Nanoparticle solutions as adhesives for gels and biological tissues

Séverine Rose[1], Alexandre Prevoteau[2], Paul Elzière[1], Dominique Hourdet[1], Alba Marcellan[1,2] & Ludwik Leibler[2]

1. Physico-chimie des Polymères et Milieux Dispersés (UMR7615 UPMC/ESPCI/CNRS), Université Pierre et Marie Curie, École Supérieure de Physique et de Chimie industrielles, 75005 Paris, France
2. Matière Molle et Chimie (UMR 7167 CNRS/ESPCI), École Supérieure de Physique et de Chimie Industrielles, 75005 Paris, France

***Nature*, 2013, 505, pp 382–385 (DOI:10.1038/nature12806)**

(16 January 2014)

nature International weekly journal of science

Introduction

- **Adhesives**

  Polymers- ensure good contact between surfaces by covering surface roughness, retard fracture of joints by dissipating energy under stress etc.

- **Gluing two polymers?**

  Difficult - needs chemical reactions, heating, pH changes, UV irradiation, electric field etc..

- **Other options**

  -Supramolecular links - self adhesive / self healing gels

  - Clay particles in polymer solutions

  Cannot meet all demands of gluing in assembly

  -At present gluing gels/ biological tissues requires complex methods – *in situ* polymerization, electrophoretic transport of polymers to the interface etc.

In this paper

• Strong, rapid adhesion between two hydrogels can be achieved at room temperature by spreading a droplet of a NP solution on one gel's surface and then bringing the other gel into contact with it.

•The method relies on the NPs' ability to adsorb onto polymer gels and to act as connectors between polymer chains, and on the ability of polymer chains to reorganize and dissipate energy under stress when adsorbed onto NPs.

•A rapid, simple and efficient way to assemble gels or tissues - desirable for many emerging technological and medical applications such as microfluidics, actuation, tissue engineering and surgery.

Self-Healing and Thermoreversible Rubber from Supramolecular Assembly

Nature, 2008, 451, 977-980

Design and synthesis of molecules that associate together to form both chains and cross-links via hydrogen bonds. Covalent cross-links or strong physical associations prevent flow and creep

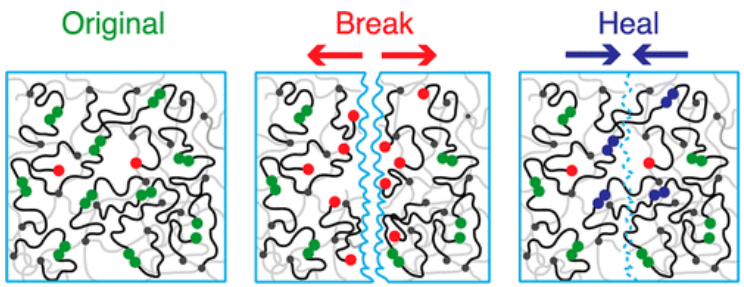
Versatile One-Pot Synthesis of Supramolecular Plastics and Self-Healing Rubbers

J. Am. Chem. Soc., 2009, 131, pp 7966–7967

A strategy to obtain through a facile one-pot synthesis a large variety of supramolecular materials that can behave as differently as associating low-viscosity liquids, semicrystalline or amorphous thermoplastics, viscoelastic melts or rubbers.

Self-Healing of Unentangled Polymer Networks with Reversible Bonds

Macromolecules, 2013, 46, pp 7525–7541

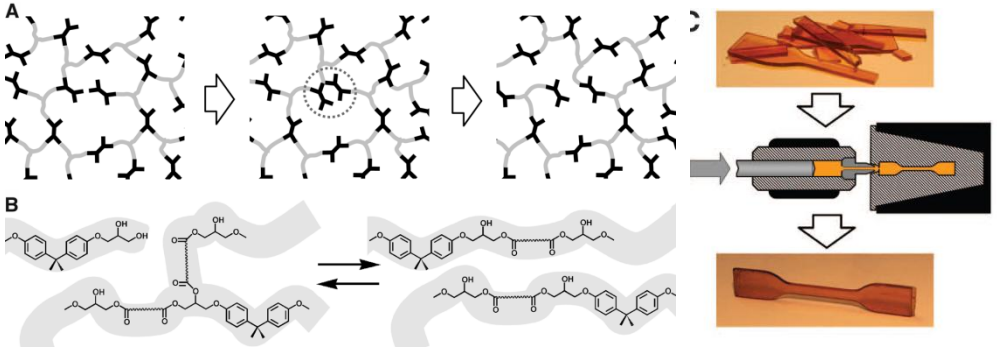


Ludwik Leibler

Silica-Like Malleable Materials from Permanent Organic Networks

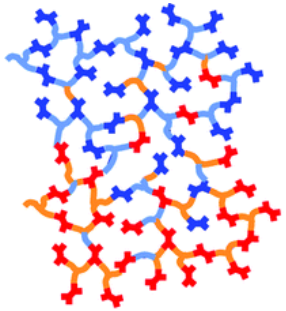
Science, 2011, 334, pp. 965-968

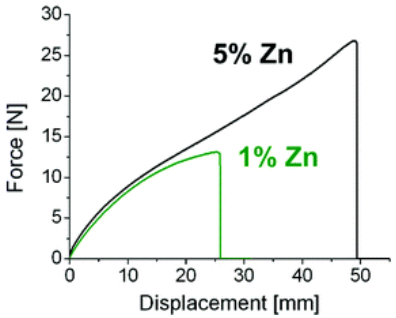
A thermoset-like material was designed that could be processed repeatedly at elevated temperatures and could even be ground up and recycled into a new shape while retaining the mechanical properties of the original material



