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Disassembly of Elastomers: Poly (olefin sulfone) – Silicones with Switchable Mechanical Properties

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An elastomeric polymer composite that can be disassembled at will into its individual components when exposed to mild bases is presented. The composite is formed of a poly(olefin sulfone) and a silicone bound together using "click" chemistry. The mechanical properties of the composites can be varied depending on their formulation. Its base-triggered decomposition is advantageous from the point of view of composite recycling and controlled release of chemicals.

Introduction

Stimulus responsive materials (often called smart materials) are materials whose properties can be changed at will by applying an external signal. Polymers and polymeric composite materials can show this behavior, and there are numerous examples of polymeric systems that exhibit piezoelectricity (generation of an electric field or potential under mechanical stress),[1] shape memory,[2] biodegradability,[3]

responses to thermal variations,[4] mechanochromism,[5] or self-healing behavior.[6] Materials that can be decomposed on demand are interesting, not only from the point of view of materials recycling, but also for drug delivery and controlled release of chemicals.[7] In this paper we present an elastomeric polymer composite formed of a poly(olefin sulfone) and a silicone linked by "click" chemistry, that can disassemble into its monomers and individual constituents when exposed to mild bases (Figure 1).
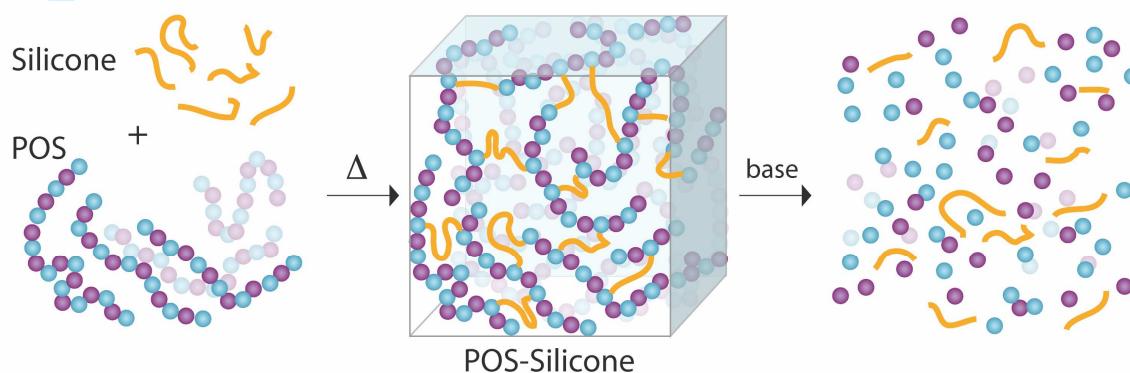

Figure 1. Formation of elastomeric cross-linked POS-Silicone composites and their decomposition via unzipping of POS when exposed to base.

