10422 *Macromolecules* **2010**, *43*, 10422–10426
DOI: 10.1021/ma101980j

Macromolecules
ARTICLE

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

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Received August 26, 2010; Revised Manuscript Received October 30, 2010

ABSTRACT: 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).

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, and 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 150 K,[12] and its cross-linked 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 cross-linking 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 (~190 °C in the presence of KOH).[17]

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 (a) by 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] and (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 photoinitiated 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)[30] has been extensively used for postpolymerization modification[31] but was only recently reported as a method for the cross-linking of silicones.[32] The method described the thermal or Cu-catalyzed "click" reaction to functionalize azide-containing silicone oligomers[33] and applied thermal conversion for the formation of elastomeric silicones.[32] That approach has the advantage that no catalysts need to be used in the process of cross-linking, so there is no need to remove/quench metal impurities after the cross-linking has occurred.

Because cross-linked 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 350 K for poly(1-hexadecene sulfone)[34b] to 450−473 K for poly(styrene sulfone).[38] However, use of POSs 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 γ rays[41−43] or exposure to

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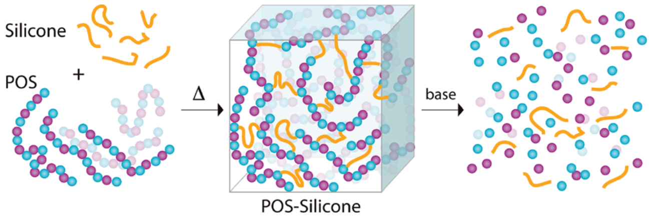
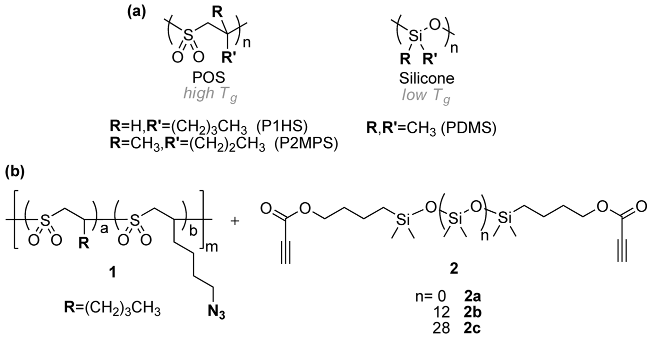


Figure 1. Formation of elastomeric cross-linked POS−silicone composites and their decomposition via unzipping of POS when exposed to base.

Scheme 1. Structure of Silicones and Poly(olefin sulfone)s (POSs)



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, nonbasic, and 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 plasticizing 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 ^1H and 77.24 for ^{13}C) or acetonitrile-d_6 (1.94 ppm for ^1H) 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 6 mm.

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 ^1H 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**.[32] In a representative synthesis, compound **2a** (1 g, 2.6 mmol or 0.5 g, 1.3 mmol for the synthesis of **2b** and **2c**, respectively) and octamethylcyclotetrasiloxane (3 g, 10 mmol) were mixed together and stirred at room temperature with a magnetic stirbar at 600 rpm for 5 min in a flask connected to a drying tube. Trifluoromethylsulfonic acid (0.4 mL, 4.6 mmol or 0.2 mL, 2.3 mmol for **2b** or **2c**) was added, and the mixture was stirred for 72 h. Magnesium oxide (0.8 g for **2b** and 0.4 g for **2c**) and 40 mL of hexanes were added to the reaction mixture and stirred for 1 h. The reaction mixture was filtered through Celite, and the solvent was removed under reduced pressure. Purification by Kugelrohr distillation at 150 °C for 2 h yielded **2b** (59%) or **2c** (57%) as transparent, colorless oils. The number of dimethylsiloxane units was determined using ^1H 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 M_n vs polystyrene standards were 2253, 4328, and 5981 for **2a**, **2b** and **2c**.

