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Exploration of solvent, volume, and catalyst effects on fluoride-catalyzed end-of-life depolymerization of silicones to cyclic monomers†

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Recycling end-of-life silicones is of interest due to the high energy cost associated with producing new materials from virgin raw materials. This work explores the chemical recycling of various commercially available silicone rubbers and fluids using catalytic amounts of tetrabutylammonium fluoride (TBAF) in different solvents and solvent volumes. This method allows for the room-temperature depolymerization of each silicone tested to cyclic siloxane oligomers, with the major product being D_4 siloxane. Suitable sustainable solvents such as ethyl acetate and cyclopentylmethyl ether were identified for the TBAF-catalyzed depolymerization, and the relationship between the solvent volume used in the reaction and the product distribution was determined and optimized, showing a 1 : 10 polymer mass to solvent volume ratio as ideal. The depolymerization was carried out on a large scale using a consumer product and silicone elastomer, and it was found that the cyclic siloxanes could be isolated *via* fractional distillation. The fluoride-induced rearrangement of D_6 siloxane was used to study the reaction kinetics by ^{1}H NMR array experiments. Alternative fluoride catalyst systems were explored which utilized a combination of a phase transfer catalyst, such as polyethylene glycol, and an alkali fluoride salt. These systems were found to convert silicone rubber to cyclic oligomers with product distributions similar to those observed for the TBAF catalyzed process.

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Sustainability spotlight

Silicones are typically made from silicon metal which is made using the carbothermal reduction process which is both energy and greenhouse gas intensive. Taking already made silicone polymers back to useful monomers is a strategy to aid in overcoming the need for extensive and repeated use of this method by giving current polymers a chance to be remade into new materials. Our work explores the use of green solvents such as ethyl acetate and fluoride catalysts, including cost effective and cheap ethylene glycol/alkali salt mixtures, as methods to take commercial silicone polymeric materials back to their cyclic monomeric forms in relatively short periods of time and at room temperature.

Introduction

Silicones have unique physical properties, leading to their extensive use in materials such as sealants, adhesives, coatings, and biomedical materials.[1–3] The production of silicones involves an energy-intensive, multi-step process.[4] The first step is the most demanding and involves the carbothermal reduction of silica to silicon metal, requiring temperatures approaching 2000 °C. These temperatures necessitate electric arc furnaces, requiring 10–15 MWh of electricity per ton of silicon metal produced.[5] In addition to the high energy cost, the carbothermal reduction process also releases 4.7–5 tons of CO/CO_2 per ton of silicon metal produced.[6] Several methods have been proposed to address the energy burden associated with the production of virgin silicones.[4,5,7] One of these strategies is to lower the temperature required for carbothermal reduction. This has been achieved by using rice hull ash as the source of silica in the reduction process. Rice hull ash is a convenient, biogenic silica source that exhibits high porosity. This allows for carbothermal reduction to take place at a lower temperature than for other silica sources, such as quartz sand. The silicon produced from the carbothermal reduction of rice hulls has

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† Electronic supplementary information (ESI) available: ^{1}H, and ^{29}Si NMR spectra, and GC-MS chromatograms supporting the structural characterization of the monomers, polymers, and degradation products discussed in this study. The ESI also includes detailed peak assignments and interpretation of the spectroscopic data. See DOI: https://doi.org/10.1039/d5su00551e

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been found to be of extremely high purity, potentially eliminating the need for further purification steps to reach semiconductor-grade silicon.[8] The treatment of rice hull ash with chlorine at high temperatures has been found to produce silicon tetrachloride in high yield, bypassing the reduction to silicon altogether.[9] While these methods greatly reduce the burden of carbothermal reduction, they do not address the problem of what is to be done with the silicones already in use when they reach their end-of-life. The process of depolymerization involves breaking the siloxane bonds to convert a polymer into monomers/oligomers. These oligomers can then be isolated and purified, if needed, before being used to prepare new silicones.

Depolymerization strategies typically involve the conversion of end-of-life silicones to either chlorosilanes or oligomers, both of which can be used to prepare new silicones. Recently, Vũ *et al.* reported that a combination of BCl_3 and a catalytic amount of $GaCl_3$ results in impressive, near-quantitative yields of chlorosilanes at 40 °C.[10] This method is limited in that it requires a feedstock of BCl_3. Methods proposed by Enthaler allowed for the generation of the desired dichlorodimethylsilane product *via* the action of acid chlorides and various iron(III) salts.[11] The limitations associated with this approach include the need for stoichiometric amounts of the acid chloride and high temperatures.

