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Thermoplastic silicone elastomers as materials exhibiting high mechanical properties and/or self-healing propensity

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ABSTRACT
Silicones are outstanding elastomers with e.g. great thermal properties and purity that make them important commercial materials. Current R&D aims at generating filler-free, non-cross-linked materials so that to bring to them transparency, reusability, and self-healing propensity. This mini review gives, after a short summary of conventional thermoplastic silicone elastomers genesis, some examples of current research in synthesis and processing of silicone-based physically cross-linked elastomers.

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Introduction

Silicones are everyday life materials disposed as fluids (in cosmetic, as textile coating, for instance) or elastomers (joints, molds, pacifiers…). Discovered just after the WW1, these polymers have developed their own synthetic pathway. In particular, the processing of elastomers involves a unique integrated process, starting from sand to silicon metal on the way to fluids, silica and final composite materials.

An academic dream not reached yet would be to generate silicone materials moldable several times so as to recycle them, and ultimately also to impart self-healing. This is not achievable with conventional silicone materials. Indeed, to generate an elastomer, two complementary steps are necessary: (i) the silicone chains are slightly crosslinked covalently in a very loose network, to prevent them from creeping. Different chemistries are available for that, namely condensation, radical or hydrosilylation reactions (Figure 1(A)); (ii) (hard) mineral filler particles are introduced into the (soft) silicone matrix, generally in large quantities, typically 30 wt. % for reinforcing particles (fumed silica) and more for non-interacting filler (e.g. quartz) (Figure 1(B)). Once these two steps are fulfilled, the material cannot be recycled: interactions between silicone and silica are so strong that the two matters cannot be separated anymore. Moreover, a selective breaking of crosslink nodes is not available in current elastomer families, although recent academic reports propose reversible crosslinking reactions (vide infra).

Thus, to generate solid silicone materials at room temperature that would be remolded thermally, one can appeal to supramolecular chemistry. It consists in

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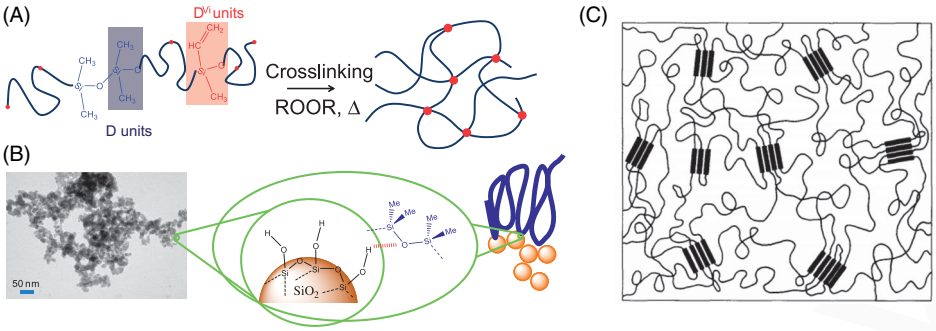

Figure 1. (A) Crosslinking reaction of silicones catalyzed by a peroxide under heat; (B) specific hydrogen bond interactions between fumed silica (see fractal structure observed by TEM on the left) and silicone chains; (C) Schematic microstructure of thermoplastic elastomers composed of hard associated blocks (thick lines) and the soft matrix (thin lines).

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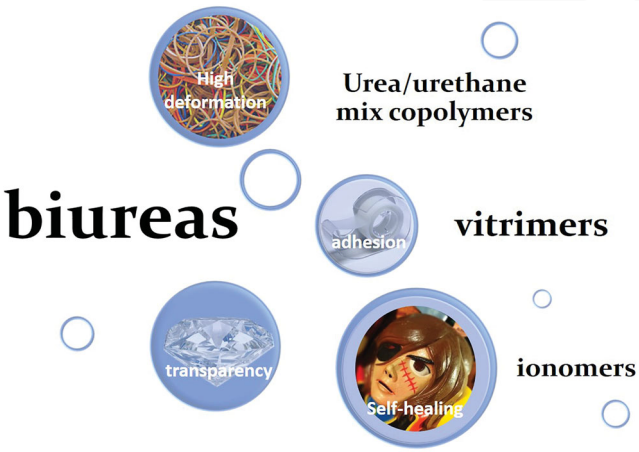

Figure 2. Summary of the content of this review.

introducing 'sticker' groups or sequences in the chains that will associate to physically crosslink the material; the stiffening of the material occurs through a clustering of the polar groups (hard segments) and their phase separation from the apolar silicone phase (soft segments) (Figure 1(C)). Several pathways can be considered: di or triblock copolymers of silicones and organic polymers, the grafting of associating groups onto silicone chains as side groups or in-between silicone chains to generate so called multi-blocks (see a recent review describing these different options [2]).

