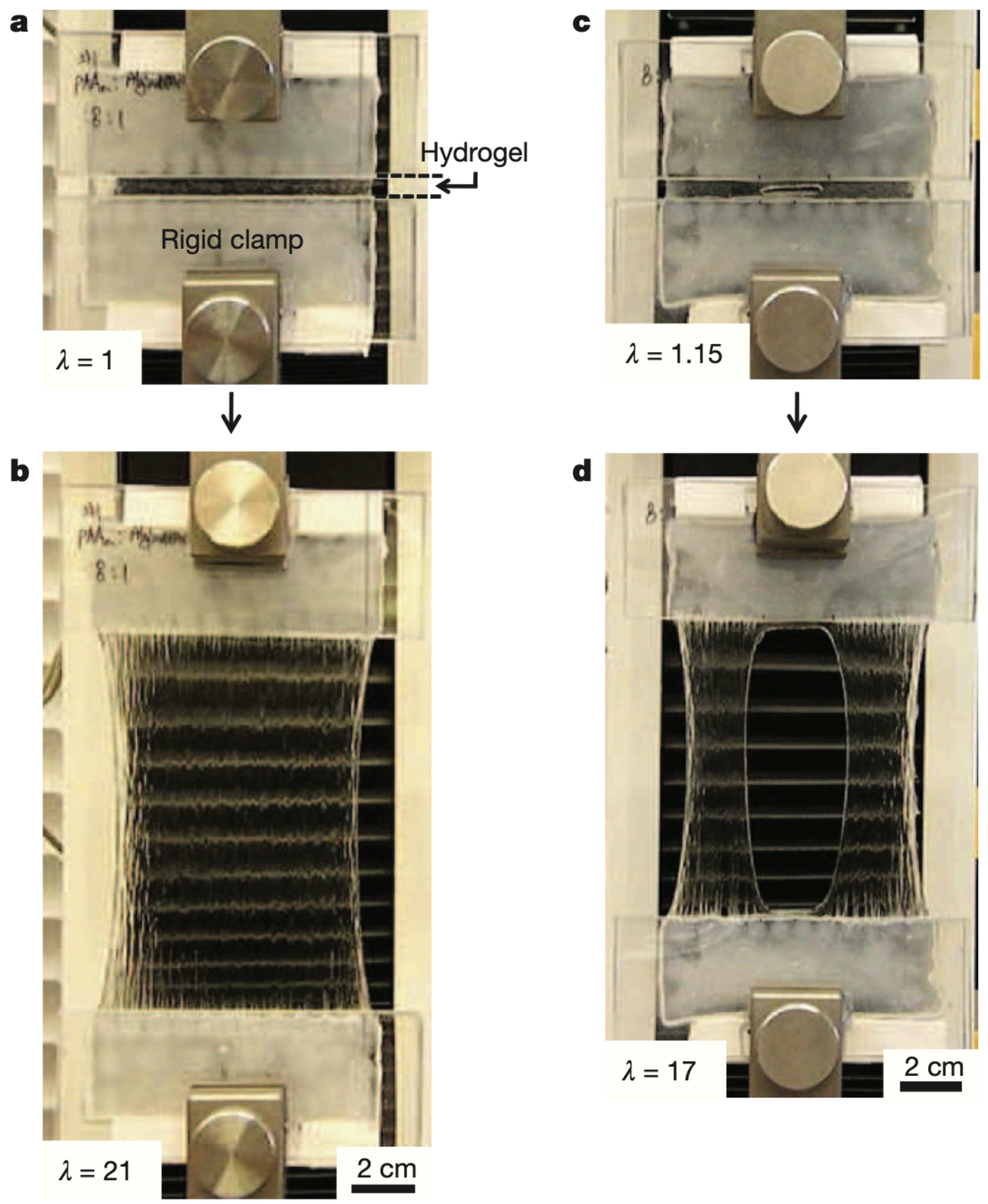
Fig. 3. Photographs demonstrating how a DN gel sustains a high compression. a) PAMPS-1-4 SN gel, b) PAMPS-1-4/PAAm-2-0.1 DN gel. Fracture stress: PAMPS SN gel, 0.4 MPa, PAMPS/PAAm DN gel, 17.2 MPa.

Simple principles can be applied to hydrogels - creating double network gels with an elastic network and a dissipative network to increase material toughness in soft water-swollen networks.

Gong *Science* **2014**, *344*, 161.
Gong et al. *Adv. Mater.* **2003**, *15*, 1155.