The depolymerization of siloxanes to cyclic oligomers is an attractive approach, as these cyclics can be readily repolymerized through ring-opening polymerization (ROP) to achieve uniform molecular weight distributions.[12] A graphical representation illustrating the depolymerization of silicones to cyclics can be found in Fig. 1.

Torgunrud *et al.* used hexylene glycol and a base as catalyst to depolymerize PDMS into cyclic silicon acetals. These acetals were then ring opened *via* the addition of an acid catalyst, such as trifluoromethanesulfonic acid, to produce a high molecular weight polymer.[13] Minyaylo *et al.* achieved conversion of silicone fluid to a mixture of cyclic oligomers using ammonia.[14] The major limitation of these techniques is that they require high temperatures. Vu *et al.* utilized a method that involved the complexation of a silanolate salt by a crown ether to depolymerize silicone oils. This method affords high yields of cyclic D-type products at moderate temperatures (>100 °C).[15] This method of reactive distillation allowed for the isolation of pure cyclic siloxane oligomers, which consisted primarily of D_4. The limitation of this technique is that it requires elevated temperatures and is optimized for waste silicone fluids *versus* silicone rubbers.

The depolymerization of silicones using a fluoride source, typically an alkylammonium fluoride salt, is a promising alternative.[16–18] Tetrabutylammonium fluoride (TBAF) was used by Krug *et al.* to recycle thermoset silicone resin coatings.[16] This method, while effective, relies on the high temperatures used during the curing process to remove the TBAF catalyst *via* Hofmann degradation. This process, in addition to requiring temperatures greater than 150 °C, can produce hydrogen fluoride and bifluoride as decomposition products.[19,20] The need for external heating and the production of toxic byproducts is eliminated by quenching the fluoride catalyst with calcium chloride, which was proposed by Rupasinghe *et al.*[17] This method effectively removes fluoride from the reaction *via* its precipitation as calcium fluoride. This quenching step stops the fluoride-induced rearrangement of the siloxane network, allowing for isolation of the products.

Previously, the TBAF catalyzed depolymerization of silicones has only been reported using tetrahydrofuran (THF) as solvent.[16,17] THF poses the problems of being produced through non-sustainable processes and being a known peroxide former.[21] In this work, we present the successful TBAF-catalyzed silicone depolymerization in several different solvents, such as ethyl acetate and cyclopentylmethyl ether (CPME), which are considered green solvents. The product ratios of cyclic oligomers using sustainable solvents were found to be identical to those obtained using THF. This finding has implications for the recycling of mixed waste, as the solvent can be selected based on the intended application and contents of the waste. Fig. 2 shows that this method is effective for the selective depolymerization of silicones in the presence of other plastics.

In this work, we also explore the effect of varying the solvent volume on the product distribution, which consists of the cyclic siloxanes D_4, D_5, and D_6 as well as linear siloxanes. This allowed for the determination of the minimum volume of solvent needed for complete conversion of a starting silicone to cyclic oligomers. This optimized depolymerization system was determined to yield similar products regardless of the commercial silicone rubber/oil used as feedstock.

In an effort to further lower the environmental impact associated with the depolymerization process, we investigated alternative catalyst systems. These systems consisted of various

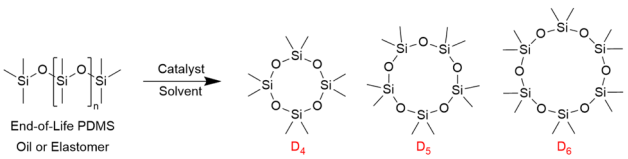

Fig. 1 The catalytic conversion of polydimethylsiloxane (PDMS) to cyclic oligomers.

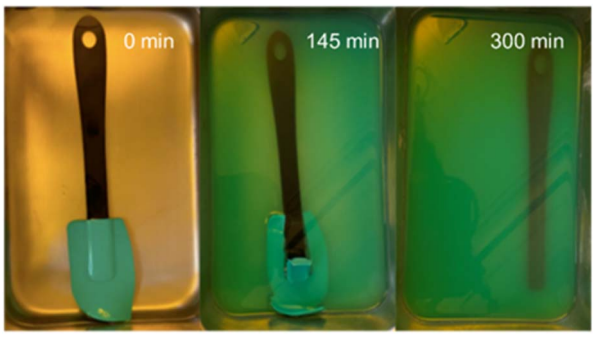

Fig. 2 Images taken throughout the depolymerization of a silicone spatula in methyl ethyl ketone (MEK) and 1 mol% TBAF. The silicone head is dissolved while the plastic handle remains unaffected.

combinations of a phase-transfer catalyst and a fluoride salt. Several suitable phase-transfer catalysts were found to allow for depolymerization, including ethylene glycol (EG), polyethylene glycol (PEG) and 18-crown-6. The depolymerization products were found to be identical to those obtained *via* the TBAF catalyzed methods and were independent of the catalyst system used.

