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Self-Healing Supramolecular Networks

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Summary: We have demonstrated recently[1] that an assembly of molecules, connected to each other by strong, but thermally reversible, hydrogen bonds, is able to show rubber elasticity and, in striking contrast to conventional rubbers, is able to self-heal when cut or torn into pieces. Self-repair is achieved by simply bringing the broken pieces into contact with no chemical reactions, no heat nor strong pressure applied. In this paper, we briefly review the design principles, synthesis and physical properties of such materials.

Introduction

The mechanical properties of rubbers spectacularly differ from those of ordinary inorganic or organic solids. Rubbers are able to deform up to few hundreds percent under stress compared with only few percent for ordinary solids. Remarkably, even after being submitted to such large strains, rubbers recover their original size when the deforming forces are removed. This is due to the ability of deformed macromolecules to return to an entropically more favorable disordered conformation when the stress is released. A conventional elastomer, such as a vulcanized rubber, is a network of long flexible chains, connected to each other by permanent cross-links. The question arises whether a system of small molecules associated into a supramolecular network *via* directional interactions could demonstrate rubber elasticity. A possible scenario would be to use multiple parallel hydrogen bonds[2–9] to assemble molecules into cross-linked supramolecular chains. Hitherto synthesized supramolecular networks showed tendency to crystallize and form partially ordered 3D organized structures rather than flexible networks. They behaved more like semicrystalline polymers than like rubbers.[10–14] In order to suppress the tendency to crystallize, we have proposed not to use two or three identical molecules that could assemble into a supramolecular network, but to change the paradigm and employ a mixture of randomly branched oligomers, equipped with a variety of H-bonding groups, in our realization, amide, 1,3-dialkyl-ureas, 1,1-dialkyl-urea and imidazolidones (see Figure 1), all able to strongly associate with each other. The challenge here was to have molecular dispersity but to also avoid phase separation. A further difficulty, faced by designing supramolecular materials, is to ensure their synthetic availability at large quantities.

A breakthrough, in this context, has been to realize that largely available Diels-Alder derivatives of natural fatty acids already provide difunctional and trifunctional precursors. Because they exist as mixtures of many isomeric forms, these molecular assemblies are homogeneous and non-crystallisable. Moreover, they are available in various compositions, depending on their vegetable origin; they are non-toxic and based on renewable bio-resources.

Synthesis

The synthesis, performed in two steps, has been described in detail in Reference[15]. The goal of the first step is to generate a

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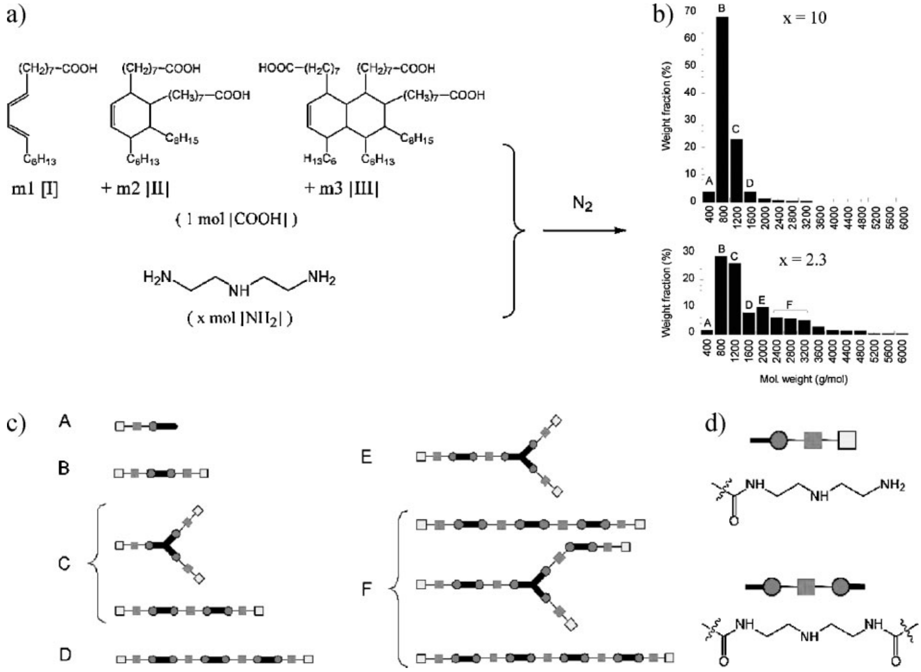

Figure 1.

