

Self-healing and thermoreversible rubber from supramolecular assembly

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Rubbers exhibit enormous extensibility up to several hundred per cent, compared with a few per cent for ordinary solids, and have the ability to recover their original shape and dimensions on release of stress^{1,2}. Rubber elasticity is a property of macromolecules that are either covalently cross-linked^{1,2} or connected in a network by physical associations such as small glassy or crystalline domains^{3–5}, ionic aggregates⁶ or multiple hydrogen bonds^{7–16}. Covalent cross-links or strong physical associations prevent flow and creep. Here we design and synthesize molecules that associate together to form both chains and cross-links via hydrogen bonds. The system shows recoverable extensibility up to several hundred per cent and little creep under load. In striking contrast to conventional cross-linked or thermoreversible rubbers made of macromolecules, these systems, when broken or cut, can be simply repaired by bringing together fractured surfaces to self-heal at room temperature. Repaired samples recuperate their enormous extensibility. The process of breaking and healing can be repeated many times. These materials can be easily processed, re-used and recycled. Their unique self-repairing properties, the simplicity of their synthesis, their availability from renewable resources and the low cost of raw ingredients (fatty acids and urea) bode well for future applications.

An attractive method of designing small-molecule systems exhibiting rubber-like elasticity is to use the concept of supramolecular polymers¹⁷. Indeed, ditopic molecules—molecules able to directionally associate with two other molecules—can form long-lived chains and show polymer-like behaviour both in solutions⁹ and in bulk^{18–20} (see also ref. 21 and references therein). By mixing ditopic and multitopic molecules—which are able to associate with more than two other molecules—a network could be formed^{10,17} (Fig. 1). Thus far, in bulk, designed small molecules that can form such supramolecular networks flow or partially crystallize and behave like plastic resins or fibres (ref. 21 and references therein, and ref. 22). Rubber-like behaviour has not been reported.

To avoid crystallization while keeping strong directional interaction is a challenge in the route towards supramolecular rubbers from small molecules. We propose the use of mixtures of molecules bearing a variety of strongly associating groups. We rely on the variety of molecular architectures to render crystallization difficult and on both entropy of mixing and directional specific interactions to avoid the macroscopic phase separation of different species. For this purpose, as a starting material we use fatty dimer acids made from natural renewable resources (vegetable oils) available in bulk quantities and various compositions²³. They are liquid at room temperature and in contrast to other classical diacids they do not crystallize, forming glasses instead. The glass transition can be varied by dosing the oil from which fatty diacids are made, and even more interestingly, these starting materials can contain variable amounts of trimer acids. We have thus solved the problem of the synthetic availability of

multitopic molecules. Indeed, our strategy is to use carboxylic-acid ends to attach functional groups able to form multiple hydrogen bonds. Our two-step synthetic pathway (Fig. 2) introduces three types of functional groups able to strongly associate via multiple hydrogen bonds, namely amidoethyl imidazolidone, di(amido ethyl) urea and diamido tetraethyl triurea.

In the first step, acid groups were condensed with a controlled excess of diethylene triamine. In the second step, the obtained product was reacted with urea. The resulting compound, called **A**, resembles a translucent glassy plastic. When heated to 90 °C, well above its glass transition temperature ($T_g = 28$ °C), it behaves like a soft rubber with strain at breaking of about 350% and it completely recovers its dimensions after being deformed to 100% strain (Supplementary Fig. 1). At still higher temperatures, above 160 °C, the material flows like a viscoelastic liquid and can be moulded, extruded and (re)shaped. Compound **A** is soluble in benzyl alcohol and