Experimental section

Materials

Solvents used for this study included acetone (Sigma Aldrich), MEK (Fisher Scientific), ethyl acetate (Fisher Scientific), toluene (Sigma Aldrich), diethyl ether (Supelco), CPME (Apollo Scientific), and THF (Supelco). The TBAF catalyst was obtained as both a 1 M solution in THF (Acros Organics) and as the solid trihydrate (Thermo Scientific). Polyethylene glycol (400 & 200 Mn), ethylene glycol (Sigma Aldrich) and 18-crown-6 (Sigma Aldrich) were employed as phase-transfer catalysts in order to solubilize various fluoride salts in organic solvent. These fluoride salts included potassium fluoride (HiMedia) and cesium fluoride (Sigma Aldrich). Anhydrous calcium chloride prills (Macron Fine Chemicals) were used for the quenching step. Acetone-d_6 (Thermo Scientific) and chloroform-*d* (Sigma Aldrich) were solvents for ^{1}H NMR experiments. Tetramethylsilane (Thermo Scientific) was used as an internal standard for ^{29}Si NMR experiments. All reagents were used as received without further purification. The Smooth-Sil 950, Ecoflex 00-30, and OOMOO 30 elastomers were prepared from silicone rubber casting kits, which were obtained from Smooth-On, Inc. GE GE012A All Purpose silicone caulk was received from General Electric, and GP-426 hydroxyl end-blocked silicone fluid was obtained from Genesee Polymers. 6000 Da vinyl end-capped silicone fluid was obtained from Alfa Aesar. Preparation and curing of the relevant silicones were conducted according to the manufacturer's instructions.

General depolymerization procedure

The depolymerization reactions were conducted at room temperature using 0.5 g of the corresponding silicone in each case (except for the 100 g direct scaleup and spatula study). The volume of solvent added corresponded to the desired ratio of silicone mass (g) to solvent volume (mL). For example, the 1 : 1 solvent system consisted of 0.5 g of silicone and 0.5 mL of solvent. The TBAF (or metal-F salt/phase-transfer agent) catalyst was then added to the mixture. Catalyst loading concentrations of 0.5 mol% (34 μL 1 M TBAF) and 5 mol% (340 μL 1 M TBAF or solid as noted) based on starting silicone mass were investigated in this study and were 0.5% unless otherwise noted. The reaction was then capped and allowed to react for 24 h. The reactions were performed in 20 mL glass scintillation vials when the total volume allowed. Upon reaction completion, the reaction was quenched with an excess of calcium chloride (~2 g). The mixture was left over calcium chloride for one day before analysis to ensure complete quenching. The mixture was then centrifuged to allow for facile decanting of the solvent, which contained the depolymerization products (see Fig. S1† for images of the various stages of the depolymerization process). In cases where solvent evaporation was required (>1 : 10), the reaction mixture was washed with a saturated calcium chloride solution followed by deionized water to ensure complete removal of TBAF and TBACl. See ESI† for characterization data and further reaction details.

Analysis techniques

The depolymerization product distributions were identified by ^{29}Si NMR using a Varian INOVA 400 MHz instrument. ^{29}Si spectra were collected at 79.452 MHz with a spectral width of 19870 Hz. ^{1}H NMR spectra were obtained using a Varian INOVA 400 MHz instrument and a Bruker Ultrashield 500 MHz instrument. ^{29}Si NMR spectra were obtained without deuterated solvent, while ^{1}H NMR spectra were obtained using acetone-d_6 and $CDCl_3$. Standard processing was applied to each spectrum, and the product ratios were determined *via* integration using MestReNova NMR processing software. GCMS was conducted on a Shimadzu QP2010 system with Zebron-5HT column. ATR-FTIR spectra were obtained on a Thermo Scientific Nicolet IS5 with an integrated ID7 ZnSe ATR. TGA experiments were performed using a Hitachi STA7200 thermal analysis system in air from 25–1000 °C at 10 °C min^{-1}.