Synthesis of the supramolecular networks, first step: **a)** preparation of the backbones by condensation of fatty carboxylic, dicarboxylic and tricarboxylic acids and ethylene diamine and urea. **b)** Histograms showing the molecular weight distributions (Monte-Carlo calculations) for two different [NH_2]/[COOH] ratios. **c-d)** Schematic view of the nine most abundant oligomers; unreacted amine units are depicted by squares.

well-controlled distribution of randomly branched oligomers. This was achieved merely by condensation of diethylene triamine (DETA)[1] with a mixture of mono-, di- and tricarboxylic fatty acids[2] (Figure 1a). Our strategy was to adjust the quantities of reactants in order to stop the polymerization at the desired point. After reaction, the monomer in excess (unreacted amine) was eliminated by washings. Branchings were obtained due to the presence of the trimers, and the size of the oligomers was controlled by adjusting the respective quantities of reactants. The expected molecular weight distributions for two different stoichiometries are illustrated in Figure 1b: When the NH_2/COOH ratio is close to unity, the size of the oligomers is very large, but also very sensitive to small variations of the experimental conditions (*e.g.* evaporation of DETA). In contrast, when using a NH_2/COOH ratio much larger than unity, the reaction is very well-controlled but the obtained oligomers are small and the amount of unreacted DETA to be eliminated is large.

In our experiments, the NH_2/COOH ratio was adjusted to 2.2; after elimination of unreacted DETA, the first step product is an assembly of oligomers with a large number of unreacted primary and secondary amine units (Figure 1c).

The goal of the second step is to bring H-bonding ability to our oligomers, which was achieved by reacting all available amine groups with urea. Urea reacts thermally in a number of ways with amine groups. In our case, the reaction was performed at

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[1] Although DETA is a triamine, it behaved as a purely bifunctional monomer in this process, as the experiments showed that acylation selectively occurred in the 1 and 7 positions (primary amine functions).

[2] The grade we used Empol 1016 was provided by Cognis with a composition of 80 wt% diacids, 4 wt% monoacids and 16 wt% polyacids (mainly triacids) which corresponds to an average functionality of about 2.03 carboxylic groups per molecule.

145-165 °C. In this temperature range, urea can indeed react either with primary amines, leading to 1,3-dialkyl-ureas, or with secondary amines, leading to 1,1-dialkyl-urea, or, else, with the whole —NH-CH$_2$-CH$_2$-NH$_2$ group leading to an imidazolidone cycle.

Thus, after the second step, molecules are equipped with essentially three different types of complementary and self-complementary H-bonding units: amidoethyl-imidazolidone, di(amidoethyl) urea and diamido-diethyl triurea (see Figure 2).

Physical Properties

Pieces of the material thereby obtained are shown in Figure 3a. At room temperature, it appears as a transparent optically isotropic solid with a glass transition temperature (T_g) of 27 °C and is thermally stable up to about 200 °C. Well above the T_g (between 120 and 180 °C) the material shows viscoelastic properties with a plateau shear elastic modulus G' of about 2.5×10^5 Pa. Our system flows like an ordinary viscous fluid above 180 °C. The system is soluble in benzyl alcohol and in CHCl$_3$/MeOH mixtures (Figure 3b - 3e).

In order to obtain elastomeric properties at room temperature, the material was plasticized with an 11 wt% amount of dodecane. The main characteristics of the resulting compound, which displays a T_g of 8 °C, were reported in reference [1] and can be summarized as follows:

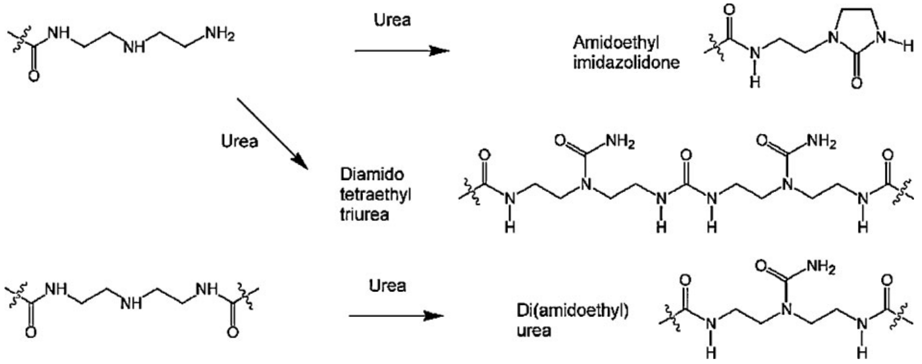

Figure 2.
Synthesis of the supramolecular networks, second step. Reactions of primary and secondary amine groups with urea, giving rise to a variety of H-bonding groups.