Metal-Catalyzed Transesterification for Healing and Assembling of Thermosets

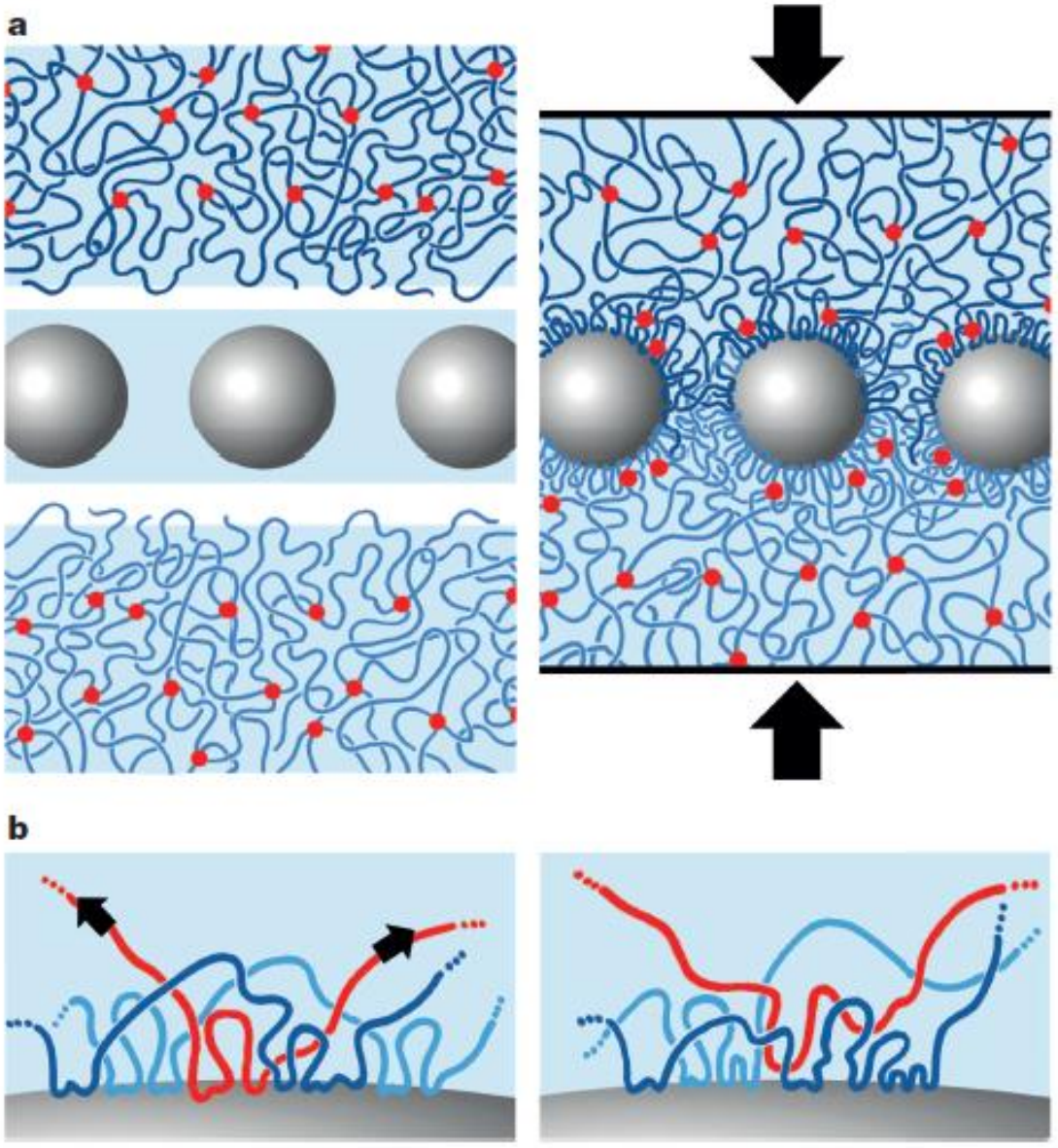
J. Am. Chem. Soc., 2012, 134, pp 7664–7667





Catalytic control of bond exchange reactions enables healing of cross-linked polymer materials under a wide range of conditions.

Gluing gels by nanoparticle solutions

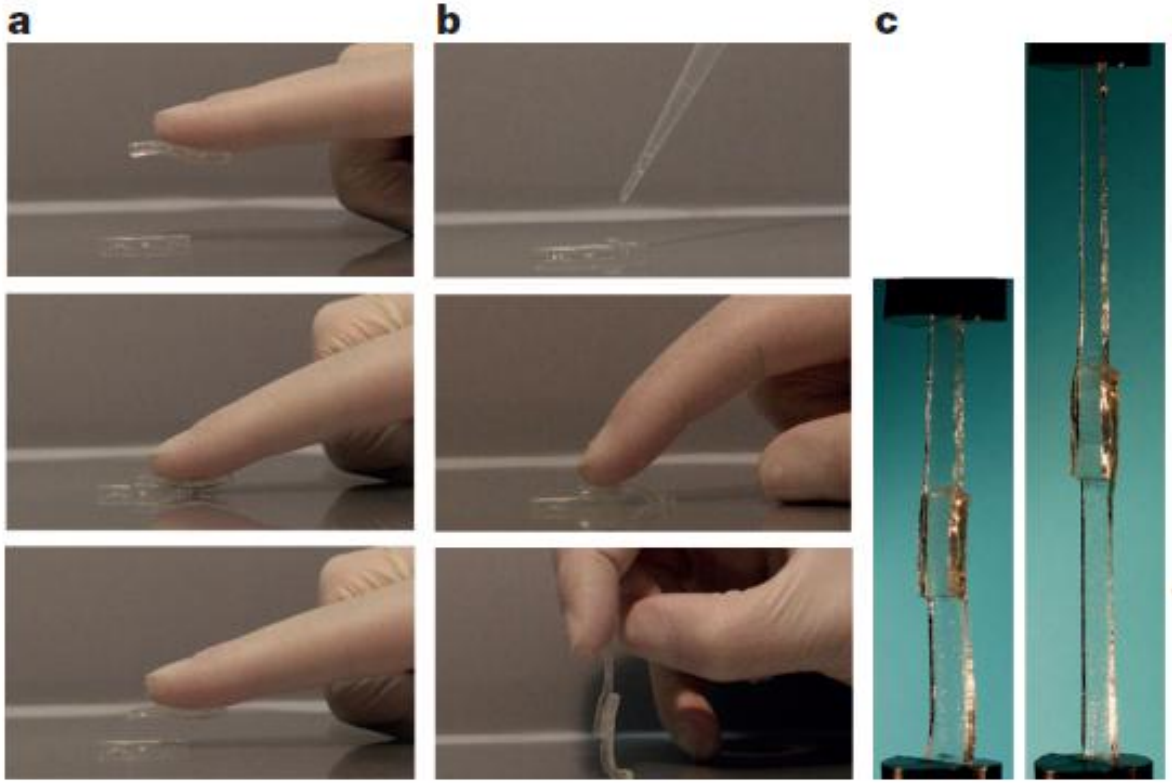


(a) Schematic illustration of the concept of gluing swollen polymer networks together using particles. The nanoparticle diameter is comparable with the gel network mesh size. Network chains are adsorbed on nanoparticles and anchor particles to gel pieces. Particles act as connectors between gel surfaces. Adsorbed chains also form bridges between particles. The black arrows indicate the pressure applied to squeeze the gel layers together.

(b) Particle adsorption is irreversible because particles are anchored to the gel networks by numerous attachments (red, light- and dark-blue strands). At equilibrium or under tension (indicated by black arrows) a monomer that detaches from a particle surface (red strand) can be replaced by a monomer belonging to the same or a different network strand (shown here as a dark-blue strand). Such exchange processes and rearrangements allow for large deformations and energy dissipation under stress.

Importance of gel chain adsorption onto NPs

Two hydrogels were synthesized –
S0.1 made of poly(dimethylacrylamide) (PDMA) and **A0.1** made of polyacrylamide (PAM).



(a) Lightly crosslinked S0.1 gels stick to the table surface and to gloves but they do not stick to themselves.