Results and discussion

Solvent study

The volume of solvent used for the depolymerization was varied, and the corresponding soluble portion of the products was identified by ^{29}Si NMR. The bulk of the insoluble products were determined to be silica and any dyes/pigments incorporated into the original elastomers (Fig. S2 and S3†). The depolymerization products vary significantly in THF, as shown in Fig. 3. It

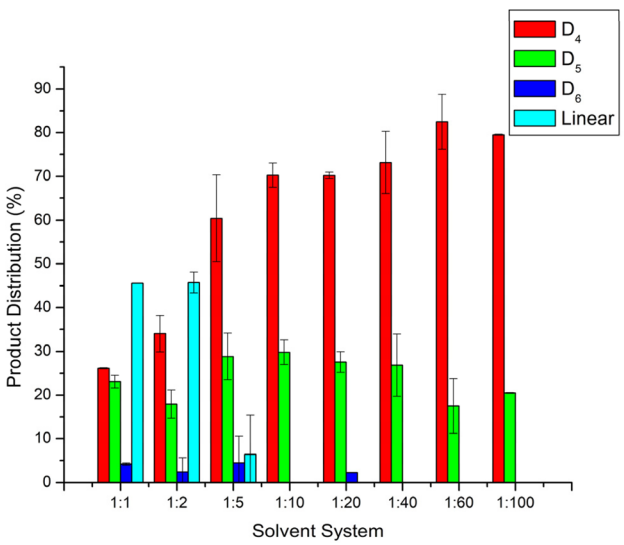

Fig. 3 Depolymerization products of Smooth-Sil 950 in select polymer : solvent ratios with THF as solvent, as identified by ^{29}Si NMR (Tables S4–S7† and Fig. S8–S23†).

was found that long-chain linear siloxanes were the dominating products when minimal solvent was added to the reaction mixture. The addition of a larger volume of solvent was accompanied by a decrease in linear products and an increase in the percentage of D_4 produced. The percentage of D_5 and D_6 produced in the reaction remained relatively unchanged. It was found that the 1 : 10 solvent system was optimal, as it corresponded to the minimum volume of solvent needed to eliminate linear siloxane products in most cases, achieving a yield of exclusively cyclic siloxanes.

Several commercially available silicone rubbers were subjected to depolymerization using the 1 : 10 solvent system to identify any differences in product distribution. Smooth-Sil 950 (Shore Hardness 50A) and Ecoflex (Shore Hardness 00–30) silicone rubbers were chosen as the platinum-cured rubbers in this study. OOMOO 30 (Shore Hardness 30A) was selected to represent tin-cured elastomers, and GE012A silicone caulk (Shore Hardness 25A) was chosen to represent a water-cured, methyltriacetoxysilane-based system. The hydroxyl-terminated GP-426 silicone fluid (100 cSt at 25 °C) was also used in this study.

The depolymerization was found to proceed to completion regardless of the type of silicone used. The product distribution remained unchanged for the various silicone rubbers, as shown in Fig. 4. The bulk of the products consisted of D_4 and D_5, with minimal amounts of D_6 and linear siloxanes being produced in some cases.

Following the successful results observed for the depolymerization of commercial silicones, an array of solvents was tested for compatibility with the reaction. The solvents that were found to be suitable for the TBAF-catalyzed depolymerization and their respective products can be found in Table 1. Further studies with mixed solvents can be observed in Table S30.† It was found that the apparent rate of depolymerization in 2-butanone (MEK) rivaled the depolymerization observed when using THF as solvent, suggesting a non-peroxide forming, and more industrially friendly solvent system for the depolymerization process. Depolymerization was also found to occur at a sufficient speed when ethyl acetate was used as a solvent. Substituting acetone for the reaction solvent resulted in significantly longer reaction times. The approximate time necessary for complete depolymerization of 0.5 g of silicone was one day in acetone compared to less than an hour using MEK or THF. The apparent reaction rate was observed to proceed more rapidly with a reduced solvent volume as well as a higher catalyst loading. Adopting mixed solvent systems resulted in varying degrees of success but were not advantageous over single solvents in conversion processes.

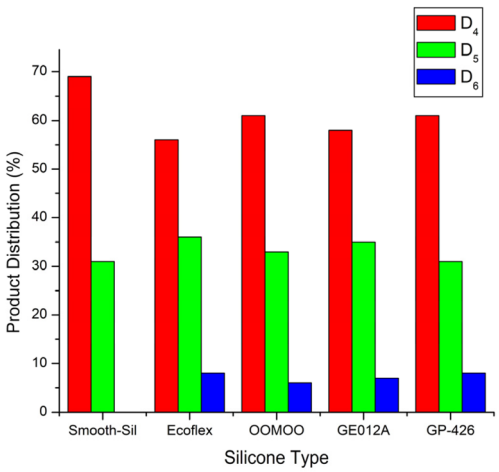

Fig. 4 Depolymerization products of various commercial silicones for the 1 : 10 solvent system using ethyl acetate as solvent (Table S24† and Fig. S25–S29†).

