International Journal of
Engineering in Computer Science

E-ISSN: 2663-3590
P-ISSN: 2663-3582
www.computersciencejournals.com/ijecs
IJECS 2024; 6(1): 216-227
Received: 21-08-2024
Accepted: 26-09-2024

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Transforming silicone waste: Depolymerization and polymerization strategies for recycling

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DOI: https://doi.org/10.33545/26633582.2024.v6.i2c.145

Abstract

Because of their structure, siloxane polymers are a valuable industrial commodity (R2-Si-O)-Because it is the initial stage in the breaking down macromolecules into tiny pieces so they can potentially be recycled, scission of the siloxane link is crucial. These extremely condition-specific reactions, which have been thoroughly investigated over the past 80 years, selectively initiate whether polymerization or breakdowns take place. The length of the backbone, the attached side groups, and the crosslinking ratio are responsible for giving the different types of silicones (Resins, fluids, or elastomers) their distinct properties. However, the environmental concerns surrounding polymer waste have increased, and so, an effective waste management has become necessary, with recycling being a key solution Studies on recycling siloxanes are still in their early stages, though. Using carbothermal reduction, traditional techniques of synthesizing silicones are quite expensive and capital intensive. The excessive release of pollutants and greenhouse gasses like CO_2 into the atmosphere is the result of these interactions. It is therefore highly desired to be able to recycle and reuse them in a meaningful way. Because of this, siloxane researchers have been working toward developing methods to deliberately break the siloxane bond into recognized compounds since the 1950s. The primary methods for introducing the siloxane's scission include hydrolysis, catalytic depolymerization, thermal depolymerization, and radical extractions link, giving rise to a variety of compounds such as cyclics, monomeric silanes, and novel polymers. This review compiles information that has been published up to May 2024 regarding the breakdown and depolymerization of polysiloxanes.

Keywords: Polysiloxanes, silicone, elastomers, recycling, depolymerization, reversion

Introduction

Silicone polymers find extensive usage in various applications, such as lubricants, electronics, medicinal formulations, automotive and construction parts, and engineering items [1-2]. Over 8 million tons of silicones were produced worldwide in 2020, with a fifteen billion dollars in US dollars value. Silicone polymers are made up of Si-O-Si units bonded to extremely durable backbones. The bond angle of Si-O-Si is broader than that of carbon counterparts, and Si-O bonds are longer than C-O bonds. As a result, these materials are extremely flexible, thermally stable, and mostly chemically inert (Apart from strong acids and bases) [3]. It is now strategically crucial to recycle these valuable inorganic polymers for both environmental and financial reasons.

The most significant silicone product is polydimethylsiloxane (PDMS). The majority of them are created by hydrolyzing chlorosilanes that are made using the "Rochow direct process". This is followed by the polymerization of the related generated cyclic monomers (mostly D3 and D4) with a basic catalytic present [4-6].

Even though silicon (Si) is a plentiful element in the crust of the Earth, producing the metal grade Si required for the "direct process" requires a very high temperature (>1400 °C) and a lot of energy. Additionally, a significant amount of greenhouse gases that are harmful to our environment are released during the process [7-8]. Thus, recycling polydimethylsiloxanes that are out-of-specification or at the end of their useful life to create value-added compounds like cyclic monomers or functional oligomers has become a highly desired and potentially sustainable alternative.

The recycling of silicone materials and polymers is still restricted and mostly consists of limited chemical recycling or down cycling by mechanical processing (e.g., powdered waste elastomers).

Although there are chemical recycling techniques that use halogenated reagents, they are only applicable to products that are produced outside of the silicone process as a whole and fall outside the purview of silicone circularity. The majority of back-to-monomer chemical recycling techniques and the related commercial processes depend on quite high "catalytic" concentrations of alkaline hydroxides, raising concerns about how effective catalysis is [9-10] or powerful acids, both inorganic and organic in nature. Therefore, in order to support a broader application of silicone chemical recycling within the context of silicone circularity, catalytic upgrading is desperately needed. Over the past 80 years, a lot of research has been done on the chemical recycling of waste silicones [11]. On the one hand, a mixture of cyclosiloxanes (D3-D8) favoring small cyclic monomers is produced by the reaction at 600 °C. Conversely, when thermal cracking occurs in air at 300 °C, the main products that are produced are silica and CO_2. Additionally, steam might be employed as a catalyst to change polysiloxanes into (Oligo) silanols at a high temperature.

The goal of this research is to depolymerize crosslinked silicone rubber that has been cured at room temperature by using the reversion process. After which it can be repolymerized to create a valuable recyclable material.