Silicones[8,9] (Scheme 1a) are among the most used elastomeric polymers and have found widespread use owing to their versatility, chemical and thermal[10] stability, and mechanical properties. One of the most widely used silicone-based elastomers is poly(dimethylsiloxane), PDMS which is transparent, chemically inert, heat resistant, can be transformed into silica by calcination, and has widely tunable mechanical properties.[11] Linear PDMS has a glass-transition temperature (T_g) of 150K,[12] and its crosslinked version is used as an elastomer. The mechanical properties of PDMS elastomers can be controlled by the length of the polymer chains, their branching, their crosslinking density, and the use of fillers.[13] Aside of applications that utilize its mechanical properties, PDMS has been crucial in the development of soft lithography[14] and in the field of microfluidics.[15] In the absence of air, PDMS starts decomposing at about 350°C into cyclic compounds consisting of 3-11 repeat units.[16] PDMS also decomposes in the presence of base, but relatively harsh conditions are required to observe weight loss and macroscopic material failure (aprox. 190°C in the presence of KOH).[17]
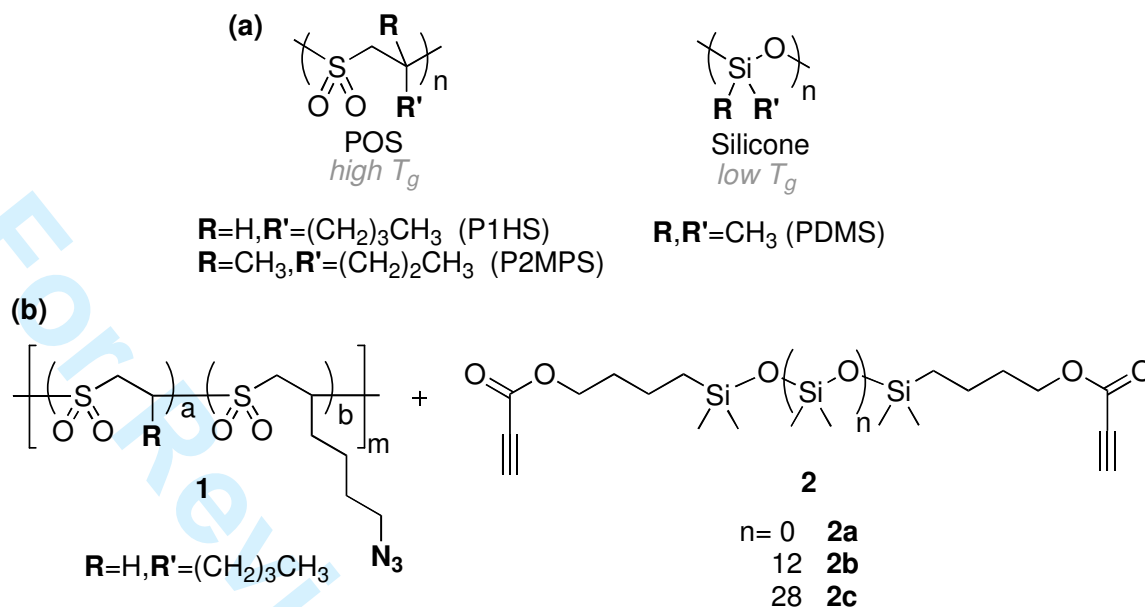
Scheme 1. Structure of silicones and poly(olefin sulfone)s, POSs.

From the synthetic point of view, silicone cyclic and linear oligomers are typically obtained from the hydrolysis of chlorosilanes,[8,18] or hydrolysis of alkoxysilanes.[16] These oligomers can be converted into higher molecular weight silicones by: a) equilibration with cyclic oligomers in the absence of a solvent;[9] b) using catalysts to polymerize oligomeric silanols either via condensation (using phosphoronitrile halides[19] or bases such as n-hexylamine)[10a] or via condensation and cleavage (using strong acids[20] or bases);[8] c) via ring-opening polymerization of cylic oligomers, either in its anionic[21] or cationic[22] form. These polymers range from fluids to very viscous liquids and are usually cross-linked to obtain resins, coatings, and elastomers. Cross-linking has been traditionally performed by a) room temperature vulcanization processes using either acid/base catalysts,[23] tin catalysts,[24] high energy electrons,[25] or photo-initiated reactions,[26] b) heat activated radical curing with peroxides,[27] or c) mixing of two different polymeric silicone components, one of which contains a transition metal catayst, typically Pt.[28]

The Huisgen 1,3-dipolar cycloaddition[29] ("click" reaction) has been extensively used for post-polymerization modification,[30] but was only recently reported as a method for the crosslinking of silicones.[31] The method described the thermal or Cu-catalyzed click reaction to functionalize azide-containing silicone oligomers,[32] and applied thermal conversion for the formation of elastomeric

silicones.[33]   That approach has the advantage that no catalysts need to be used in the process of crosslinking, so there is no need to remove/quench metal impurities after the crosslinking has occurred.

Because crosslinked elastomeric silicones are chemically robust and do not degrade easily with temperature, they are not generally attractive components for recyclable materials.   As a result, an equivalent material with similar properties that could be easily transformed into its processable precursors on demand is a worthy goal.