Table 1 Smooth-Sil 950 depolymerization products in various solvents using the 1 : 10 solvent system. (Fig. S31–S35)

Solvent	D_4	D_5	TBAF (mol%)
Diethyl ether	78	22	0.5
THF	72	28	5.0
CPME	70	30	0.5
Ethyl acetate	69	31	5.0
Toluene	69	31	5.0
Acetone	68	32	0.5
MEK	63	37	0.5

Large scale reaction

The depolymerization of Ecoflex 00-30 was conducted on a 100 g scale using 0.5 mol% TBAF and 1L of ethyl acetate as solvent (1 : 10 solvent system). The mixture was stirred for 24 hours, although the polymer mass appeared dissolved entirely within the first hour of the reaction. The reaction was quenched with an excess of calcium chloride and left to stir for two days. The solution was then extracted with 300 mL of deionized water three times to remove TBACl and $CaCl_2$/CaF_2 completely. The organic layer was collected, and the solvent was gently removed by rotary evaporation, recovering the solvent. After solvent evaporation, the contents remaining in the flask consisted of the depolymerization products and silica particles. The volatile products were isolated *via* fractional vacuum distillation with the setup shown in Fig. S36.† The composition of the distillate was analyzed *via* ^{29}Si NMR. (Fig. S37–S45†) The product distribution and total yield for each fraction can be found in Table 2. Products labeled "Other" owe their ^{29}Si NMR signals to trimethyl-terminated capping groups.

The isolation of D_4 siloxane proved facile due to its low boiling point under vacuum, which was just over room temperature. The collected D_4 was observed to crystallize upon contact with the chilled receiving vessel held at 0 °C in an ice bath. The significant difference in the boiling points of D_4 and D_5 also made it possible to collect a fraction of pure D_5 after D_4 had finished distilling over. The isolation of pure D_6 proved challenging, as D_6-containing fractions were always observed to contain residual D_5. The highest boiling fraction was found to be devoid of any cyclic products and consisted primarily of linear siloxanes. This fraction comprised 10% by mass of the yield of distillable products. End group analysis utilizing the

Table 2 Boiling ranges, recovered masses, and determined product distributions for the fractions collected

Fraction	Boiling range (°C)	Mass (g)	D_4 (%)	D_5 (%)	D_6 (%)	Linear (%)	Other (%)
1	23–39	23.3	100	—	—	—	—
2	41–50	16.0	—	100	—	—	—
3	50–55	1.5	—	78	18	—	4
4	55–63	1.5	—	65	30	—	5
5	63–67	0.9	—	28	64	—	8
6	67–70	1.0	—	14	80	—	6
7	>70	5.0	—	—	—	86	14

^{29}Si NMR spectrum for this fraction indicated an average molecular weight of approximately 925 g mol^{-1} for the linear products identified in fraction 7 (Fig. S45, eqn (S46)–(S47)†). The viscosity of this silicone oil was measured to be 7 cSt at 20 °C, which corresponded well with the determined molecular weight.[22] For practical application this process can be used to strip D_4 and the remainder further rearranged itself or with new silicone to produce more D_4.

Rearrangement of cyclics

To better understand equilibration in these systems, we used a model system starting with D_4, D_6, and vinyl-capped linear silicone to study the redistribution of cyclic structures or depolymerization from polymer. Initial trials with the linear silicone were difficult to follow clearly (Fig. S48†), so the cyclics rearrangement was favored to follow the process.[23] The previously observed trend of the products shifting to D_4 as the reaction volume increases was also observed for the TBAF-induced rearrangement of cyclic siloxanes. The product distributions for the rearrangement of the cyclics were very similar to those observed for the depolymerization of commercial silicones. The rearrangement of D_4 using a 1 : 10 solvent system caused a shift to 51% D_4, 32% D_5, and 17% D_6 (Fig. S49†). The same rearrangement on D_6 resulted in a change to 64% D_4 and 36% D_5 (Fig. S50†). The rearrangement of D_6 was studied *via* ^{1}H NMR, and the products were identified by ^{29}Si NMR. These results can be found in Fig. 5. An increase in the D_4 peak area accompanies the steady decrease in peak area observed for the D_6 peak. The reaction was completed after approximately 37 minutes, as indicated by the no longer changing peak areas.