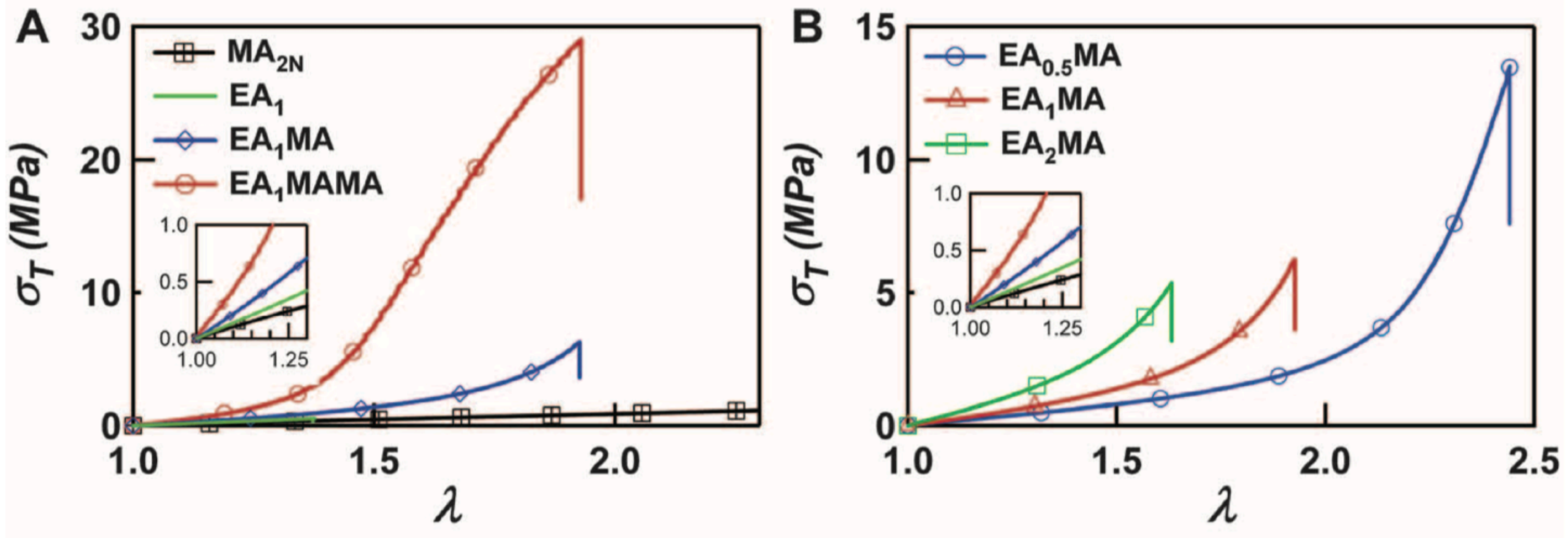
Tough double network hydrogels





Sun et al. *Nature* **2012**, *489*, 133.