Poly(olefin sulfone)s (POSs)[34] (Scheme 1a) can be used as expanded foam insulation materials,[35] to improve the compatibility of certain materials with polymeric hydrocarbon chains,[36] and as antistatic additives for fuels.[37]   POSs have tunable glass-transition temperatures (T_gs) depending on the olefin moiety, although they are usually relatively high with T_gs ranging from 350K for poly(1-hexadecene sulfone)[34b] to 450-473K for poly(styrene sulfone).[38]   However, POS use has been limited because they have low ceiling temperatures and tend to depolymerize, with polymer chains unzipping into volatile monomers (sulfur dioxide, SO_2 and an olefin)[39] when an external stimulus produces chain scission (radical formation or ionization).[40]   Events that lead to depolymerization are exposure to ionizing radiation, either in the form of high energy electrons[41] or gamma rays,[41-43] or exposure to base.[44]   Their tendency to degrade has been exploited in the creation of electron beam resists[41,45] and sensors.[43]

POSs are commonly synthesized by radical chain growth polymerization of SO_2 and an olefin. Typically, bulk polymerization at low temperatures is performed with condensed liquid SO_2 as the solvent and tert-butyl hydroperoxide as the initiator.[39]   Polymers so produced display a 1:1 ratio of perfectly alternating sulfone and olefin units when there is an alkyl moiety directly linked to the olefinic residue.[45b]   The precise alternation is a consequence of the propagating radicals alternatively having clear electrophilic and nucleophilic character.   As a result, olefin candidates for copolymerization with SO_2 must be electron-rich, sterically unhindered, non-basic, and be moderately soluble in SO_2.[45b]

Given that POSs degrade into their volatile monomers with base, an elastomeric POS could be used as a material capable of being disassembled.   However, POSs have high T_gs and elastomeric POSs have not been reported.   The low T_gs of silicones are usually attributed to the long Si-O bond and the wide Si-

O-Si angle.[46] In contrast, the rigidity and high T_gs of POSs are the result of strong electrostatic interactions between adjacent sulfone dipoles, which induces a higher degree of order.[47] Even POS copolymers using hexadecane as a long alkyl chain plastizicing element are brittle powders at room temperature. We recently reported that POSs with azide functionalities in the side chains (1, Scheme 1b) can be easily synthesized.[43] Copolymerization of azide-containing monomers with SO_2 and an olefin gave a family of random terpolymers with monomodal molecular weight distributions, and since it is an ideal azeotropic copolymerization, the ratio of azide incorporation into the polymer can be precisely controlled by the feed ratio. As a result, we set to explore the possibility of using a polymeric POS-silicone composite formed using azide-alkyne cycloaddition reactions as a "smart material" capable of being decomposed upon exposure to base.

Experimental Methods

Materials and Instrumentation. Unless otherwise stated, reagents were purchased from Sigma-Aldrich and used as received. Bis(hydroxybutyl)tetramethyldisiloxane and octamethylcyclotetrasiloxane were obtained from Gelest and used as received. NMR spectra were obtained on a Bruker Avance (400 MHz). NMR chemical shifts are given in ppm referenced to either CDCl$_3$ (7.24 ppm for ^{1}H and 77.24 for ^{13}C) or acetonitrile-d6 (1.94 ppm for ^{1}H) for the polymer degradation studies. Polymer molecular weights were determined at room temperature on a HP series 1100 GPC system in THF at 1.0 mL/min (1 mg/mL sample concentrations). Approximate molecular weights were estimated using a polystyrene calibration standard. Hardness measurements were performed using a Rex 1500A Durometer Shore A type on samples with a thickness of 6mm.

The synthesis of POS **1** was previously described.[43] In the composite formation experiments a polymer of M_n=6.9K, PDI=1.38 was used. The ratio of 6-azido-1-hexenyl repeat unit to 1-hexenyl repeat unit was determined by ^{1}H-NMR (Figure S1), and found to be of 12% azide-containing repeat unit unless otherwise specified.