In the following, we will first summarize the features of the main family of silicone thermoplastic materials, bisurea segmented copolymers. Then we will describe recent studies that propose to introduce stronger associating groups (including covalent links) that are nevertheless reversible mostly with temperature. In every part of this minireview, we will focus mainly on the mechanical and/or self-healing properties of the different materials as a mean of comparison. Figure 2 summarizes the scope of this review.

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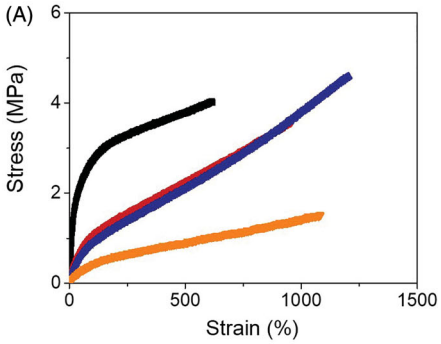

	●	●	●	●
Urea content (wt. %)	9	10	2	11
Hard block precursor	IPDI	HMDI	HMDI	TMXDI
Average molar mass (g/mol)	50 000	44 000	160 000	90 000
Đ	1.8	1.5	3.1	2
Tg (°C)	-118	-119	-120	*ND*
Tc (°C)	-	-	-80	140

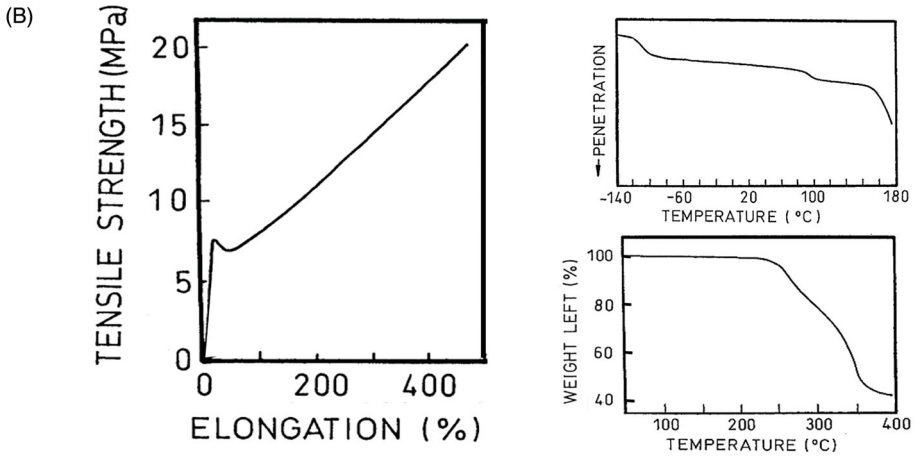

Figure 3. (A) Structure and intrinsic properties (Table) vs. mechanical properties (stress/stress curves) of representative multiblock copolymers. Names of precursors: IPDI: isophorone diisocyanate; HMDI; 4,4′-methylene bis(cyclohexylisocyanate); TMXDI: tetramethylxylene diisocyanate; ND: not detected. Microstructures deduced by ^{1}H NMR, molar masses by SEC in THF and thermal transitions by DSC. (B) Best reported silicone –urea thermoplastic elastomer (see structure details in the text). Left: tensile test; top right: Vicat hardness versus temperature; bottom right: TGA curve (from ref. [5]).

Silicone-urea segmented copolymers

Multiblock conventional synthesis and properties

Based on thermoplastic polyurethane copolymers developed in the 1940s, Yilgör and other researchers have intensively worked from the 1980s to the 2010s on multiblock copolymers, principally made of silicone-urea sequences [3]. These polymers are relatively easy to prepare by reacting commercial aminosilicones with different types of conventional diisocyanates classically in isopropanol, which is a common solvent for precursors and final block copolymer [4]. The main difficulty here is to find the right polyaddition conditions to promote large molar mass production. Typically, polymers presented in Figure 3(A) were prepared by reactive extrusion i.e. in absence of solvent. Chains beyond 30,000 g/mol entangle to favor good mechanical properties even

Table 1. Comparison of ultimate mechanical properties between silicone-urea copolymers (bloc PDMS of 2500 g/mol, acronym PSU for PDMS-based urea copolymer) and conventional polyurea copolymers (bloc PEO of 2000 g/mol, acronym PEU for polyethylene oxide-based urea copolymer) according to the diamine used as chain-extender.