Toughening by combining elastic and dissipative networks



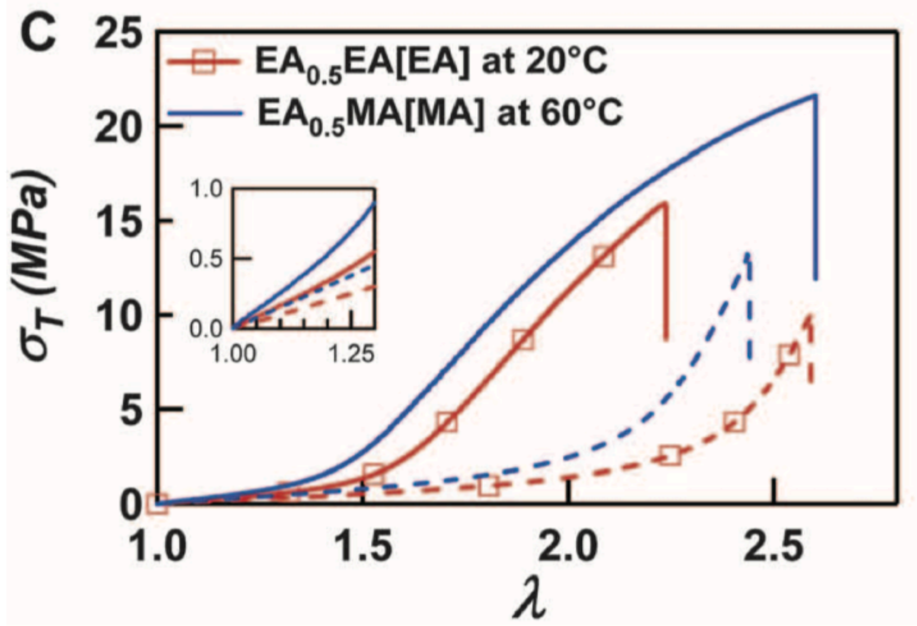
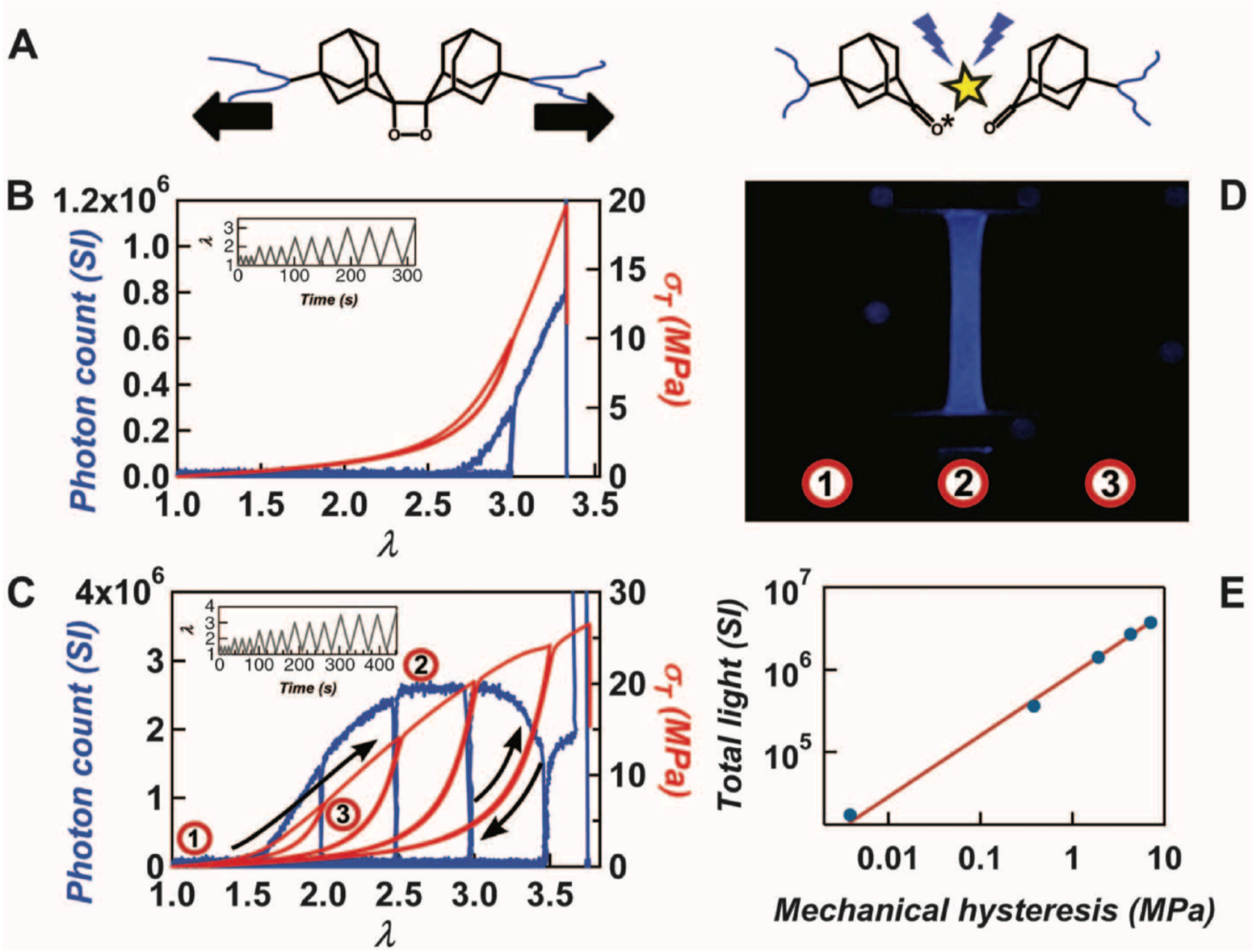