Objective

1. Recycling is the process of gathering spent materials, disassembling them into waste products, and preparing them for reuse. This substitute reduces energy and production costs in addition to reducing the quantity of garbage that ends up in landfills. Lower expenses and minimize the damaging impact of virgin material mining and utilization on the natural world.
2. In the modern world, recycling polymers is essential because of their high consumption, which means that their production is unlikely to decline anytime soon, and since they often take decades to decompose in the environment due to their non-biodegradable nature substance. Since silicones are one of the polymers whose consumption is steadily increasing, it is essential to create recycling techniques for them. Since silicones are thermosets, they cannot be recycled mechanically, unlike thermoplastics. Reprocessing this polymer into new items requires breaking the chemical bonds that were created intra-and/or between chains during the curing process. An intriguing recycling path it is by going backward.
3. The first step in using depolymerization on an industrial scale is to comprehend the criteria that must be met therefore, in order to design a protocol for the process, the goals of this study are to gain a better understanding of the reversion circumstances of a room temperature vulcanized silicone elastomer. Next, the silicone should be repolymerized in order to recover a useable recycled material. Analyzing the differences between the recycled and original products will be created by testing for edema and mechanical issues. Rheology and SEC will also be used to define the products that result from reversion.

General Information about Silicone

The silicones are mineral-based polymers whose fundamental structure consists of polyorganosiloxanes, in which silicon atoms are joined to oxygen atoms to form a bond known as a siloxane. This alternating silicon-oxygen backbone can be connected to many functional groups, including hydrides, alkyls, vinyls, and aryls, which are what give each silicone its unique characteristics. The majority of silicone goods sold in the market are derived from a single polymer system called polydimethylsiloxane, or PDMS, which alternates the siloxane bond. i.e., a recurrent unit of the main polymer chain, where every silicon atom is connected to both methyl groups.

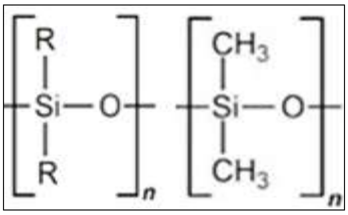


Fig 1: Chemical structure of silicone

It is feasible to distinguish between them based on the quantity of bonds that one silicon atom from the main chain has with oxygen. According to fig 1, there are four different kinds of polysiloxane structural units: M stands for monofunctional, D for difunctional, T for trifunctional, and Q for tetrafunctional. Different kinds of materials are created by combining these various architectures. Like the oils, resins, and elastomers (Rubbers) [13]. The structural arrangement of silicone chains-whether they are branching, cyclic, linear, or cross-linked-is one method used to categorize them. Nonetheless, their physicochemical characteristics are the most often used method of classification. There are three distinct categories: elastomers, resins, and fluids [14]. The fluids have modest to high molecular weight chains that are linear or slightly branched. Since their viscosity rises with the degree of polycondensation, they can be separated into gels, oils, and rubber. When a chemical agent is added, the elastomers' linear chains are joined by covalent or ionic bonds; this process is known as cross linking or vulcanization.

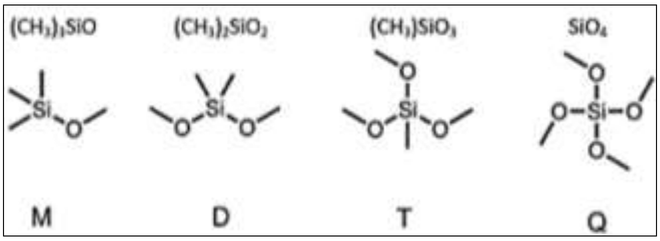


Fig 2: Siloxane structural units

The elastomers can be classified as HTV (high temperature vulcanization) or RTV (room temperature) depending on the temperature at which this process occurs vulcanization. The characteristics of this kind of silicone are determined by the length of the chains and the quantity of cross links created.

Additionally, the silicone resins are cross-linked. Because of the many T and Q units, they have a three-dimensional branched chain structure. The groups bound to the silicon atom significantly impact the properties of the resin.

Both the resins and the elastomers are designed as intricate multi-component systems (Figure 3), to which fillers and additives can be added to guarantee particular qualities (Color, rheology, etc.) and to reinforce the material, for instance.