	Soft segment	Urea content (%)	Tensile strength (MPa)	Strain at break (%)
PSU-DY-20	PDMS	20	7.9	205
PSU-HM-20	PDMS	205	8.1	195
PSU-ED-19	PDMS	19	8.3	180
PEU-DY-20	PEO	20	25.4	1320
PEU-HM-20	PEO	20	25.8	1325

ED: ethylene diamine; HM: hexamethylene diamine; DY: 2-methyl-1,5-diaminopentane (taken from [3])

without reinforcing fillers (Figure 3(A)). One can notice that dissymmetric-based (from isophorone diisocyanate or IPDI) and symmetric-based (from 4,4′-methylene-bis(cyclohexylisocyanate) or HMDI) copolymers of similar structure behave the same in tensile tests. Crystallizable hard blocks (based on tetramethylxylene diisocyanate or TMXDI) give much stronger elastomers (stress at 100% is 3 times the one of other elastomers) whereas a material with five-time less urea content is really soft (tensile strength of less than 2 MPa). Alike other conventional organic polymers (polyisobutylene, polyisoprene), the marked hydrophobicity of silicones promotes an efficient phase separation of bisureas, according to the difference of solubility parameters between hard and soft segments.[5] On the other hand, the lack of interactions between the matrix and the polar clusters limits the final mechanical properties of these block copolymers, compared to conventional polyurethanes for which the strong interphase between soft and hard segments is promoted by hydrogen bonding between urea and polyoxyalkylene chains (Table 1 and [3]). Tensile test values are nevertheless comparable to those measured for conventional thermoset silicone materials, typically a tensile strength (σ) of few MPa and elongation at break (λ) reaching as high as above 1000% (Figure 3(A)). The best reported material that we found in the open literature is obtained from a large content of hard segments made of HMDI (HS of about 33 wt.%) and soft segments composed of small silicone units (molar mass of silicone precursor is about 900 g/mol). The overall molar mass was not given in this study, but we estimate it at above 50,0000 g/mol according to its intrinsic viscosity, using recently reported Mark-Houwink parameters [6]. In that case, σ tops 20 MPa with a fair λ of about 400% (Figure 3(B)) [5]. The rubbery plateau is very large (from −120 °C, the Tg of the soft segment, to 150 °C, corresponding to the relaxation of hard segments), as observed by Vicat measurement. The thermal stability under nitrogen, as obtained by TGA, is remarkably large with an onset of degradation around 250 °C, comparable with conventional silicone elastomers.

These copolymers can also be prepared industrially by reactive extrusion. Wacker Chemie Gmbh company has launched since 2004 an ambitious program of commercialization of thermoplastic silicone elastomers (TPS) under the tradename of Geniomer©. One challenge that Wacker has solved prior to this product selling was to synthesize telechelic aminosilicones of perfect end-functionality thanks to an inhouse functionalization technique. To our knowledge, these are the only thermoplastic elastomers based on silicone-urea technology currently available on the market.

Variations around urea-based multiblock copolymers

One embodiment to generate longer polymer chains is to synthesize these copolymers in two steps:

i. first, addition of diisocyanates in excess on aminosilicone chains
ii. second, post-reaction of these precursors with simple organic diamines, also called 'chain-extenders'. By doing so, one increases the size of the soft blocks and favor entanglements, which ultimately significantly depress hysteresis in cyclic stress-strain curves, a known weakness of thermoplastic elastomers [4,7]. By incorporating urea-oxamide groups, the same tendency in decreased hysteresis has been observed, this time thanks to a greater phase separation [8]. In other studies, some researchers have tried to combine silicone blocks with other soft segments, namely, poly(propylene oxide) (PPO) or poly(ethylene oxide) (PEO), either directly in a solution copolymerization of corresponding diamines synthons, [9] or by extruding commercial thermoplastic urethane copolymers (TPU) with aminopolysiloxane (90/10 in wt.%) at high temperature [10]. In the first case, a better compatibilization between the soft and hard segments in optimized materials allowed reaching larger strains at break. Materials from the second pathway show nodules of small sizes (<250 nm) by SEM, suggesting possible reshuffling between the two polymers, as also proved by the apparition of urea groups within the copolymer. It is worth mentioning the works of the Multibase company, subsidiary of Dupont, that commercializes different masterbatches of organic thermoplastic polymers (polypropylene, polyurethane.) and (in-situ cross-linked) ultrahigh molecular weight silicones, mixed by extrusion [11].