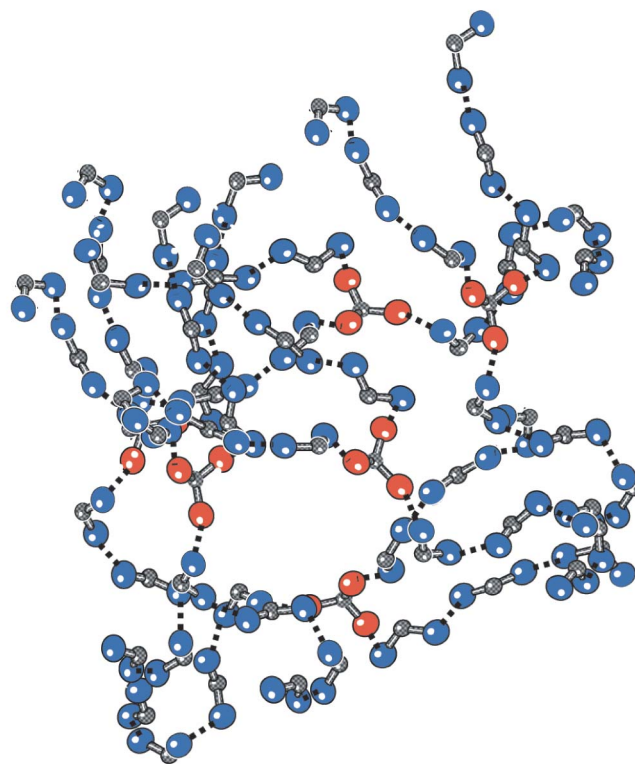


Figure 1 | Supramolecular network. Schematic view of a reversible network formed by mixtures of ditopic (blue) and tritopic (red) molecules associating by directional interactions (represented by dotted lines).

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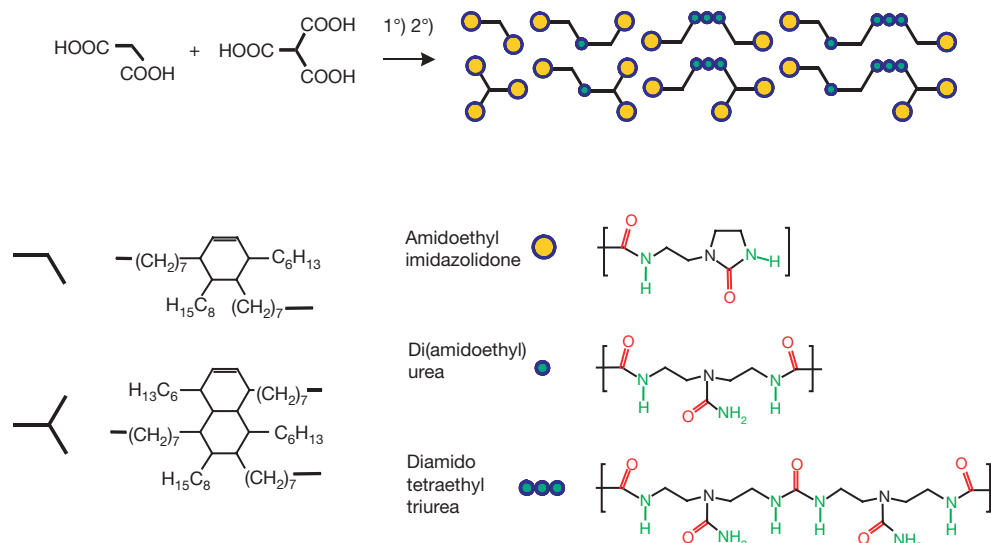


Figure 2 | Synthesis pathway. A mixture of fatty diacid and triacid is condensed first with diethylene triamine and then reacted with urea giving a mixture of oligomers equipped with complementary hydrogen bonding

groups: amidoethyl imidazolidone, di(amidoethyl) urea and diamido tetraethyl triurea. The hydrogen bond acceptors are shown in red, donors in green.

methanol/chloroform mixtures and insoluble in water, with water uptake of ~ 14 weight %. The narrowness and detectable fine structure of nuclear magnetic resonance (NMR) signals (Supplementary Fig. 2) reveal that **A** is made of small molecules: oligomers. This is confirmed by size exclusion chromatography and intrinsic viscosity measurements (Supplementary Fig. 3). Infrared spectroscopy shows the presence of multiple hydrogen bonds between N–H and C=O groups (Supplementary Fig. 4).