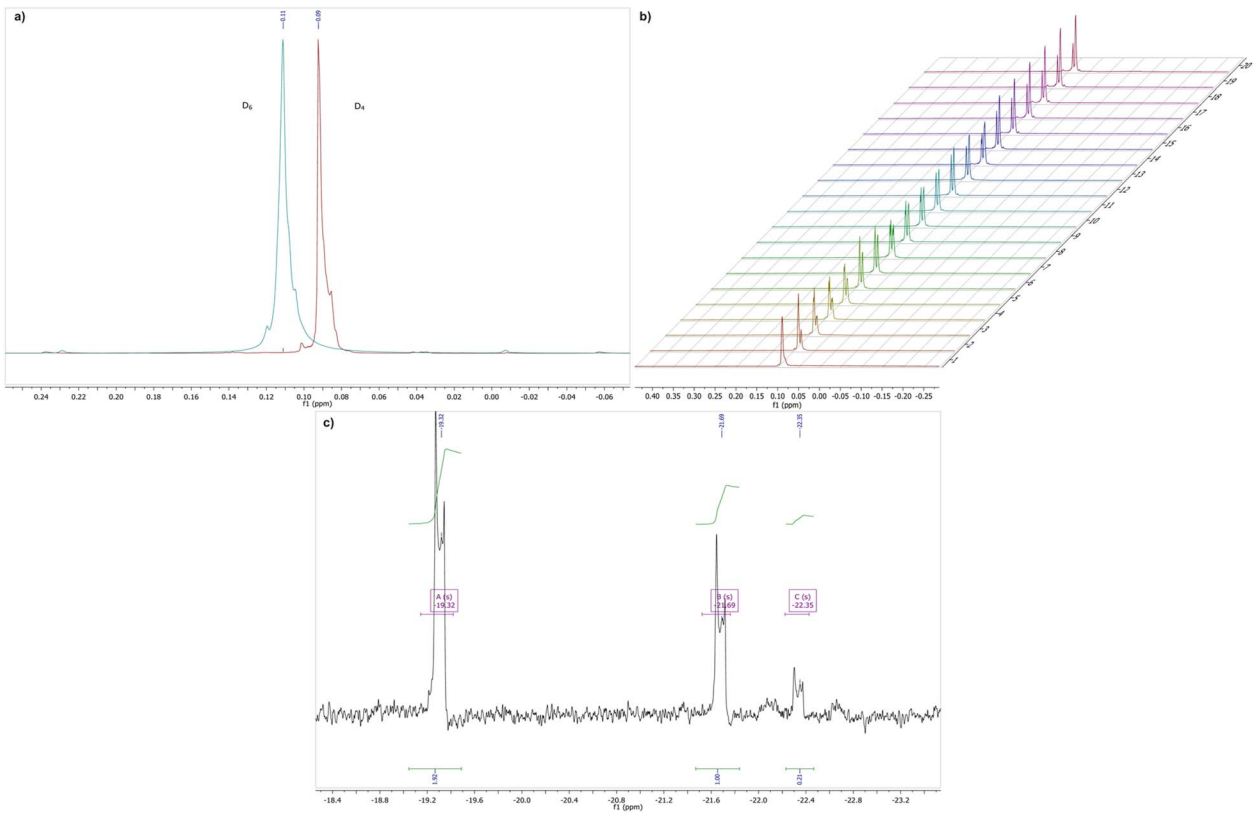

Fig. 5 (a) Reference ^{1}H NMR spectra of D_4 and D_6 in acetone-d_6, (b) ^{1}H NMR array experiment following the rearrangement (1 : 10) of D_6 over 50 minutes at −5 °C, (c) ^{29}Si NMR spectrum of the products of this rearrangement showing D_4 (A), D_5 (B) and D_6 (C).

The addition of 0.5 mol% TBAF to neat D_4 resulted in the formation of a highly viscous, nearly gel-like resin.[24] The results indicate that, in the absence of solvent, D_4 rearranges to form predominantly long-chain linear siloxanes (Fig. S51†). The viscous mass dissolved with added solvent and reformed upon solvent evaporation, highlighting the reversibility of this conversion between cyclic and linear siloxanes. A similar observation was made when tetramethylammonium silanolate was incorporated into a siloxane polymer to create a "living network" capable of self-healing.[25]

Temperature study

The depolymerization reaction was conducted at various temperatures to investigate the effect on the product distribution. Toluene was the solvent of choice in these trials, with a 1 : 10 ratio of polymer mass to solvent volume being used. The temperature was held constant, including during the quenching step, to ensure that the products did not re-equilibrate upon being brought back to room temperature. The appreciable thermal decomposition of TBAF at elevated temperatures limited the experiment to relatively mild heating.[26] It was found that the product distribution for the reaction performed at 60 °C did not differ significantly from that observed at room temperature (Fig. S52†). However, the dissolution of the polymer appeared to occur relatively faster at 60 °C, with no visible polymer remaining after 30 minutes. The depolymerization at −20 °C was extremely slow, with large pieces of silicone still visible after one week. The products of the low temperature depolymerization consisted primarily of linear siloxanes (92%) with a small fraction of D_4 (8%). (Fig. S53†) The linear siloxanes in this case were attributed to the soluble fraction rather than depolymerization products (Fig. S54–S58†).