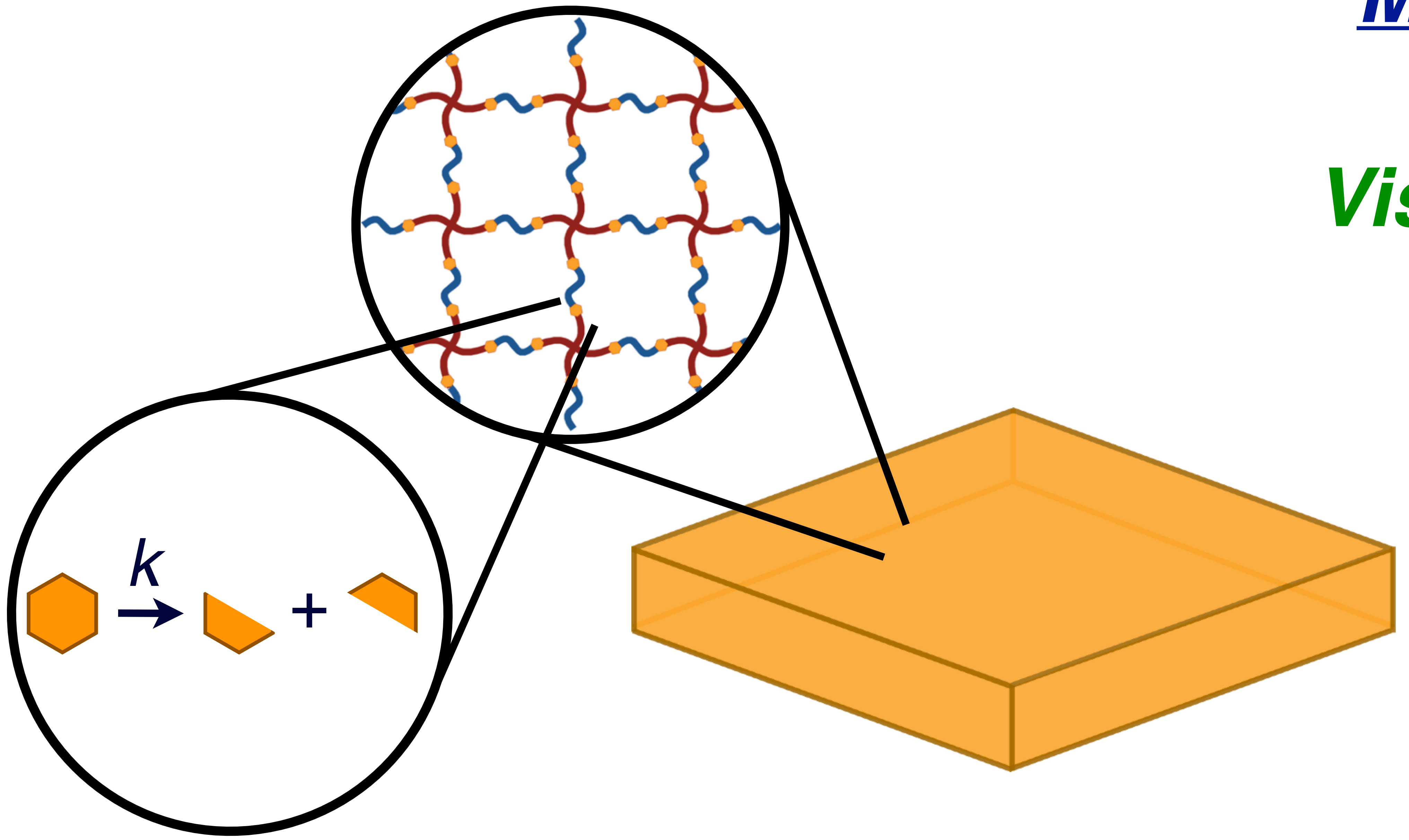
Fig. 1. Mechanical behavior of tough elastomers in uniaxial tension. (**A**) True stress/stretch curves of the EA_1, EA_1MA, EA_1MAMA, and PMA second network alone at 60°C. (**B**) Effect of changing the level of cross-linker in the EA first network on the EA_xMA DN. (**C**) Comparisons between $EA_{0.5}MA[MA]$ and $EA_{0.5}EA[EA]$ at equivalent $T - T_g$. Solid lines represent the TN, and dashed lines represent the DN.



Intelligent design of dissipation in elastomers can significantly increase network toughness.

Ducrot et al. *Science* **2014**, *344*, 186.

Macroscale properties are controlled by molecular details



Macroscale Properties

Viscoelasticity

Diffusivity

Surface chemistry

Swelling

Degradation

Macromolecular details inform material properties and provide a tunable handle in their design.