To lower the glass transition temperature, we plasticized compound **A** with varying quantities of dodecane. With 11% w/w dodecane, T_g is about 8°C and the resulting compound, called **B**, is a non-tacky rubber-like material. Differential scanning calorimetry and X-ray scattering confirm that the material is not crystalline (Supplementary Fig. 5). A broad scattering event at 0.17 \AA^{-1} indicates a short-range organization with characteristic length of 36 \AA , comparable with the molecular size. The frequency dependence of the oscillatory shear moduli for storage, G' , and loss, G'' , clearly shows the polymer-like behaviour (Fig. 3a). Its behaviour at high frequencies indicates the proximity of the glass transition, whereas

at low frequencies, the elastic rubbery character dominates. At plateau, the storage shear modulus is about $3 \times 10^4\text{ Pa}$ and the relaxation time extrapolated from these data are not less than $3 \times 10^6\text{ s}$ (a few weeks) at 50°C .

The rubber-like properties of this material are confirmed at large deformations. Figure 3b shows stress–strain curves that resemble those of soft rubbers. The strain at break exceeds 500%. After elongation to 300% with a speed of 2.5 mm min^{-1} and release of stress, the residual strain is less than 5%. When the cycle is repeated, the sample recovers completely without any residual strain. Finally, the inset of Fig. 3b shows that during uniaxial deformation the volume of the material is preserved just as for ordinary rubbers.

Figure 3c shows the results of creep experiments performed at 50°C . When a stress of $5 \times 10^3\text{ Pa}$ is applied for $8 \times 10^4\text{ s}$ the strain is about 32% and it increases at a rate of 0.04% per hour. This value is consistent with the relaxation time extrapolated from linear rheology. When the applied stress is released, the sample completely recovers its dimensions; the residual strain is negligible, less than $5 \times 10^{-2}\%$. For a higher load of $2 \times 10^4\text{ Pa}$ applied for as long as

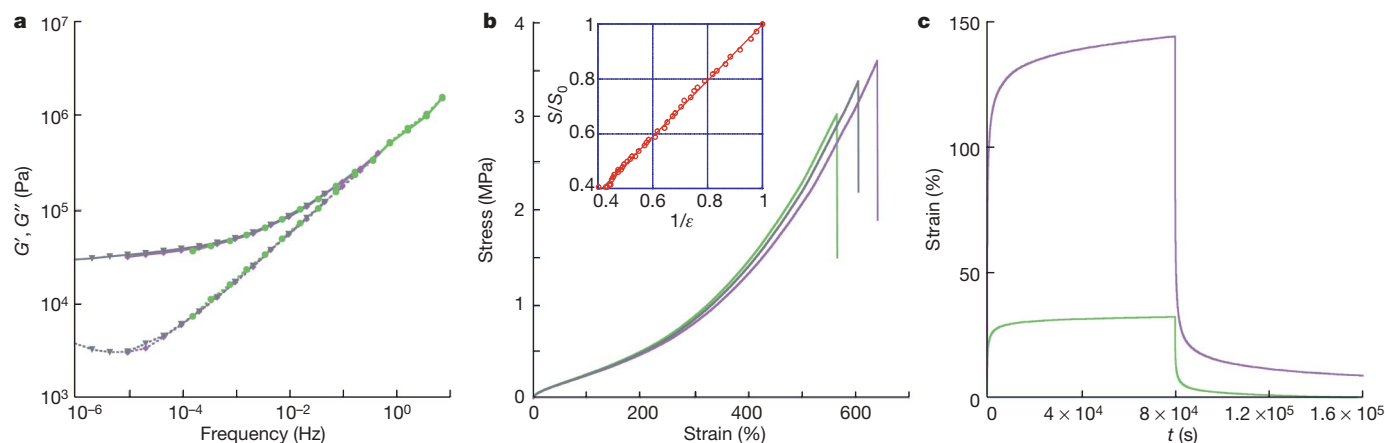


Figure 3 | Rheological and mechanical properties. **a**, Frequency dependence of the storage (top, G') and loss (bottom, G'') moduli of compound **B** obtained by classical time–temperature superposition shifts. The reference temperature is 50°C and measurements were performed at 50°C (green circles), 70°C (purple diamonds) and 90°C (black triangles). **b**, Stress–strain curve of supramolecular rubber **B**. Data for three samples are