Alkynyl-silicone **2** of different lengths was obtained using modified conditions for the equilibration

reaction of **2a**.[33]   In a representative synthesis, compound **2a** (1g, 2.6 mmol or 0.5g, 1.3 mmol for the

synthesis of **2b** and **2c** respectively) and octamethylcyclotetrasiloxane (3g, 10mmol) were mixed

together and stirred at room temperature with a magnetic stirbar at 600 rpm for 5 minutes in a flask

connected to a drying tube. Trifluoromethylsulfonic acid (0.4ml, 4.6 mmol or 0.2ml, 2.3mmol for **2b** or

2c) was added and the mixture was stirred for 72 hours. Magnesium oxide (0.8 g for **2b** and 0.4 g for

2c) and 40ml hexanes were added to the reaction mixture and stirred for one hour. The reaction mixture

was filtered through Celite and the solvent was removed under reduced pressure. Purification by

Kugelrohr distillation at 150°C for 2 hours yielded **2b** (59%) or **2c** (57%) as transparent, colorless oils.

The number of dimethylsiloxane units was determined using ^{1}H-NMR, by comparison of the integration

signal of the terminal 2 alkynyl protons at 2.88 ppm to the signal of the silicon-linked methyl groups at

0.03 ppm to make 14 $Si(CH_3)_2$ repeat units (**2b**, n=12), or 30 $Si(CH_3)_2$ repeat units (**2c**, n=28) (Figure

S2). The increase in molecular weight was also characterized by THF-GPC and the Mn vs. polystyrene

standards was 2253, 4328, and 5981 for **2a**, **2b** and **2c**.

Results and Discussion

Base Initiated Depolymerization.   The tendency of POSs to depolymerize with base depends on

several factors, including the choice of base. Even though the pKa of the protons in the backbone of a

poly(1-alkenyl sulfone) are expected to be between the pKas of bis(methylsulfonyl)methane (15.0 in

DMSO)[48] and dimethylsulfone (31.1 in DMSO),[49] POSs can be degraded into their monomers by milder

bases. This can be seen by following the depolymerization of poly(2-methyl-1-pentene) P2MPS chains

by ^{1}H-NMR (Figure 2a). The disassembly of the polymer is revealed by the increase of the signal for

the olefinic monomer (2-methyl-1-pentane) at 2.8 ppm over time. After 30 min at r.t with 0.7 M of base

a clear signal can be seen for the olefinic monomer when using butylamine or piperidine as the base, and