Self-healing of multiblock copolymers at room temperature

Starting from the seminal work of Yilgör et al. [2,3], numerous teams around the world have proposed some variations of initial formulations to enhance the dynamics of the elastomers and thus promote trigger-free, room temperature self-healing. One efficient strategy consists in using different diisocyanate precursors and/or silicone oligomers to generate multiblocks with weaker (i.e. reversible) H-bonding ability. For instance, combining a strongly associating symmetrical methylene bis(cyclohexylisocyanate) (HMDI) with an asymmetrical one, isophorone diisocyanate (IPDI) allows modulating the interaction strengths within the clusters [12]. Equally, mixing bisamino- and bisalcohol-terminated silicones with HMDI introduces both strongly associating urea and weaker urethane groups within the same copolymer chain [13]. Both types of elastomers heal in few days without any external stimulus (Figure 4(A)). Another way of doing consists in introducing in a commercial TPS some additives called 'stoppers', namely monosubstituted urea-based silicone oligomers so as to break the large supramolecular edifices and 'dynamize' the materials. A full cauterization is observed in few days (Figure 4(B)) [14].

Isocyanate-free chemistries and subsequent self-healing

The high reactivity of diisocyanate precursors pairs with harm and toxicity. Two synthetic pathways have been recently proposed to avoid using these while still generating

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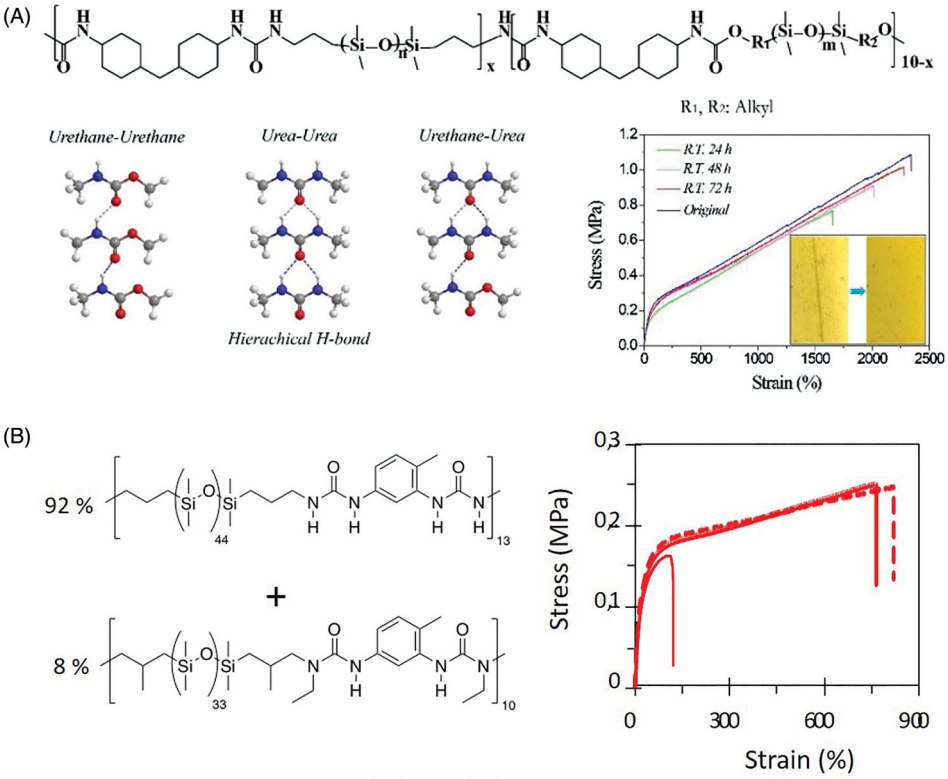

Figure 4. Recent strategies to bring self-healing properties to silicone-urea multiblock copolymers. (A) Urea-co-urethane-silicone copolymer (base HMDI) shows moderate association strength of the hard blocks (from [13]). (B) Mix of a commercial thermoplastic elastomer (Geniomer 80, TDI-based) and a 'stopper' to promote self-healing as seen in stress-strain curves (dashed line: genuine material, thin line: right after tearing the material; bold line: after 48°h healing at RT) (from [14]).