shown to illustrate the reproducibility. The inset shows that the cross-section area varies as the inverse of the tensile deformation. During deformation the sample volume is conserved as in conventional rubbers. **c**, Creep–recovery experiment of compound **B** for an applied stress of 5,000 Pa (green) and 20,000 Pa (purple).

8×10^4 s, the strain is about 144% and it increases by 0.36% per hour. After release of the stress, the residual strain is less than 8% (but even after 8×10^4 s, the relaxation still continues). Tensile stress relaxation experiments (Supplementary Fig. 6) confirm this picture. Because of the proximity of the glass transition, viscous dissipations are important in both stress and strain relaxation experiments and samples recover their dimensions rather slowly.

All the above mechanical features show that material **B**—although it is made of oligomers—behaves very much like a rubber. In contrast to classical rubbers, however, material **B** exhibits unique self-healing properties: when a sample is broken or cut into pieces and the pieces are brought into contact together for some time at room temperature (20 °C) they self-heal without the need to heat or press strongly. The mended samples are able to sustain large deformations and recover their shape and size when stress is released. Figure 4a illustrates that longer healing times lead to better healing, but even when contact time is as short as fifteen minutes a repaired sample can be deformed up to about 200% without breaking. Interestingly, for all healing times, stress–strain curves superpose and only show elongation at break changes. Although healed scars are not visible, repaired samples break at the scar location except after long healing times (Supplementary movie 1). The cycle of stretching, breaking and healing can be repeated many times.

These observations seem to confirm our design principles: to be self-mending the supramolecular rubber has to be made from small molecules and the supramolecular associations have to be strong and long-lived so that at equilibrium, the fraction of non-associated groups in the network is low. However, the strength of the associations has to be lower than that of covalent bonds so that when broken, many non-associated groups are present near the fracture surface. Self-healing is efficient because a large number of groups ‘eager’ to link is available. At shorter healing times fewer bridges across the interface are formed and the elongation at break is lower.

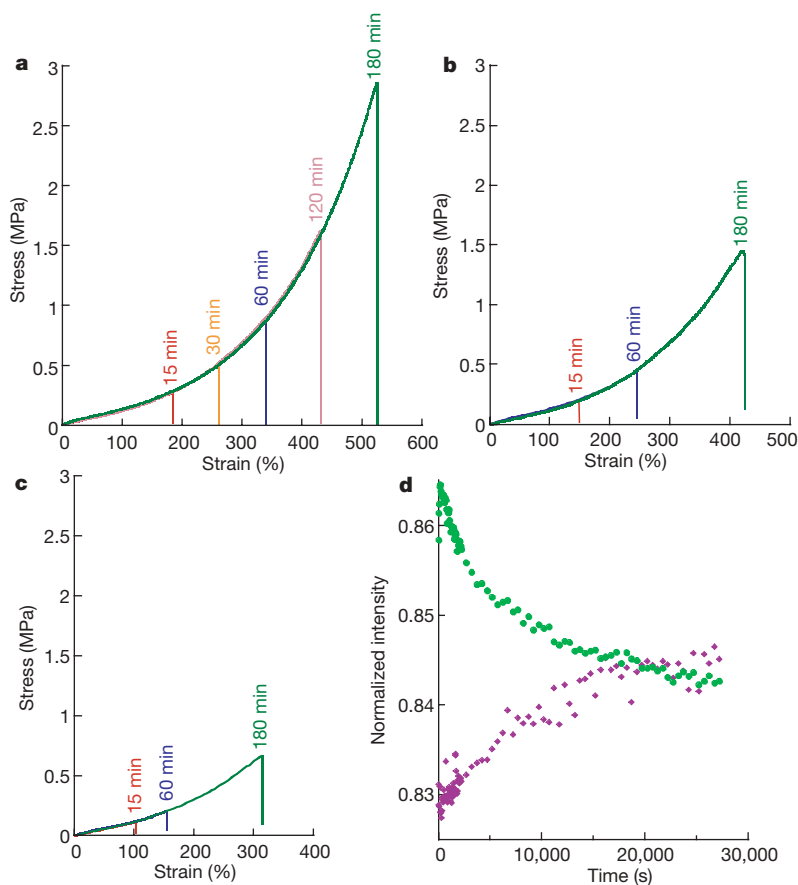
Of course, the above mending mechanism also implies that when the sample is not mended immediately after being broken but only after some waiting time, the number of non-associated groups available for healing decreases. Indeed, during the waiting time, some free groups find partners within the broken part. But, as shown in Fig. 4b and c, broken samples can still efficiently heal after waiting for 6 h or even 18 h. When the waiting time is varied, the stress–strain curves again superpose and the elongation at break of mended samples remains impressive.