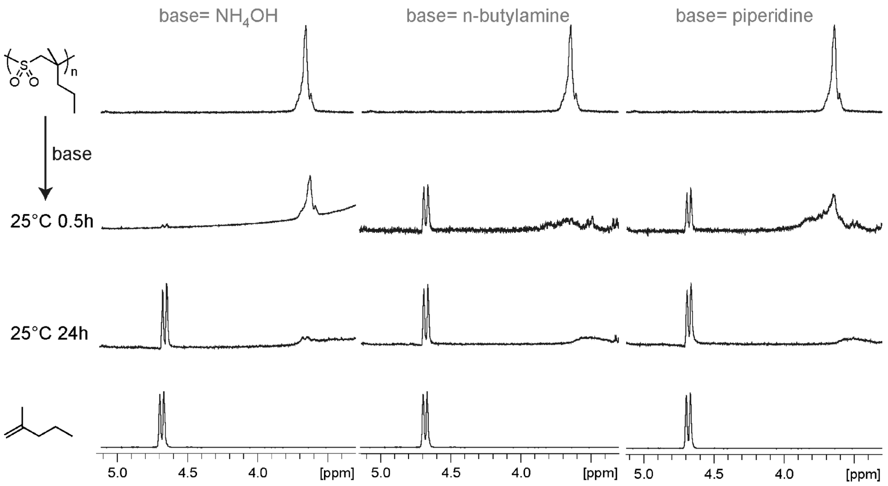
In a typical composite synthesis, POS **1** and alkynyl silicone **2** were mixed in the desired ratio and dissolved in a minial amount of THF (usually homogeneous solutions can be obtained with concentrations up to 400 mg/mL). The solution was vortexed for 15 min and poured in a Teflon mold. The composite was cured at 80 °C in a vacuum oven for 120 min, after which time the composite could be easily removed from the mold.

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 pK_a of the protons in the backbone of a poly(1-alkenyl sulfone) are expected to be between the pK_as 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 ^1H 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 4.7 ppm over time. After 30 min at rt 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 20 h even the comparatively less basic NH_4OH has almost completely degraded the polymer chains.

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 ^1H NMR

(a) Choice of Base



(b) Choice of Comonomer

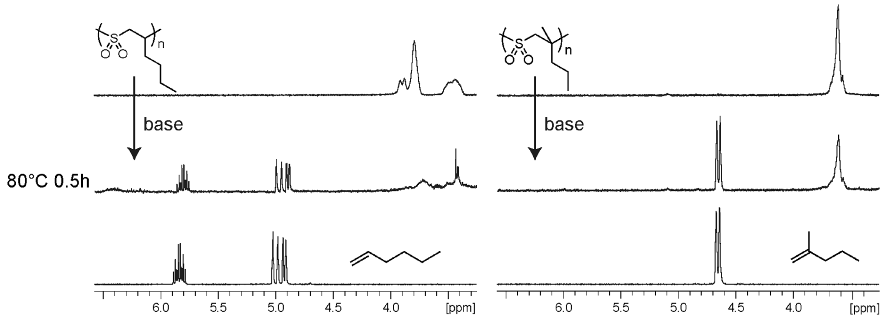


Figure 2. ^{1}H NMR study of the decomposition by base of POSs in deuterated acetonitrile. (a) Decomposition of P2MPS by different bases under different conditions. (b) Decomposition of P1HS and P2MPS after treatment with 0.3 equiv of piperidine at 80 °C after 30 min.

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 be less prone to degradation 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 dialkynyldimethylsiloxane 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).

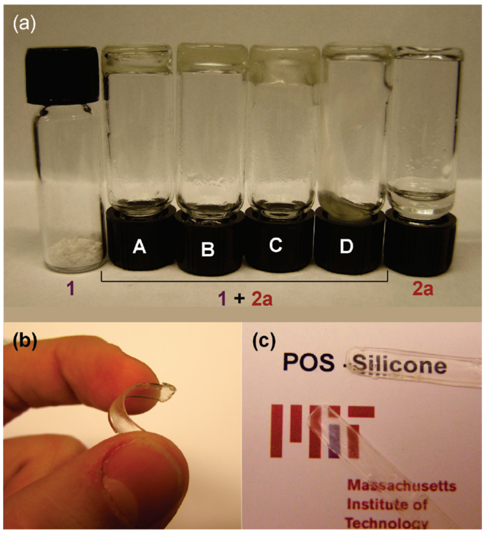


Figure 3. POS−silicone elastomeric composites. (a) Vials containing **1** (far left), **2a** (far right), and composites of **1** and **2a** (composition in wt %: A: 88% **1**, 12% **2a**; B: 78% **1**, 22% **2a**; C: 50% **1**, 50% **2a**; D: 33% **1**, 66% **2a**). (b) Flexible film of **1** + **2a** composite. (c) Transparent films of **1** + **2a**.