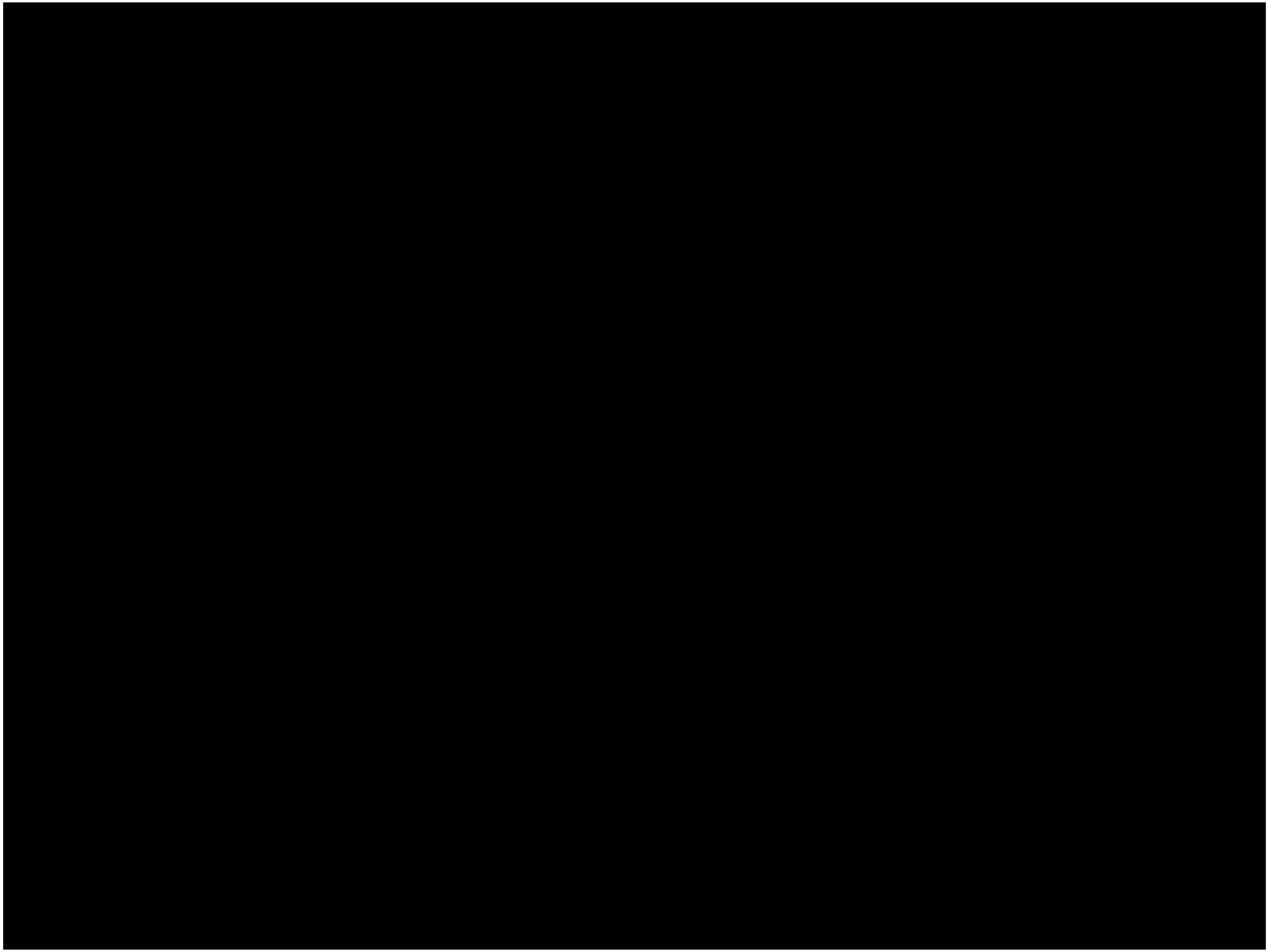
(b) By spreading a drop of TM-50 silica solution on the gel surface, two gel pieces are glued together after being brought into contact for few seconds.

(c) Used lap joint is able to sustain large deformations.

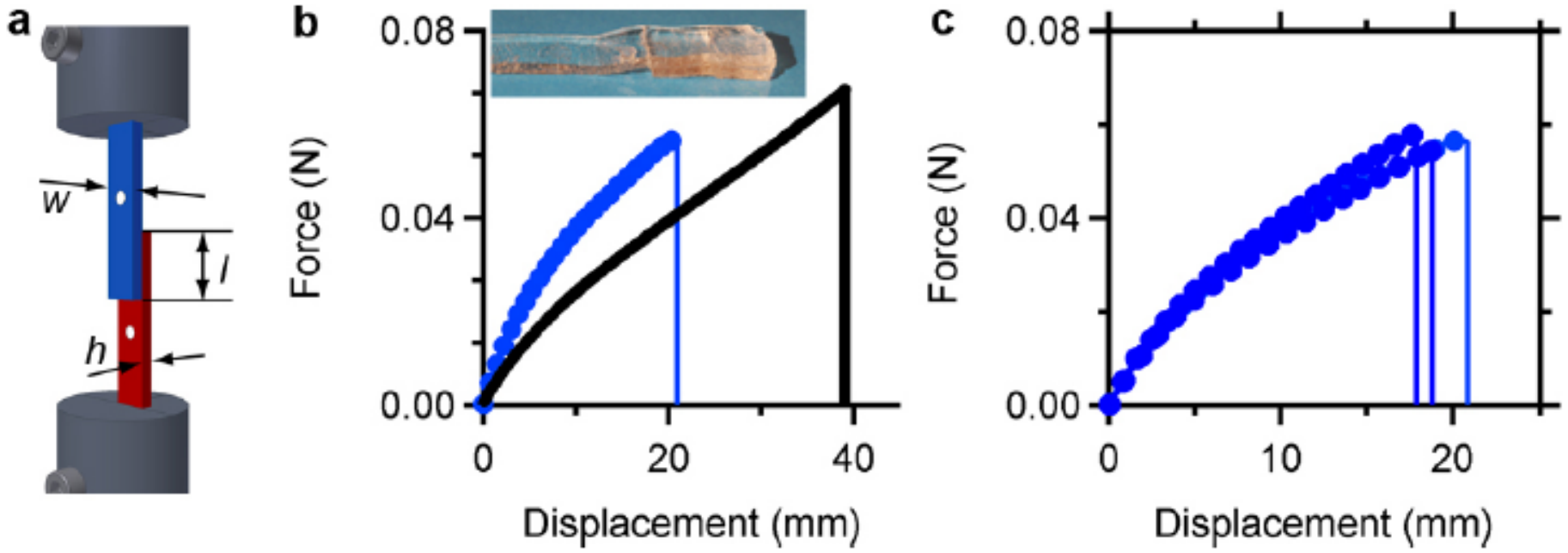
• Both gels have the same crosslinking density and similar swelling degree and do not adhere to themselves **(a)**.