TPSs. The first route proposes to react urea directly on a telechelic aminated silicone at high temperature and under inert atmosphere. A variety of groups, including urea-bridging moieties and other associating groups such as imidazolidone, monoalkyl- and dialkyl-ureas, are thus generated. This chemistry, which has been described for a long time in the literature, was applied mainly by two groups to generate materials. One team started from homemade carboxylated silicones in two steps [15], following the protocol of Leibler et al. [16] Another team has proposed to start from di- or octa-functional aminosilicones to promote efficient chain-extension (Figure 5(A)) [17]. In both cases, the thus prepared weak materials (σ below 1 MPa) showed self-healing properties. This urea-based chemistry is still partially mastered and understood, some authors even suggesting that covalent crosslinking reaction would occur through the synthesis of biuret groups [15b]. Another simple reaction puts in play aminated silicones with a simple cyclocarbonate to generate telechelic hydroxy-urethane terminated chains that naturally phase-separate into a material (Figure 5(B)) [18]. These elastomers self-heal almost completely after 24 h (80%) even after 5 consecutive cycles. Finally, to be complete, we can quote the works done on silicone modification by ureido-pyrimidone groups (UPy) originally published by Meijer et al. [19]. Even when

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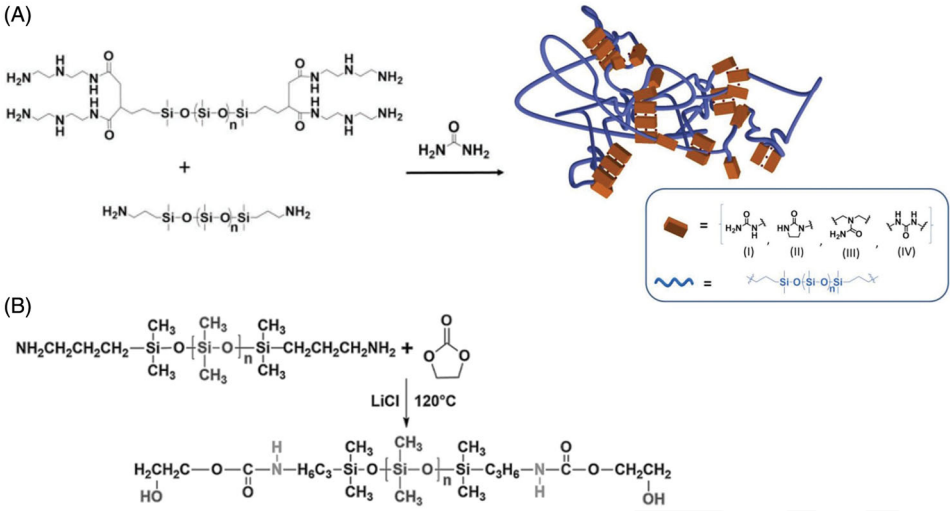

Figure 5. Isocyanate-free silicone (co)polymers. (A) direct reaction of urea on a mix of differently-functionalized aminated silicones to generate a panoply of associating groups (shown in the frame) while favoring chain extension and phase separation (reprinted from [17]). (B) amine-cyclocarbonate applied to a silicone to generate α-hydroxylate urethane-silicone polymers that spontaneously auto-associates (from [18]).

using quadruple bridges, these simple synthons are not promoting material building through phase separation. Other strongly binding lateral groups such as bis-ureas or benzocarboxamides [20] actually do the job.

Towards stronger associations

Simple ionic interactions

Coulombic-like associations can be highly polar and of high energies (to the level of covalent ones). Both factors favor an important demixion of the clusters from the matrix leading to strong thermoplastic elastomers. The simplest synthetic pathway consists in mixing an aminated silicone with molecular organic carboxylic acids. Starting from amino-side-functionalized silicones and trifunctional citric acid, rather smooth materials are generated (σ around 0,5 MPa and λ averaging 350%) [21]. Combining oxalic (di)acid with a high molar mass silicone bearing high amine content strengthens significantly the mechanical properties (σ up to 4 MPa and λ above 1000%), most likely thanks to partial crystallization of the organic clusters. Unexpectedly, these elastomers are also remarkably stable thermally, as revealed by TGA under nitrogen atmosphere, which could possibly be due to a covalent linking reaction at high temperature (namely, conversion of some ionic pairs into amide groups) [22]. Another strategy, reported in two articles, mixes aminated and carboxylated silicones. The materials thus formed are mechanically weak (σ in the order of 0.2 MPa) but of particular interest for their dielectric properties brought by the high ionic conductivity of amine/acid pairs [23].