Attempts were made to follow the reaction over time using ^{29}Si NMR and ^{19}F NMR but were unsuccessful. Problems were also encountered with overlapping peaks in ^{1}H NMR. Fortunately, it was discovered that the ^{1}H NMR signal associated with D_6 could be discerned clearly from those of the other cyclics. The TBAF-catalyzed rearrangement of D_6 was then used to mimic the depolymerization procedure in several ^{1}H NMR kinetic array experiments. In each case, 50 mg of D_6 was added to an NMR tube, followed by 0.5 mL of acetone-d_6 (1 : 10 system). A small volume (4 μL) of TBAF was added to the tube, and the measurement was promptly started. The depletion of D_6 over time is shown in Fig. 6.

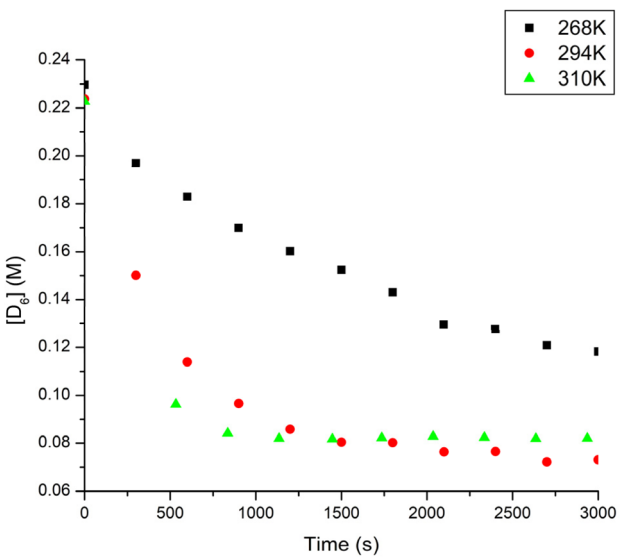

Fig. 6 The depletion of D_6 siloxane over time due to fluoride-induced rearrangement.

Table 3 Calculated first-order initial rate constants for the depletion of D_6 in the fluoride-catalyzed rearrangement

Temp. (°C)	k_0 (s^{-1})
−5	2.0×10^{-4}
20	9.0×10^{-4}
37	2.7×10^{-3}

At temperatures approaching room temperature, the rearrangement process rapidly reaches equilibrium. At room temperature, the fluoride-catalyzed rearrangement of D_6 is practically complete within the first 25 minutes following TBAF addition. Equilibration time was reduced to less than 15 minutes by heating the reaction to 37 °C. Further testing at higher temperatures was limited by the relatively low boiling point of acetone-d_6, which was used as a solvent. It was observed that the time required for equilibration was increased to beyond 50 minutes by cooling the reaction to around −5 °C. The initial rate constants (k_0) were calculated for the rearrangement of D_6 and can be found in Table 3 below (Fig. S59–S61†).

Depolymerization with alternative catalysts

To further try to improve the sustainability of silicone depolymerization, alternative fluoride catalyst systems were used. The depolymerization of Smooth-Sil 950 was conducted using several combinations of a phase-transfer catalyst and a fluoride salt. These phase-transfer catalysts included EG, PEG (Mn = 200 & Mn = 400), 18-crown-6, and poly(vinylpyrrolidinone, PVP). The fluoride salts tested included KF, CsF, NaF, LiF, and CaF_2. A catalyst loading of 0.5 mol% was used for both the phase-transfer catalyst and the fluoride salt, with later experiments at 3–5 mol% giving higher conversion rates (Fig. S70–S74†). Experiments were performed using ethyl acetate and MEK as solvent. The 1 : 10 ratio of polymer mass to solvent volume was used in each experiment.

In every case, the reaction was found to occur significantly slower than the TBAF catalyzed reaction. The product distributions for the various phase-transfer catalyst trials can be found in Fig. 7 below.