•PAM does not adsorb onto silica whereas PDMA adsorbs readily. When a 15 µL drop of TM-50 silica suspension was spread on the PDMA gel surface and another PDMA piece was pressed to form a lap junction, a strong adhesion was observed after a few seconds of contact **(b, c)**.

Video 1: Lap-shear test of adhesion for a PDMA S0.1 hydrogel assembly glued with TM-50 silica solution



Lap-shear and tensile tests of PDMA S0.1 gels

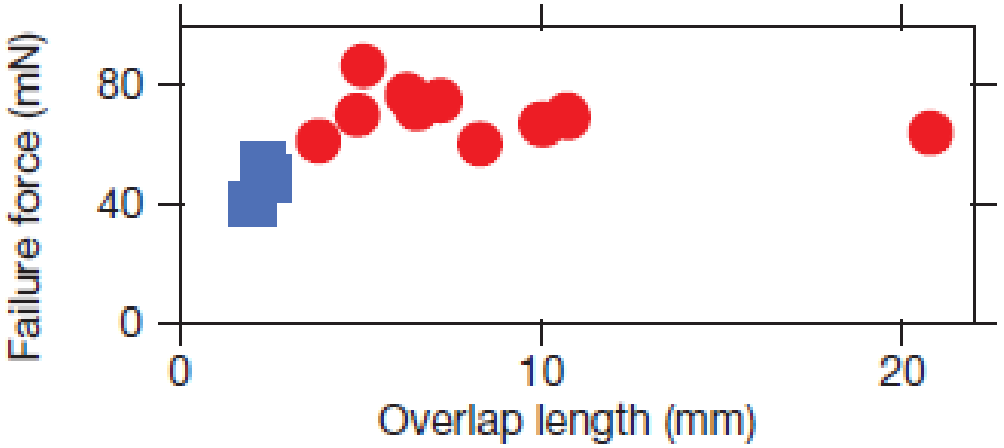


(a) Lap-joint geometry. Displacement was measured by a video extensometer that followed two markers (white dots), which were placed at a distance of 5mm from the edge of the lap joint. The total length of the assembled ribbons was 40mm. w denotes the width and h the thickness of gel ribbons. l is the overlap length.

(b) Comparison of force–displacement curves for PDMA S0.1 ribbon (black line) and for the lap joint glued by spreading 15 ml of TM-50 silica solution (blue circles).
Displacement was measured by optical extensometer from two markers, initially spaced by 20mm and centred on the joint. The PDMA S0.1/S0.1 assemblies broke outside the joint (inset).

(c) Lap-shear adhesion test reproducibility.
Force–displacement curves of PDMA S0.1/S0.1 lap joint illustrating lap-shear test reproducibility. All gel ribbons were cut from the same plate. Bulk failure outside the joint was systematically observed.

Effect of overlap length of lap joints

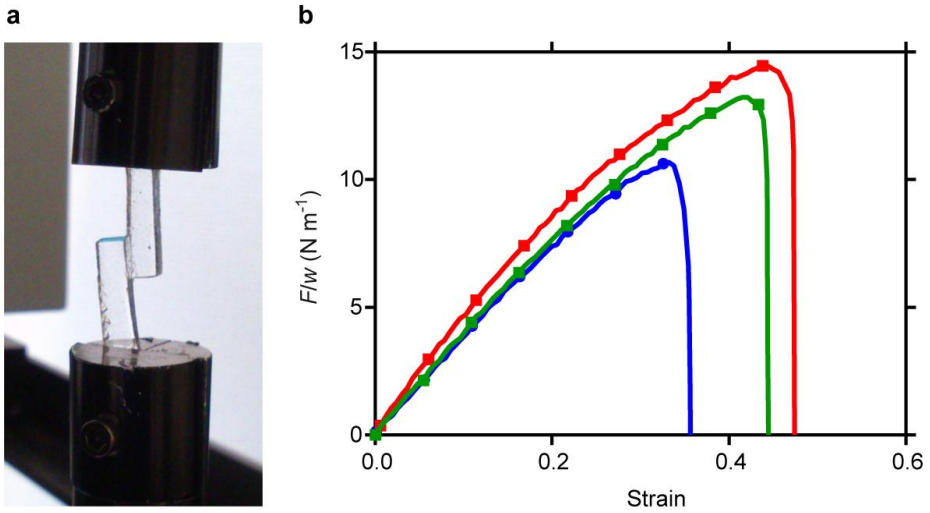


The failure force measured by the lap-shear adhesion test for lap joints of various overlap length. Red circles indicate fracture outside the joint; blue squares indicate interfacial failure by peeling.

- Joints made of S0.1 gel were stronger than the gel itself and failure occurred outside the bonding junction.

- Only when the overlap length was made comparable to the ribbon thickness did interfacial failure by peeling occur .

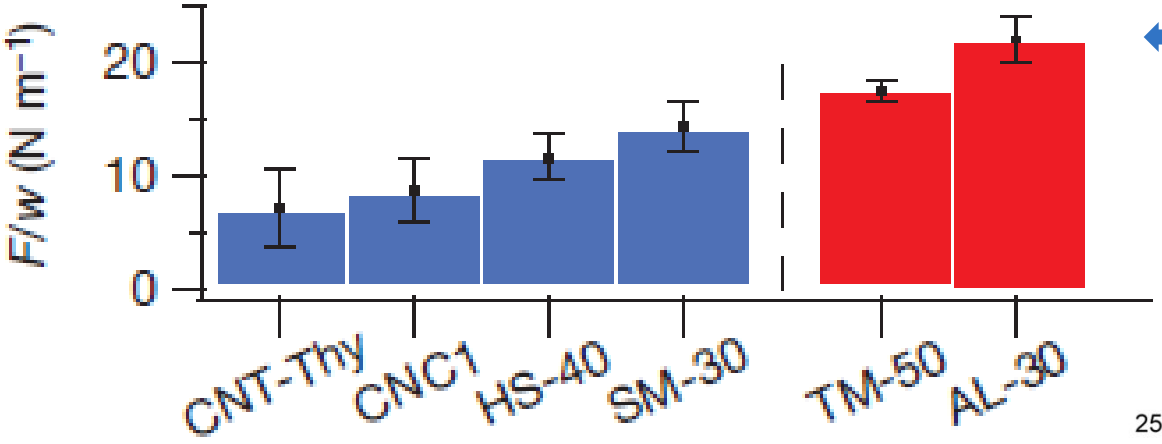
Measurement of adhesion energy of PDMA S0.1 gels



(a) Lap-shear test geometry in which interfacial failure by peeling was observed for S0.1 gel ribbons glued by spreading 6 μL of TM-50 silica solution(l = 5mm, w = 2mm and h = 5mm).