The mechanical properties of the final composites depend on the weight ratio of POS (**1**) to alkynyl silicone (**2**), the length of both polymers, and the cross-linking density (Figure S5). The measured hardness can range from that of a 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).

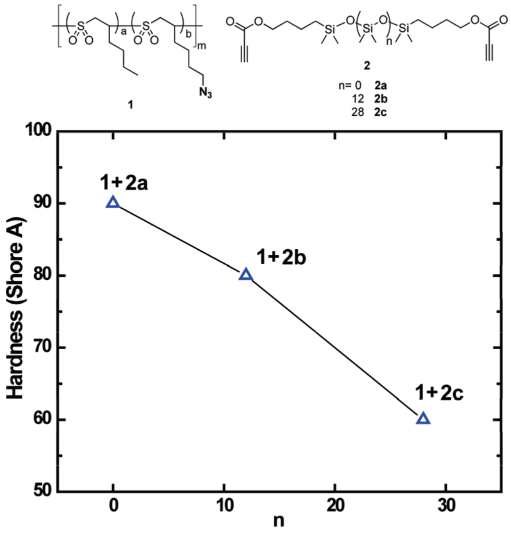


Figure 4. Shore A hardness of composites formed of equimolar mixtures of azide and alkynyl moiety of the respective POS and silicone where the silicone has different lengths. The longer the silicone chain, the lower the measured hardness. This has to do with the incorporation of more flexible linkers in the composite, as the length of the silicone grows.

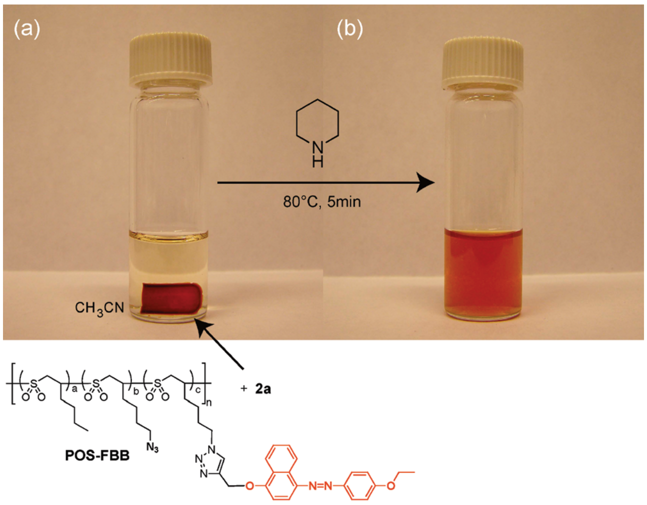


Figure 5. Composite of FBB-tagged azide-containing POS with silicone **2a** (88 wt % of POS−FBB, 12 wt % of **2a**) in acetonitrile solution (a) before base addition and (b) after base addition. Only 5 min at 80 °C is required so that no macroscopic pieces of composite are observable, and the dye is completely leached into the solution.

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 wt % 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 Information Figure S6).

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 cross-linked 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 min in a 0.03 M solution of piperidine in acetonitrile, macroscopic mechanical failure was observed, and no macroscopic pieces of elastomer could be noticed (Figure 5b).

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.

Acknowledgment. We thank the Army Research Office and National Science Foundation for funding.

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, IR spectra of polymer POS **1** and a POS−silicone composite, Shore A hardness values for composites with different compositions and component ratios, detailed synthesis and characterization of dye alkynyl-FBB. This material is available free of charge via the Internet at http://pubs.acs.org.

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