after 20h even the comparatively less basic NH$_4$OH has almost completely degraded the polymer chains.
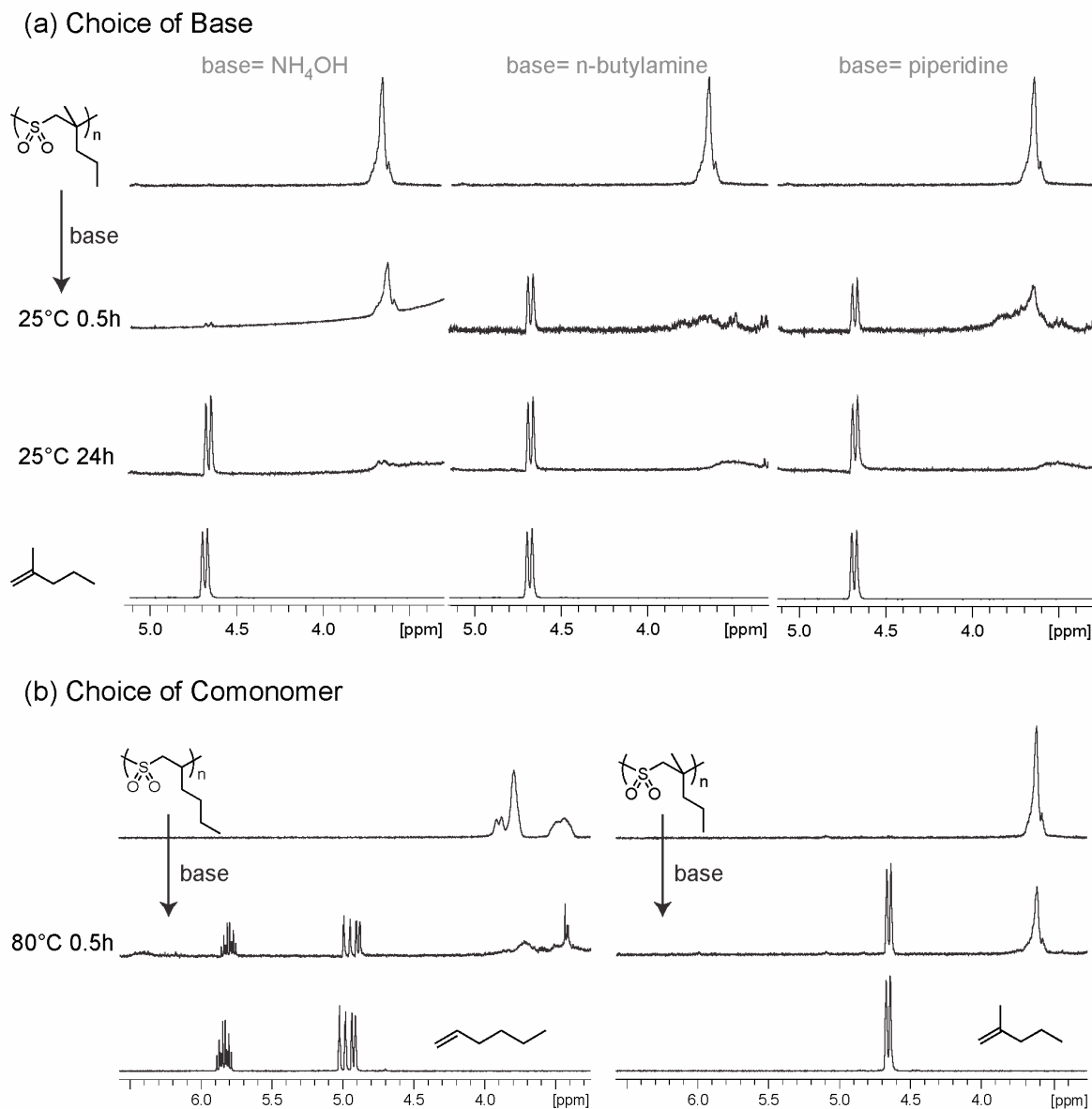
Figure 2. ^{1}H-NMR study of the decomposition by base of POSs in deuterated acetonitrile. (a) Decomposition of P2MPS by different bases under different conditions. (b) Decomposition of P1HS and P2MPS after treatment with 0.3 eq of piperidine at 80°C after 30 min.

Another factor that dictates the ease of degradation of POSs with base is the choice of olefin comonomer. Upon comparing the degradation of poly(1-hexene sulfone) P1HS to poly(2-methyl-1-pentene) P2MPS at 80°C after 30 min (Figure 2b), it is clear from the ratio of monomer to polymer ^{1}H-NMR signals that P1HS degrades faster. As expected, the degradation is even more accelerated when using a higher concentration of base (Figure S3).

The extent to which depolymerization occurs also depends on the depolymerization temperature. After 60 min of stirring with piperidine at room temperature, almost no degradation of the polymer can be observed (Figure S4). However, when heated to 80°C the signal for the olefinic monomer can be clearly seen for both POSs studied.

P1HS based copolymers were chosen for composite preparation due to their superior tendency to be degraded by base. The fact that P1HS is more prone to base degradation than P2MPS is at first counterintuitive, since this is the opposite effect that one would expect when comparing the ceiling temperatures of both polymers. Specifically, P1HS with an observed T_c of 60°C should degrade slower than P2MPS with an observed T_c of -34°C.[50] As a result, the slower reaction of P2MPS is attributed to higher steric hindrance that decreases deprotonation rates.