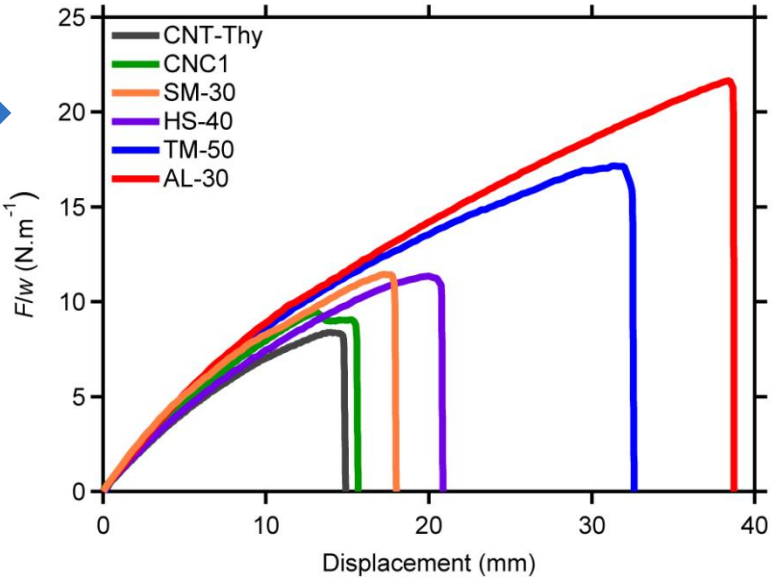
(b) Force–displacement curves for PDMA S0.1/S0.1 lap joints. Adhesive failure by interfacial peeling was observed. All gel ribbons were cut from the same gel plate and the tensile modulus was measured to be E is ~8.1 ± 1.0 kPa. From the measured failure force, the adhesion energy can be estimated to be 6.2 ± 1.4 Jm^{-2}.

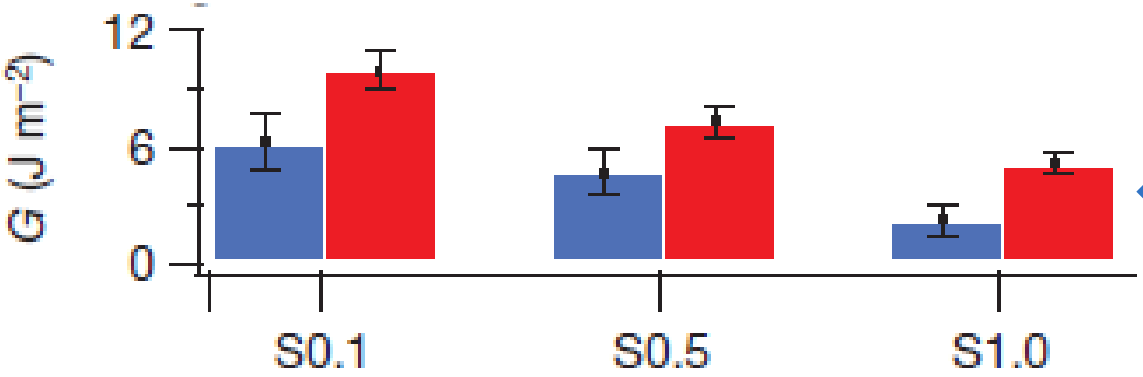
Adhesion strength dependence on particle size, surface chemistry & gel properties



Failure force, F, normalized by the width of the joint, w, for lap joints glued using solutions of various particles.
Red bars indicate fracture outside the joint; blue bars indicate failure by peeling.

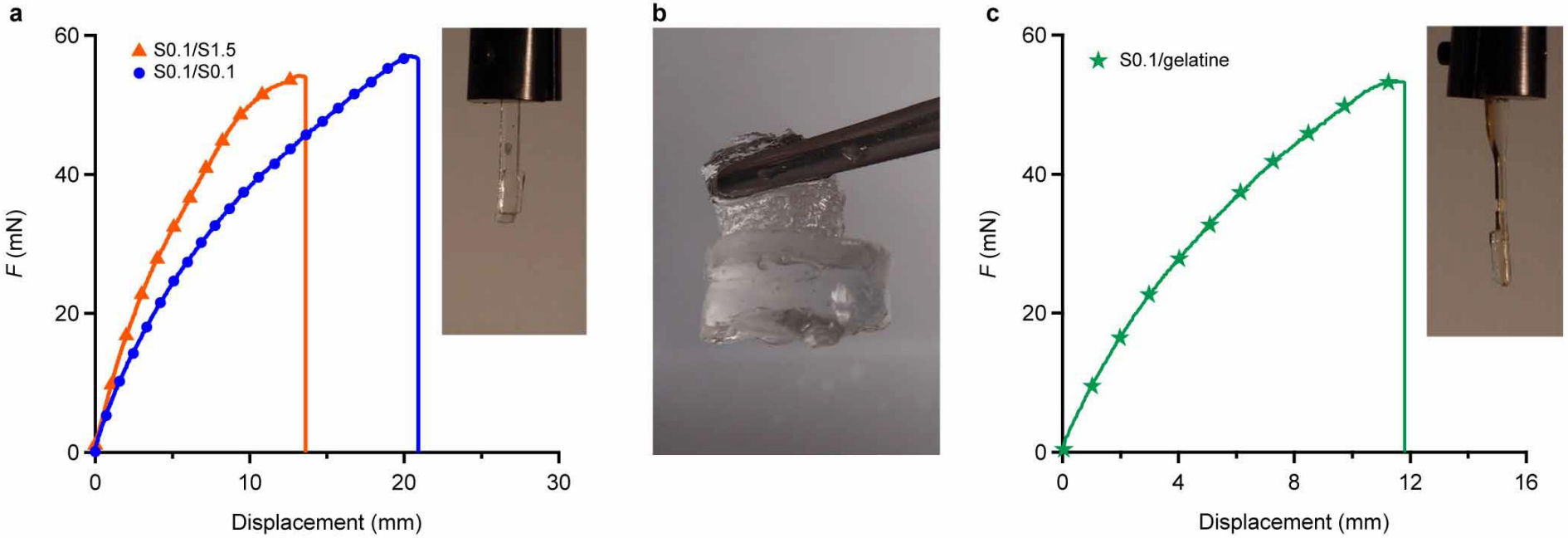
Lap-shear test of PDMA S0.1 gels glued by various particle solutions. In order of increasing deformation at the breaking point are shown the adhesive failure by interfacial peeling in CNT-Thy, CNC1, SM-30 and HS-40. Fracture outside the junction occurred for TM-50 and AL-30.





Adhesion energy G_{adh} (in blue) measured by the lap-shear test and fracture energy G_c (in red) measured by the single-edge notch tensile test for PDMA gels of various crosslinking densities.