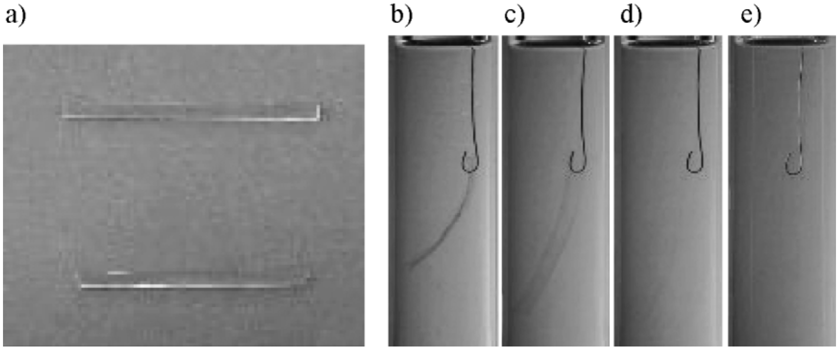

Figure 3.
Supramolecular network: Visual aspect of the neat material **a)** and during its slow dissolution in benzyl alcohol **b)** initial aspect at 60 °C, **c)** after 8 h at 60 °C, **d)** after 72 h at 60 °C, **e)** after 72 h at 60 °C + 8 h at 120 °C.

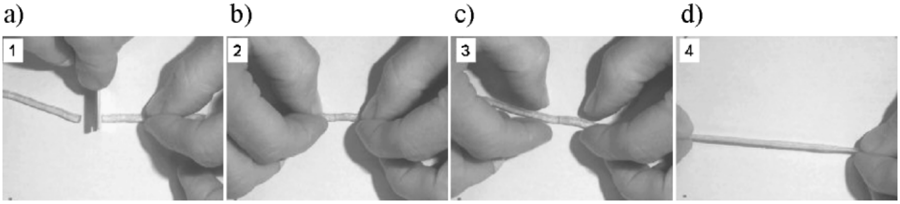

Figure 4.
Self-healing supramolecular rubber: **a)** cutting, **b)** mending, **c)** healing, **d)** stretching.

- At low deformations (rheological experiments in the parallel plate geometry and 50–90 °C temperature range), the material exhibits a rubbery plateau with a storage shear modulus of about G' $\approx 3 \times 10^4$ Pa. The relaxation time, extrapolated from the time-temperature superposition was not less than 3×10^6 s (a few weeks) at 50 °C.
- At large shear deformations (creep experiments at 50 °C), for an applied stress of 5,000 Pa for 22 hours, the material displays no creep and almost complete recovery. At larger stresses (20,000 Pa for 22 h), the material exhibits a slow creep of about 0.36% per hour and a residual deformation of about 8% after release of the stress.
- In response to a uniaxial stress (tensile tests at 50 °C), the material can be reversibly deformed up to several times its original length. The stress-strain plots show a linear regime with an elastic modulus of about E' $\approx 5 \times 10^4$ Pa up to about 200% deformation, followed by a stress-hardening regime; an elongation at break of about 600% and a stress at break of about 0.3 MPa; moreover, the deformation is isochore in the whole elastic range.

Thus, the plasticized material clearly behaves as a soft rubber. However, in striking contrast to a conventional elastomer, made of cross-linked polymer chains, it is able to self-heal after a damage. Remarkably, the new material does not show self-adhesion on timescale of weeks. However, when cut or broken into pieces, it can be simply mended in a few minutes by bringing together fractured surfaces to self-heal without the need of applying heat or strong pressure[3] (Figure 4).

Repaired samples recover their extensibility up to several hundreds percent. The process of breaking and healing can be repeated many times and, even more strikingly, the repair can be performed even several hours after breaking.

Conclusion

This design from small molecules confers to the novel supramolecular networks a very unusual property, self-healing, which, we hope, will be useful in a number of applications such as adhesives, protecting coatings, building industry, or even civil engineering. Another notable aspect is that these new rubbers can be obtained from rather simple starting materials and using simple synthetic techniques. Different chemistry schemes can be proposed to synthesize supramolecular materials from fatty acids. Reference[16] presents one such possible scheme: in a one-pot versatile procedure, materials ranging from supramolecular semicrystalline plastics to hybrid networks (with both physical and chemical cross-links) *via* viscoelastic resins and self-healing rubbers are obtained simply by varying stoichiometries.

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[3] The non-plasticized material also shows the self-healing property. However, in that case a small pressure is necessary to bring the broken pieces in close contact.

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