Composite Synthesis and Characterization. THF solutions containing azide-POS (**1**, Scheme 1b) and dialkynyl dimethylsiloxane oligomers (**2**, Scheme 1b) in different ratios were thermally cured in the oven at 80°C. After 120 min, depending on the initial ratio of polymers in the mixture, composites of different hardness ranging from elastomeric monoliths to highly viscous oils were obtained (Figure 3a). The elastomeric nature of the monoliths contrasts with the brittle nature of the POS solids, and the liquid oligomeric silicones (Figure 3a). The polymer mixture can also be cured in different molds, yielding flexible and transparent films (Figure 3b-c).
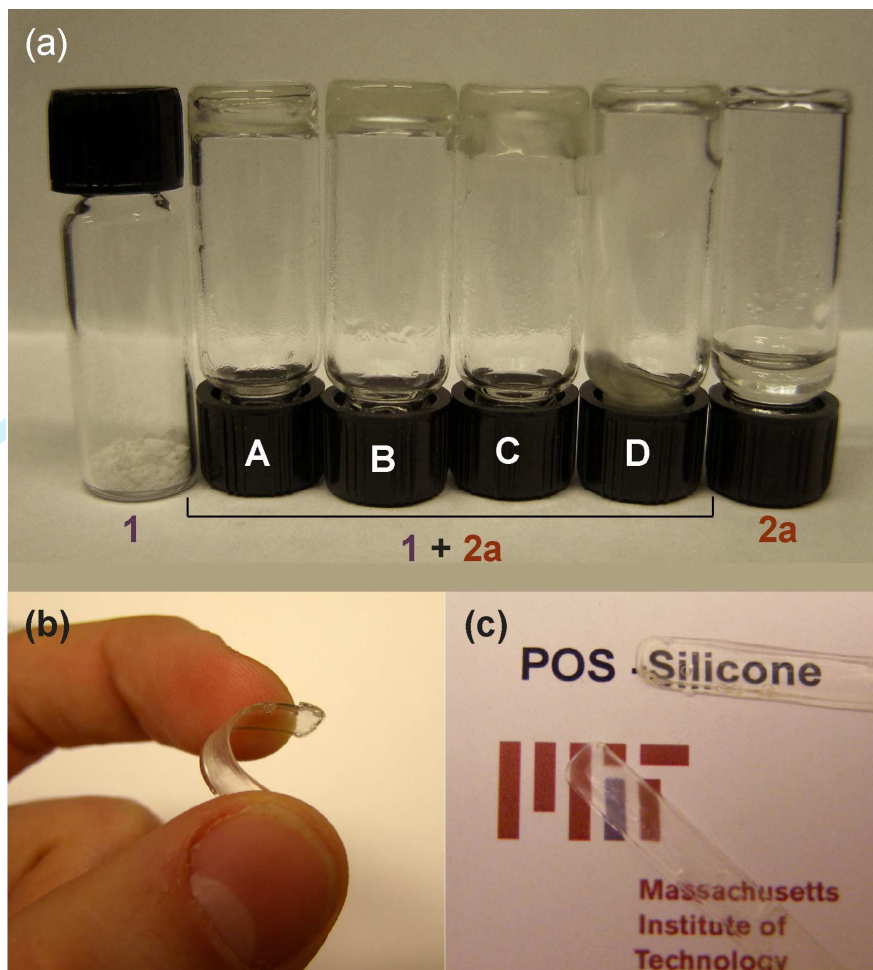
Figure 3. POS-silicone elastomeric composites. (a) Vials containing **1** (far left), **2a** (far right), and composites of **1** and **2a** (A: 88%**1**, 12%**2a**; B: 78%**1**, 22%**2a**; C: 50%**1**, 50%**2a**; D: 33%**1**, 66%**2a**) (b) Flexible film of **1+2a** composite (c) Transparent films of **1+2a**.