Gluing gels of different stiffness or chemical nature



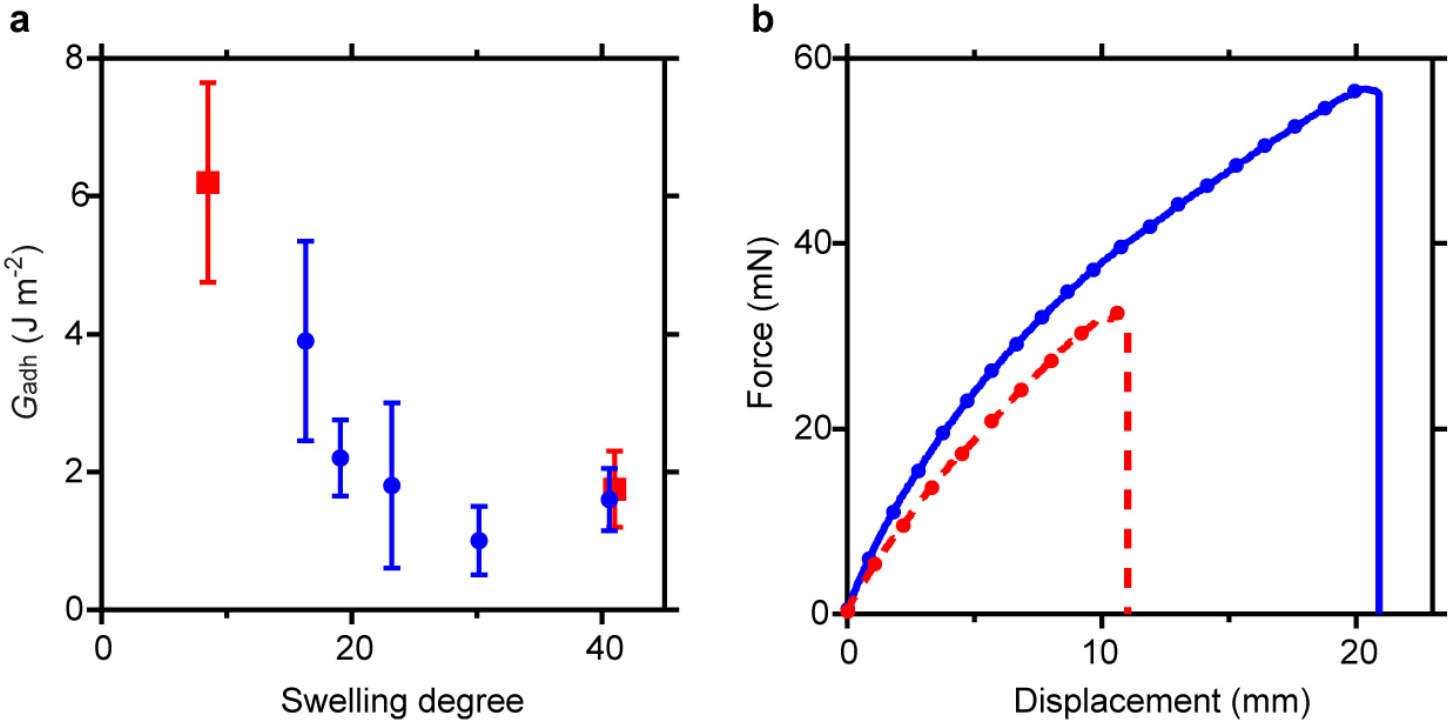
(a) Force–displacement curve for an assembly made of soft PDMA S0.1 and rigid PDMA S1.5 (red triangles) gels glued by TM-50 solution. For comparison the results obtained under identical conditions for the symmetric PDMA S0.1/S0.1 assembly are plotted (blue circles).
Lap-joint dimensions were l=10mm, w=5mm and h=2mm. 15µL of TM-50 solution was spread to make the junction.

(b) Glued at their preparation state, both PDMA S0.1 and PDMA S1.5 gels initially had the same size (diameter of about 10mm). The picture shows gels after 5 h of swelling in deionized water. The highly crosslinked PDMA S1.5 gel (top piece) is less swollen than the PDMA S0.1 gel (bottom piece).

(c) Lap-shear force–displacement trace for the gelatine and S0.1 PDMA gel assembly (green stars) glued by spreading TM-50 silica solution.
The failure occurred outside the lap joint and the fatal crack propagated in tension mode.

Gluing overswollen gels and overswelling glued gels

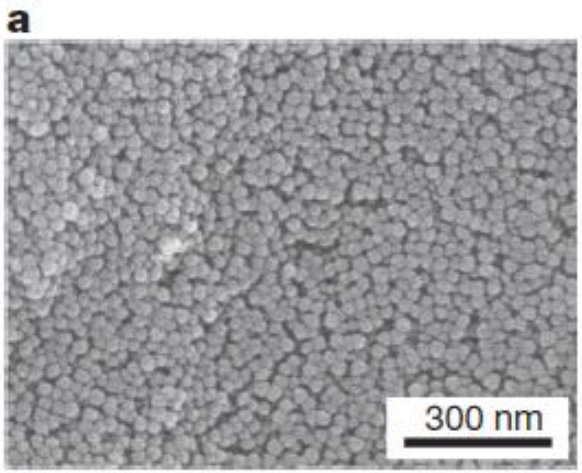
By choosing particles (AL-30) of the ideal size and gel affinity, completely swollen S0.1 gels containing as much as 97.6 v/v% of water was also achieved.

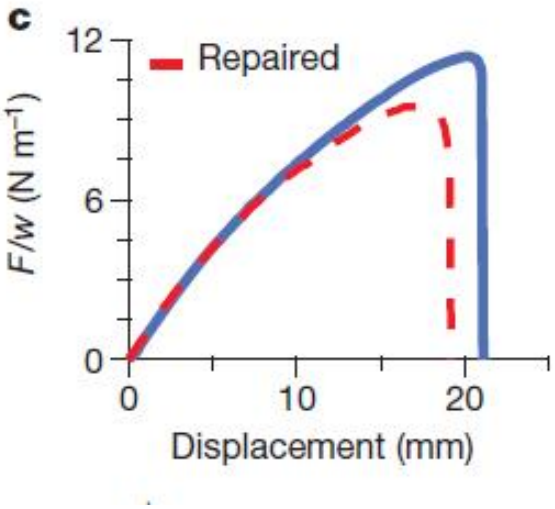


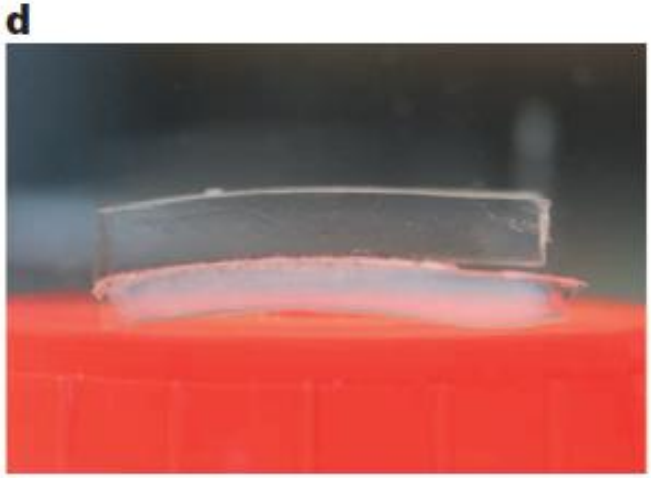
(a) Adhesion energy of joints made of PDMA S0.1 hydrogels swollen before being glued with AL-30 silica solutions to various degrees of swelling Q (in blue) and adhesion energy of joints made of S0.1 hydrogels glued withTM-50 silica solutions at as-synthesized swelling degree (Q_0<8.5) and after being immersed in water and swollen to reach the maximum, equilibrium swelling degree,Q_e<41 (in red). When S0.1 gels were glued with AL-30 particles at the as-synthesized state, bulk failure systematically occurred outside the junction even when the joints were very short, narrow and thick. To induce peeling (interfacial failure) making cuts at the interface was necessary.