There is a maximum waiting time after which self-healing is no longer possible in a reasonable time. During this maximum waiting time thermal equilibrium is reached, and so few free groups remain available for partner exchange across the scar and for bridging. To confirm this mechanism, we increased the temperature at which samples were held during waiting time and then performed the healing operation after cooling the pieces back to room temperature. The maximum waiting time after which healing is no longer possible decreased, from more than one week at 23 °C, to about 48 h for waiting time at 40 °C, 95 min at 60 °C, 15 min at 90 °C, and 5 min at 120 °C. This is because equilibrium is reached much more quickly when temperature is raised, and so broken associating groups find partners within the broken piece much faster. Finally, to confirm that it is necessary to have non-equilibrated free groups on both of the surfaces to be joined together, we checked that a freshly cut surface does not adhere to the surface of a non-broken sample at room temperature.

It is difficult to obtain direct spectroscopic evidence of an excess of non-associated hydrogen bonds at a freshly cut surface because even reflectance infrared techniques probe and average over a depth comparable to the radiation wavelength, that is, a few micrometres. Nevertheless, using time-dependent infrared spectroscopy we were able to confirm the slow dynamics of hydrogen-bond re-association (which we consider to be the mechanism of self-healing). This

Figure 4 | Self-mending at room temperature.

a, Cut parts are brought into contact at 20 °C immediately after being cut (waiting time less than 5 min). Curves represent stress–strain behaviour measured for convenience at 40 °C after different healing times. **b**, Stress–strain behaviour at 40 °C of mended samples; mending was performed at 20 °C after keeping broken samples apart for 6 h. **c**, As in **b** but cut samples were kept apart for 18 h and then mended at 20 °C. Coloured vertical lines in **a** to **c** correspond to elongation at breaking for given healing times (for all healing times, stress–strain curves superpose almost exactly and show elongation only at break changes). **d**, Time-dependent infrared experiments. The sample was heated to 125 °C for 10 min and then quenched to 25 °C. Infrared absorption spectra evolutions were recorded. The intensity at $1,524\text{ cm}^{-1}$, characteristic of free N–H bending motions (green) decreases, whereas the intensity at $1,561\text{ cm}^{-1}$, characteristic of associated N–H bending motions (purple) increases. These data confirm the long lifetime of open hydrogen bonds when they are created in excess.



slowness accounts for the most striking feature of self-healing materials: their ability to mend rapidly even after a rather long waiting time, even though the samples do not flow (creep) at these timescales.

Indeed, in a temperature-jump experiment (Fig. 4d), the sample was heated at 125 °C for 10 min and then quickly cooled down to 25 °C and the evolution of the infrared spectrum was observed. Figure 4d shows that characteristic bands of free N–H and bound N–H bending motions evolve in opposite directions with a long characteristic time of about 10⁴ s. A similar evolution was observed for C=O stretching bands, thus confirming that when excess free hydrogen groups are created, they associate slowly and the association times are compatible with times during which healing is possible. We emphasize that the characteristic decay time of the number of non-associated bonds is much smaller than the mechanical relaxation time. The ratio of these two times is expected to be high for strongly associating systems, especially when some short-range organization is present²⁴.