The depolymerization was found to proceed much more quickly in MEK than in ethyl acetate. It was found that when 18-crown-6 was used in combination with KF, the reaction proceeded to completion over the course of several days in MEK. When the phase-transfer catalyst was changed to PEG-400, the reaction took several weeks to reach completion. When CsF was used in place of KF, the PEG-400 catalyzed reaction occurred

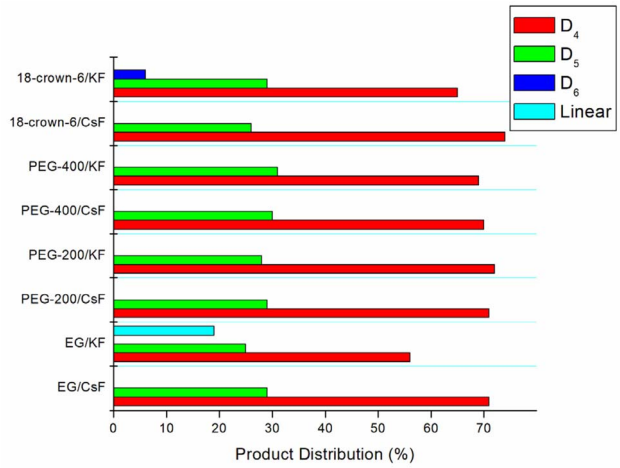

Fig. 7 Smooth-Sil 950 depolymerization products in MEK as determined by ^{29}Si NMR. (Fig. S62–S69†).

much faster than the 18-crown-6 catalyzed reaction. The overall improved reactivity observed for the CsF trials can likely be attributed to the expected greater solubility of CsF in organic solvent in the presence of a phase-transfer catalyst.[27] The depolymerization using PEG-200 took approximately one month to reach completion. When EG was used, the depolymerization appeared to become stalled after several months. This indicates that, in order to achieve timely depolymerization, the PEG phase-transfer catalyst must have an average molecular weight greater than 200 g mol^{-1}. Attempts with PVP 10,000 g mol^{-1} as the phase transfer agent failed to yield silicone depolymerization.

When the catalyst loading was increased to 3 mol%, the depolymerization was observed to occur much faster for PEG systems. Note that studies in which CaF_2, NaF or LiF were used as the fluoride source in conjunction with the phase-transfer catalysts above resulted in negligible depolymerization over 1 month. In all cases of metal-F salts no depolymerization was observed without a phase-transfer agent.

Conclusions

The dependency of the product distribution of the TBAF-catalyzed depolymerization on starting silicone mass and solvent volume was identified. Understanding this relationship made it possible to optimize the reaction conditions to allow for maximum D_4 production (up to 78%) while minimizing the volume of solvent required to a 1 : 10 polymer to solvent ratio. Several solvents were identified as capable of replacing THF in depolymerization, including the more sustainable solvents CPME and ethyl acetate. The product distributions remained relatively constant regardless of the solvent used or catalyst loading, suggesting that solvent plays a minor role in the cyclization process, *versus* the importance in the swelling/solubilization of catalyst/polymer intermediates. Alternative catalyst systems were identified which involved the combination of a phase-transfer catalyst and a fluoride salt. The system of PEG-400/CsF in MEK was found to allow for timely depolymerization of commercial platinum-cured silicone, albeit at a slower rate than that observed for the TBAF catalyzed system.

The cyclic siloxane reaction products were successfully isolated on a 100 g scale *via* fractional vacuum distillation. The determined average molecular weight and viscosity for the high-boiling silicone fluid fraction were determined to be reasonable when compared to known values for trimethyl-terminated PDMS oil.[22]

The action of TBAF on the cyclics themselves resulted in an equilibration between ring sizes, similar to the results observed in the depolymerization product distributions. Performing this rearrangement in solventless conditions or by completely evaporating the solvent resulted in the product distribution shifting to linear siloxane products.

This work demonstrates a step forward in developing sustainable methods of silicone recycling by using green solvents and readily scalable catalysts to lower the environmental costs of both producing and recycling silicone-based materials.

Data availability

All data supporting the findings of this study are available within the article and its ESI.† Additional raw data or materials can be provided by the corresponding author upon reasonable request.

Author contributions

Andrew C. Deller – Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, United States – conducted the kinetic model, temperature studies, and wrote manuscript. Herenia Espitia Armenta – Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, United States – Current: Danish Technical University, Lyngby, Denmark – conducted the mixed plastic studies and some of the solvent system studies. E. A. Kalani D. Edirisinghe – Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, United States – Current: Johnson and Johnson MedTech Inc., Raritan, New Jersey, United States, – conducted the original studies on the various solvent systems and ratios explored in this study. Mitchel E. Deller – Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, United States, – conducted depolymerization studies using phase-transfer catalysts. Aided in the preparation of silicone samples and performing replicate experiments. Kristan L. Major – Department of Agricultural and Life Sciences, Central State University, Wilberforce, Ohio 45383, United States, – aided in the preparation of silicone samples and exploration of heating and catalyst methodologies. Buddhima Rupasinghe – Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, United States, Current: Eurofins Inc., Kalamazoo, MI,

United States, – acted in a consulting role on these studies to help guide experiments.

Conflicts of interest

Joseph C. Furgal and Buddhima Rupasinghe retain a financial interest in this work through US 2024/0117143 A1.

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