(a) Lap-shear test for PDMA S0.1/S0.1 assembly glued by TM-50 silica at the preparation state, Q_0 (blue circles) and after swelling in water for three days and attaining maximum equilibrium swelling Q_e (red circles).

Water-resistant and self-repairing glue







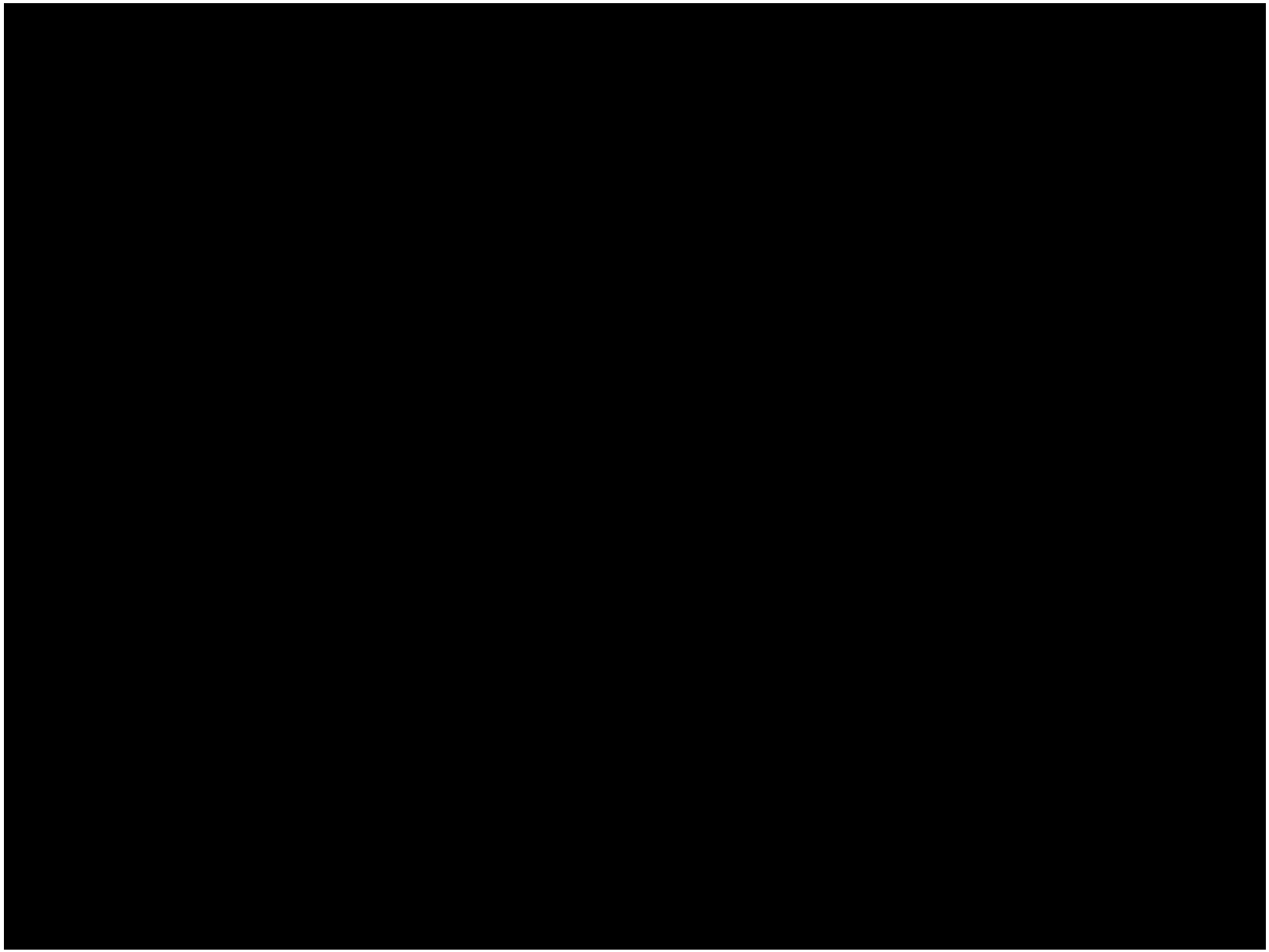
(a) SEM image showing presence of TM-50 silica layer adsorbed on a S0.1 gel surface after multiple washing and soaking of the gel in water for several days.

(b) After reaching the maximum swelling and being immersed in deionized water for four weeks, the PDMA S0.1/S0.1 assembly glued together usingTM-50 silica held well.

(c) Lap-shear test showing that after adhesive interfacial failure by peeling (blue line), the S0.1/S0.1 joint glued using HS-40 silica solution was repaired by bringing ribbons back into contact with finger pressure for about 30 s (red line).

(d) Gelatine/PDMA S0.1 junction glued with TM-50 silica after immersion in water for one week to reach maximum equilibrium swelling.

Video 2: Lap-shear test of adhesion for a PDMA S0.1 hydrogel swollen in water to maximum swelling degree Q_e