Compared to covalently crosslinked rubbers, the supramolecular rubbers described here cannot indefinitely hold stress without creep (even though characteristic relaxation times can be as long as weeks) and the strain recovery is slow. However, different compromises can be achieved while retaining unique self-mending and high extensibility characteristics. For example, we found that when water rather than dodecane is used as plasticizer the glass transition is lowered to –15 °C and 500% strain is completely recovered in a few seconds when stress is released, much as in conventional rubbers, and stretched samples can maintain stress for about ten hours without appreciable creep (Supplementary movie 2). It is also possible to attach other associating groups to fatty di- and tri-acids, instead of the three groups proposed here, and to vary the energy and lifetime of associations. Finally, the diversity of fatty acids made from vegetable oils and the additional flexibility of choosing the diacid/triacid ratio provides a useful tool with which to tune properties. This versatility is not only an asset for industrial development but also offers the opportunity to improve our understanding of the challenging physics of unusual elasticity, glass-like dynamics and relaxations, adhesion and supramolecular structures formation^{25–30}.

METHODS SUMMARY

Compound A is obtained at the 100 g scale in two steps. 175 g of Empol 1016 supplied by Cognis (mixture of 4% monoacid, 79% diacid, 17% triacid and polyacids) was condensed with 70.3 g of diethylenetriamine at 160 °C under nitrogen over 24 h. 72 g of *oligo*-amidoamine with a [CH₂–CONH] to [CH₂–NH₂] ratio of 1.8 as determined by NMR obtained after elimination of unreacted amine (chloroform/water extractions) was then reacted with 17 g of urea at 135–160 °C for 7.5 h under nitrogen, whereupon ammonia and unreacted urea were extracted by vacuum stripping and water washings. The material was dried under vacuum and pressed at 120 °C into 100 cm² area × 2 mm thickness steel moulds. Swelling with dodecane was achieved at 60 °C over 24 h.

¹H, ¹³C and correlation NMR spectra were recorded from CDCl₃/CD₃OH mixtures (50/50 by volume) using a 400 MHz Bruker spectrometer. Infrared spectra were recorded using a Bruker Tensor 37 Fourier transform-infrared spectrometer (4 cm^{–1} resolution) equipped with a Specac Golden Gate ATR heating cell. Thermal analyses were performed at a heating rate of 10 °C per min under helium with a TA Instruments DSC Q1000 apparatus. Size exclusion chromatography experiments were performed at 40 °C in CHCl₃/BzOH at a flow rate of 1 ml per min using a Waters set-up equipped with a differential viscometer and a differential refractometer.

ARES Rheometrics was used for rheological frequency sweeps (10^{–2} to 10 Hz) with 1% applied strain in the parallel plates geometry. Creep–recovery tests were performed using a Haake RS100 rheometer. Tensile tests were performed on ISO 527-3 normalized specimens using an Instron 5564 apparatus. The Poisson ratio was determined by measuring the sample cross-section and deformation at fixed time intervals using a digital camera. Healing experiments were performed at room temperature (20 °C) by bringing cut samples together and pressing for less than 15 s. The pressure applied by hands was about 6 × 10⁴ Pa.

Received 14 August 2007; accepted 11 January 2008.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgements We thank P.-G. de Gennes for interest and support. We thank M. Cloitre, J.-M. Lehn, K. Matyjaszewski and S. Stupp for discussions. We also thank M. Milléquant and S. Girault for their help with chromatography and X-ray scattering experiments, respectively. We are indebted to Arkema and in particular to M. Hidalgo for enlarging our views on some industrial aspects of this project. CNRS, ESPCI, Arkema and DGA are thanked for financial support.

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