Aza-Michael reaction has so far been scarcely proposed to generate supramolecular materials, particularly based on silicones (see a recent review here [24]). This reaction

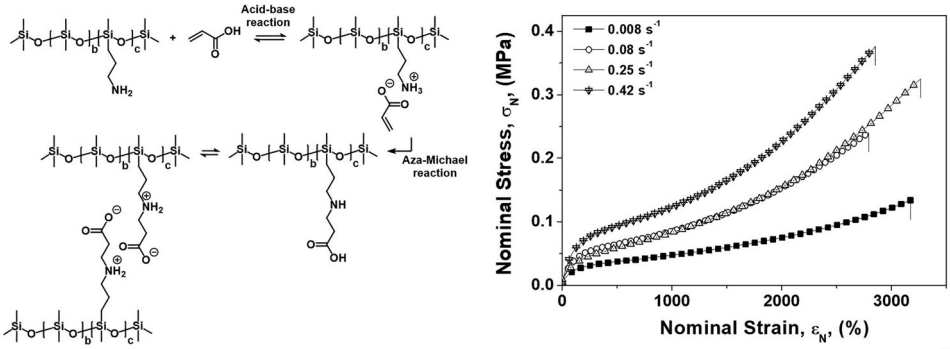

Figure 6. Zwitterionic silicones obtained by Aza-Michael reaction to generate nanostructured, transparent soft elastic materials of remarkable elongation [25].

is solvent-free, catalyst-free and is efficient even at room temperature, making it really interesting in the context of green chemistry's principles. For instance, the grafting of acrylic acid onto aminosilicones bring zwitterionic chains that associate and demix into an elastomeric material with remarkable elongation at break (Figure 6) [25]. Both TEM and X-ray diffraction have shown the presence of a myriad of clusters of size below 20 nm.

All materials quoted in this part self-mend at room temperature, albeit partially.

Interactions with metallic ions

(Hopefully non-toxic) metallic salts associated with ionic aggregates (non-specific interactions) or specific ligands (dative interactions) in the polar clusters allow strengthening significantly the materials. A first strategy makes use of carboxylated silicones mixed with multivalent cations to generate very strong ionic pairs, a strategy often used in aqueous acrylic-based paints. The former silicone chains can be prepared either by thiol-ene reaction on vinylated PDMSs [26], or aza-Michael reaction of (meth)acrylic acid on aminosilicones [27]. Both divalent (zinc) or trivalent (iron and aluminum) cations associate strongly to produce stiff (σ of few MPa) but strongly viscoelastic elastomers, as cyclic stress-strain tests have shown it. An elaborated second strategy consists in introducing specific ligands (generally oxygen and/or nitrogen-based aromatic molecules) promoting dative interactions with different types of cations [28]. Not all combination however leads to phase demixion and elastomer building, the clusters being non-ionic and thus of lower polarity. Moreover, the materials are generally highly colored and hence of less interest for industry. We shall still quote the work of Bao's team who have prepared amazing elastomers breaking at more than 10.000% [28a], as well as the proposition of J.-M. Lehn, back in 2008, to redistribute supramolecular networks by ligand exchange [28b]. All materials self-heal at room temperature.

Reversible covalent crosslinking

Since the pioneering review article of Engle and Wagener [29] that was presenting back in 1993 different types of covalent links thermally reversibly unbonded, time has passed