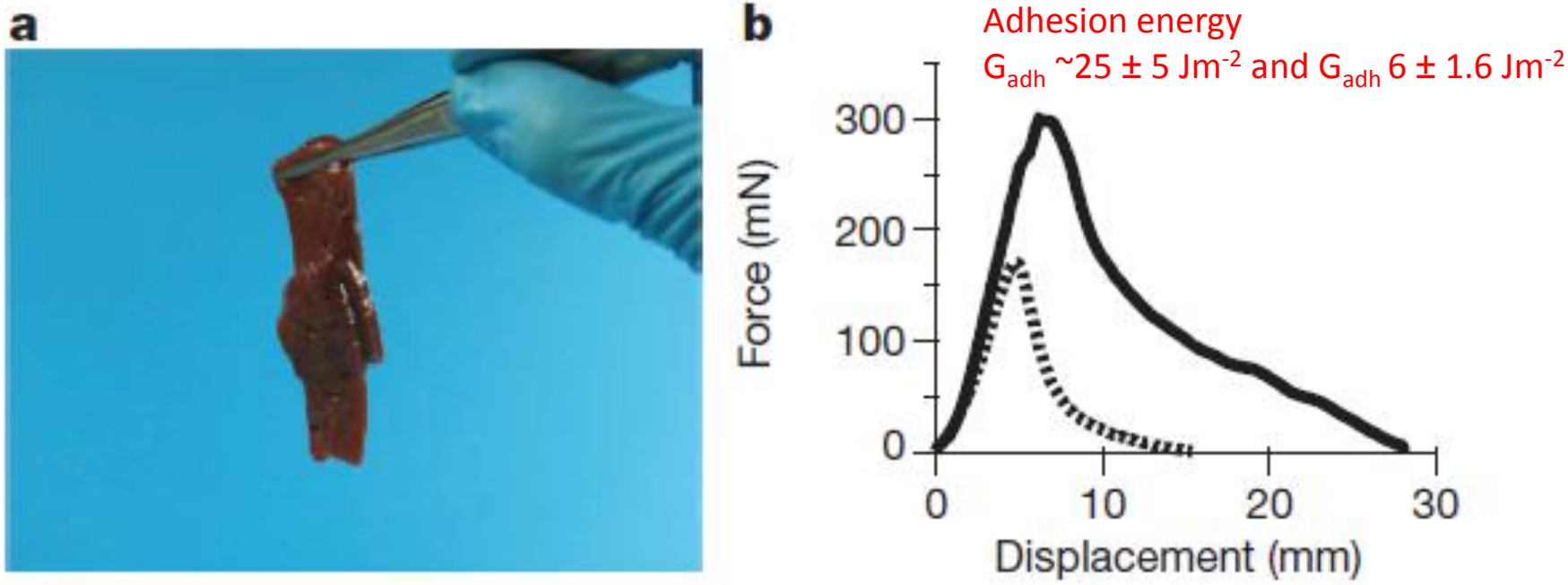


Gluing biological tissues

•Soft biological tissues, although more complex, both mechanically and osmotically, resemble gels in many respects.

•To test the gluing potential of NP solutions we cut two ribbons 45mm*18mm*3mm of calf liver. Cut pieces do not adhere to each other and cannot be glued by water at pH9.

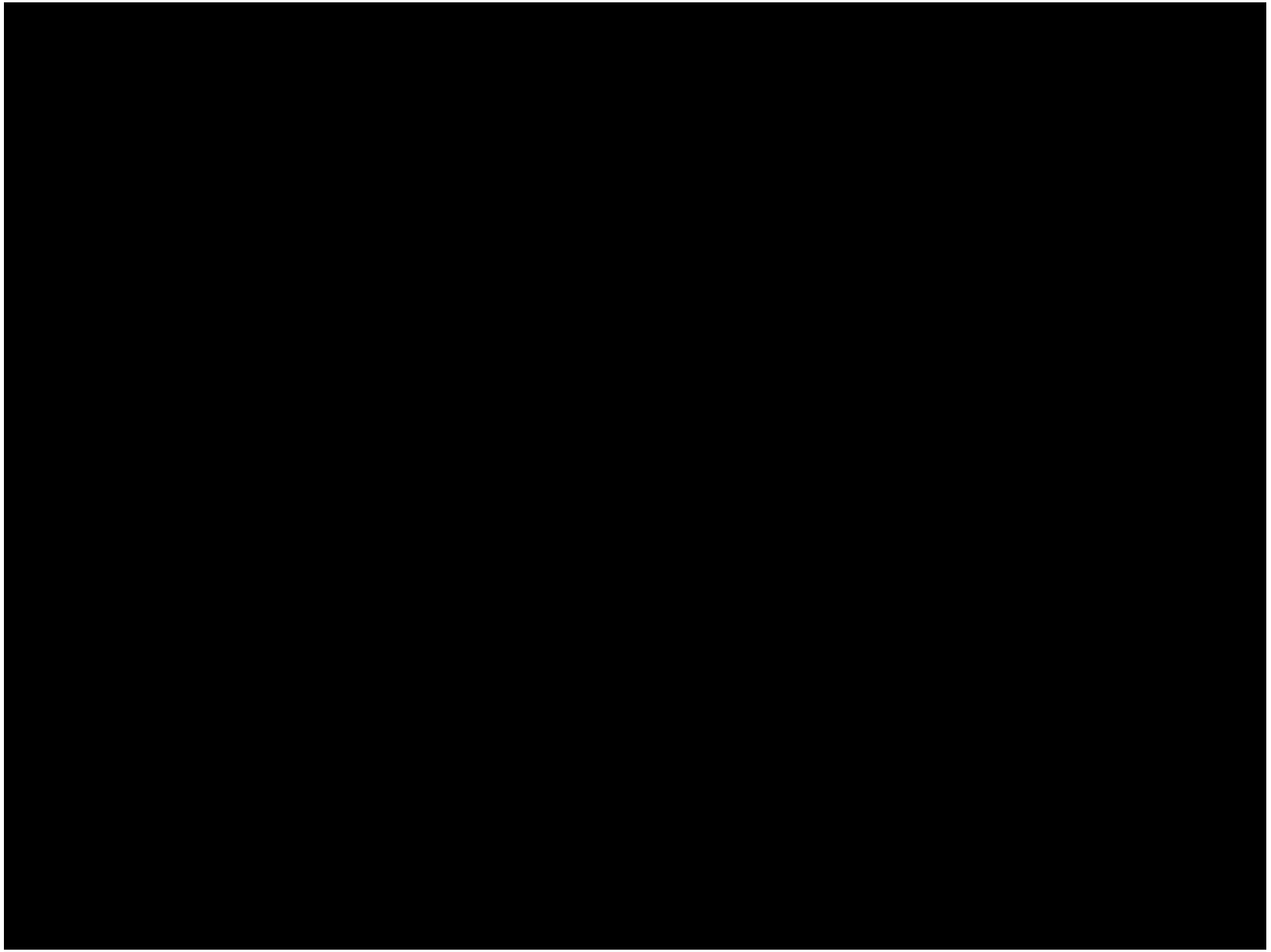
• 60 µL of silica TM-50 solution was spread on the cut surface (without any pre-treatment or special drying) to make a lap joint with overlap length l=20 mm.



(a) Two pieces cut from calf liver were glued together by spreading TM-50 nanosilica solution between them and then pressing them with a finger. After 30 s of contact the assembly was manipulable and the bond held well.

(b) Normalized force–displacement curves for lap joints made of ribbons cut from calf liver and glued by spreading TM-50 silica solution between them and then pressing ribbons with a finger for 30 s. The ribbons were cut with a scalpel blade and no treatment was applied to liver surfaces before gluing. Results for two livers are presented.

Video 3: Lap-shear test of adhesion of calf liver ribbons glued with TM-50 silica solution



Summary

• The results suggest that nanoparticle solutions provide a simple way of assembling synthetic and biological hydrogels as well as biological tissues without affecting substantially the rigidity or permeability of the assembly.

• Powerful methods exist to tune and control the surface chemistry of inorganic particles and latexes to achieve optimal particle adsorption and bonding.

• The possibility of self-repairing and re-positioning peeled adhesive joints is an additional boon.

• Given the importance of wet adhesion in biomedicine and biotechnology as well as in more traditional coating and material technologies, these results suggest ways to develop new applications by simply assembling many kinds of chemically and mechanically mismatched tissues and gels.

Thanks