   The mechanical properties of the final composites depend on the ratio of POS (**1**) to alkynyl silicone (**2**), the length of both polymers, and the crosslinking density. The measured hardness can range from that of an high viscosity oil like D, depicted in Figure 3a, to a composite of a measured Shore A hardness of 90 (PDMS has a Shore A hardness of 50). Increasing the length of **2** has the effect of decreasing the hardness of the composite (Figure 4). The measured yield modulus for composites of 1 and 2a (n=0) with 80% weight of POS was in the 10 mPa range, which is in accordance with the incorporation of the high T_g POS in the polymeric network. Measured yield modulus values of commercial PDMS using the same conditions and sample configuration were an order of magnitude lower. The monolithic composites were not transparent when the longest alkynyl silicone, **2c** is used.

This latter result is probably due to microprecipitation induced by phase segregation of both polymeric

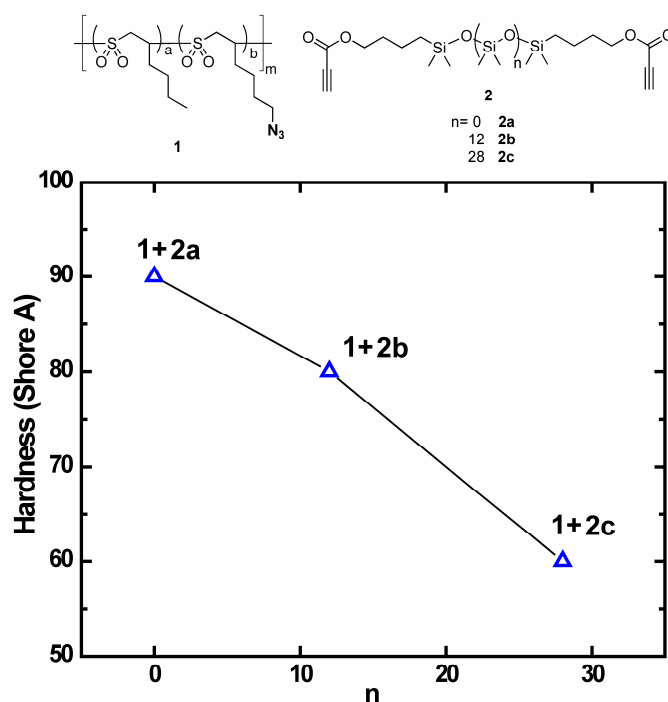components (See Supporting Info Figure S5).

Figure 4. Shore A hardness of composites formed of equimolar mixtures of azide and alkynyl moiety of

the respective POS and silicone where the silicone has different lengths. The longer the silicone chain,

the lower the measured hardness. This has to do with the incorporation of more flexible linkers in the

composite, as the length of the silicone grows.

The decomposition of these composite materials when exposed to base was studied using a composite

labeled with a dye, Fat Brown B (FBB). To form this composite alkynyl-FBB was covalently tethered to

the side chain of POS **1**,[51] and then the composite was formed by reaction with compound **2a**. The

colored crosslinked composite was expectedly insoluble in acetonitrile (the solution was not colored,

Figure 5a). After addition of piperidine, the elastomer decomposed into its monomeric counterparts,

releasing the monomer-tethered dye (FBB) into the acetonitrile solution. After only 5 minutes in a

0.03M solution of piperidine in acetonitrile, macroscopic mechanical failure was observed, and no