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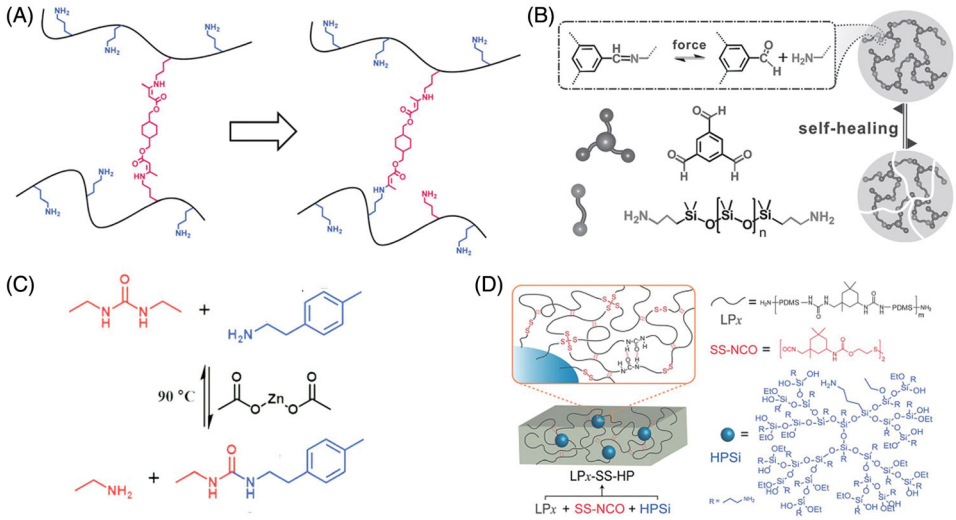

Figure 7. Some examples of reversible covalent chemistry: (A) vinylogous functions [31b]; (B) aromatic imine groups [30a]; (C) redistribution of urea functions [31d]; (D) disulfide bridges [31c]. One can note in the last case the use of silicone dendrons to generate a horde of cross-links so as to reinforce the final material.

but this research theme has received a boost recently, and specifically on silicone materials. Two possibilities are described in the literature. One approach considers only covalently-reversible links [30], which corresponding materials are relatively weak mechanically; another approach brings together supramolecular and covalent networks, which properties clearly compete with conventional elastomers [31]. Figure 7 shows few examples of original chemistries to create these materials. Several studies report the generation of imine derivatives [30a,30d,31e] arising from the reaction between an aromatic aldehyde and amine or carbohydrazide groups. More specific chemistries, including thiol-based groups [30c,31c], vinylogous [31b] or boron-oxygen [30e] links (present in the well-known "Silly Putty" materials), have been published. Healing of the materials depends on the generated networks, with reaction thermally controlled or at room temperature, in bulk or in water, with or without catalyst. On the double network strategy, we have distinguished the study of silicone-urea polymers crosslinked with tricyanurate functions that are redistributed thanks to a zinc-based catalyst [31d]. Note that for imine and disulfide bonds, direct exchanges between these bonds occur through temperature debonding, reshuffling and reformation, whereas, for vinylogous and crosslinked urea-based materials, an excess of original reactive functions, e.g. aminated groups, is required for substituting the split junction into a new one (Figure 7). A very interesting and recent review details these different strategies and others [32].

Upcoming challenges

As we showed in this review, combining strong mechanical properties with an upfront self-healing behavior seems at once antagonist in polymer materials, including thermoplastic silicone elastomers. One way to make ends meet would be to integrate in the supramolecular matrix a second network of percolating filler particles. Few examples

reported in the literature on a conventional silicone-urea [33], an ionic material [21] and a reversible covalent network [34] show that the upgrade in mechanical properties is relatively small but real. In the last case typically, introducing 20 wt.% of kaolin particles in the material multiplies its tensile strength by 5 (from 0.1 to 0.55 MPa) and its stress at break by almost 2 (from 110 to 180%) [34]. Another means of reinforcing the elastomers without affecting the chemical network makes use of silicone resins that locally introduce strong hardening points (e.g. Figure 7(D).

In term of applications, thermoplastic elastomers are of precise interest for their 'easy' transformation by extrusion or injection. The fact that thermoplastic silicone elastomers are now available on the market should certainly allow similar development as seen before in TPUs. Many applications of bulk or coated-TPS polymers were envisioned lately by academic researchers in electronics, anti(bio)fouling or actuators [35]. Another particular domain concerns 3D printing, a fast-rising process covered both in industry and in academia where TPS could certainly have their share. The filament deposing technique (FLD) [11b,36] is one technique for which a precise matter/machine couple must be designed; complex rheology and dynamic properties of the materials open a great deal of investigations in the near future.

Final word

Jean-Pierre Pascault liked to ask this fundamental question about thermoplastic polyurethanes: 'is the phase separation responsible for enhanced supramolecular associations or is it the other way round?' This 'egg-and-chicken' question definitively remains open …

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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