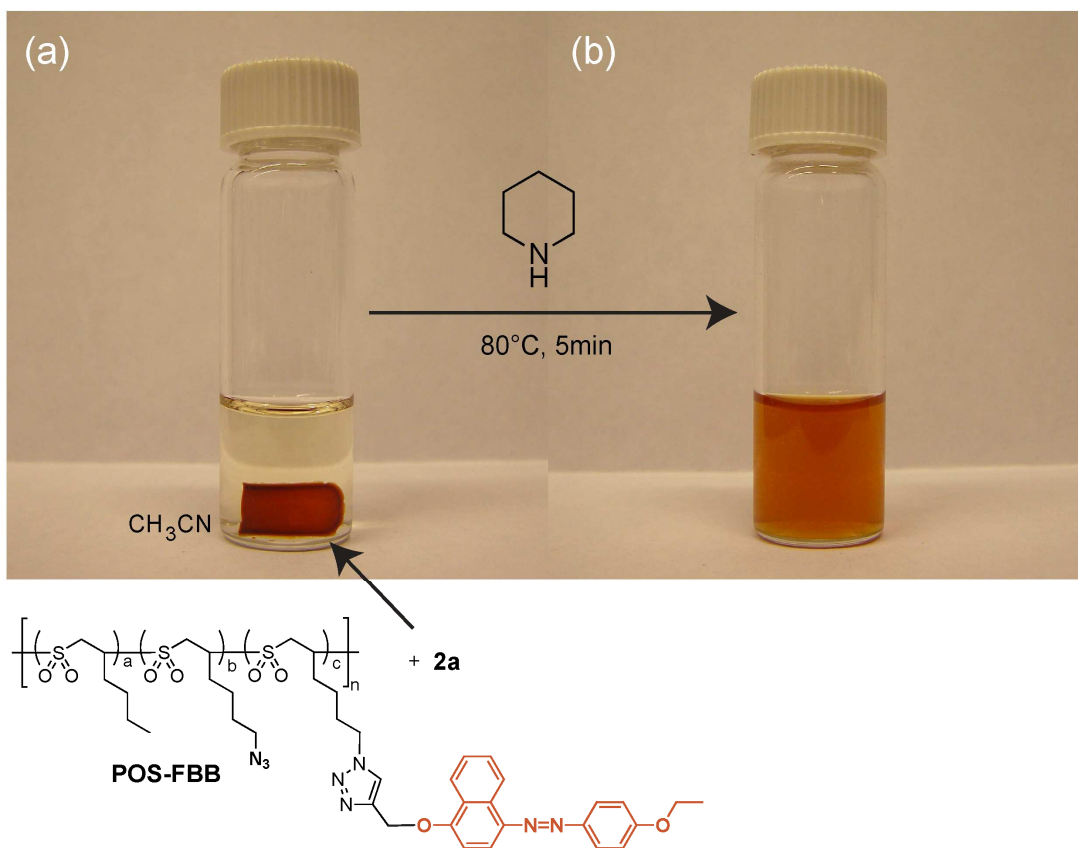macroscopic pieces of elastomer could be noticed (Figure 5b).

Figure 5. Composite of FBB-tagged azide-containing POS with silicone **2a** in acetonitrile solution (a) before base addition and (b) after base addition. Only 5 minutes at 80°C are required so that no macroscopic pieces of composite are observable, and the dye is completely leached into the solution.

Conclusions

We have shown the synthesis of an elastomeric polymer composite that can be disassembled into its individual components when exposed to a mild base (piperidine). The composite is formed by curing a poly(olefin sulfone) and a silicone using "click" chemistry, and its components can be tailored to impart different properties to the final mixture. Different ratios of the two polymer components yield composites with varying mechanical properties/hardness. Its base-triggered decomposition is advantageous from the point of view of composite recycling and controlled release of chemicals.

Supporting Information Available. NMR studies on the length and composition of polymers **1** and **2**, ^{1}H-NMR studies of base initiated unzipping of POSs under different conditions, Shore A hardness values for composites with different compositions and component ratios, detailed synthesis and characterization of dye alkynyl-FBB.

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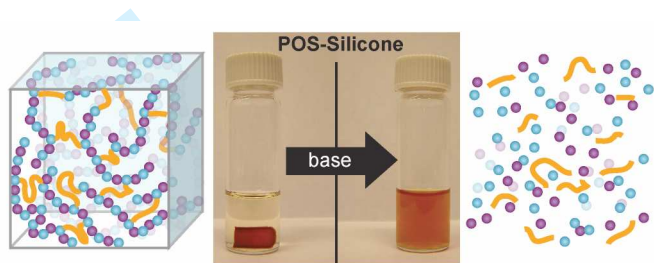
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containing 12% azide on the side chain was used, with a ratio of azide to alkynyl-FBB of 10 to 1 for the

click-chemistry reaction.

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