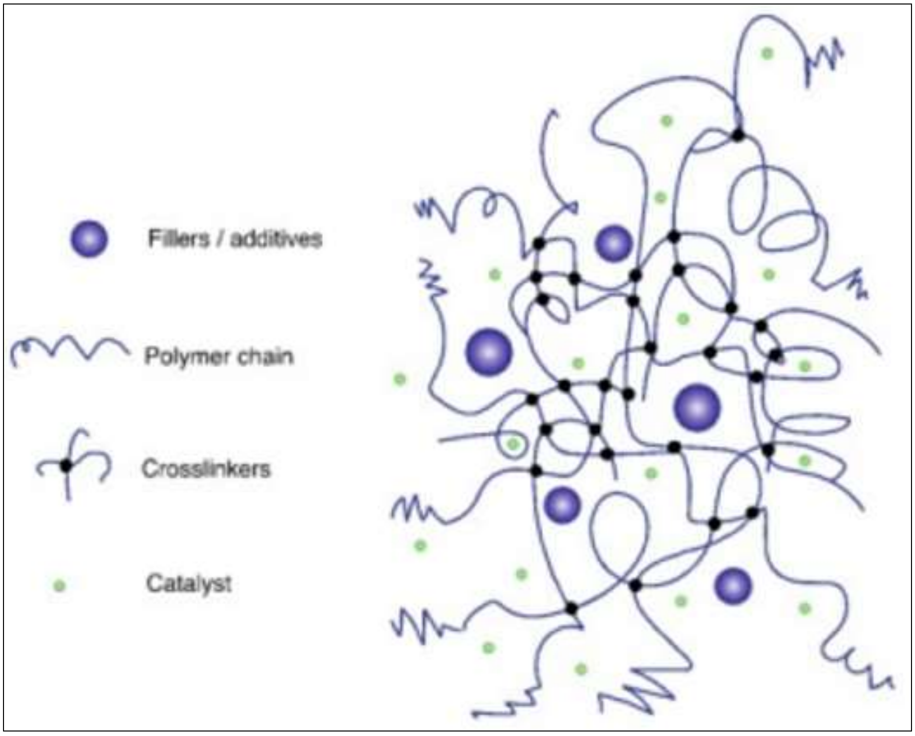
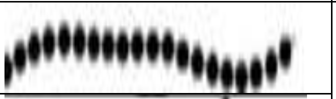
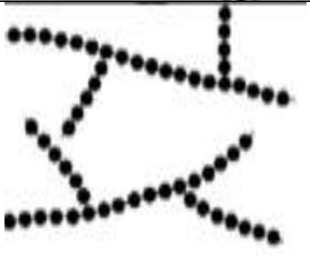
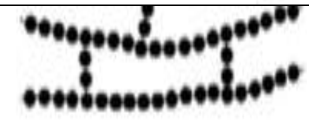
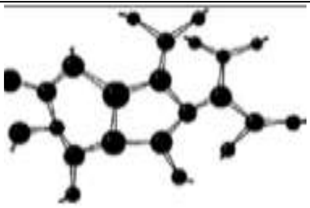


Fig 3: Multicomponent network of a silicone elastomer

Both the many classes and their schematical structure are visible.

Table 1: Silicone classification and structure

Chain organization classification	Schematic structure	Physicochemical classification
Linear silicone		Fluid
Branched silicone		
Cross-linked silicone		Elastomer
		Resin

Properties and Application

In numerous industrial and household applications, polysiloxanes are the preferred material due to their remarkable characteristics and excellent modifiability. These characteristics will vary depending on the kind of silicone, fluid, elastomer, or resin, but there are some common characteristics that are offered by the silicon-rich skeleton and the Si-O backbone. For instance, the inorganic sequence Si-O-si is polarized and extremely strong, with a bond energy of 452 kj/mol. This is caused by the difference in electronegativity between the oxygen (3, 44) and silicon (1, 90), which results in very good chemical inertia, thermal stability (With a temperature range of -100 to 250 °C), and resistance to aging (Oxidation, hydrolysis, ozonolysis, and photo-dissociation). Large Si-O-Si bond valence angles, long Si-O interatomic distances, and the lack of oxygen atom substituents result in a mobile and flexible chain with low temperature evolution, an unusually low glass transition temperature (Around -120 °C), elastic-like behavior, and relatively high gas permeability. Additionally, processing is made easier by the organic groups bonded to silicon by Si-C bonds and enhances the qualities that make it water repellent. The low surface tension, electrical isolation, and non-toxicity of polysiloxanes are also well-known attributes. Chemically, the fundamental characteristics of silicone can be enhanced by adding various organic groups, fillers like titanium oxide and carbon black, or additions like silicates, fumed silica and silicon metal oxides, as previously described.

The aforementioned has led to the widespread usage of silicones in a wide range of applications, as table 1 illustrates.

Table 2: Usage of silicones in a wide range of applications

Properties	Physico-chemical characteristics	Area & Example
Anti-Forming	Lower surface tension	Industrial process
Flexibility	Very flexible o-si-o bonds,	All types of seals
Low in flammability	Melting point: 205 ˚C to 260 °C	Automotive, Construction, Seals
Volatility	Extremely low to high molecular weight vice versa	Pharmaceutical, cosmotics
Electrical isolation	Non polar macromolecules	Automotive, Construction, High voltage lines, engine ignition circuits
Lubrication	Branched macromolecules	Lubricants (Oil, Fats)
Surfactants	Decrease of surface tensions of substractes	Textiles, Automoblie, Polish
Hydrophobicity	Low surface tension & Presence of methyl groups; water repellency, Permeability to gases & water vapour	Construction, Textile
Weather resistance	Methyl absorption below 300 nm (UV stability)	Car seals;

Recycling of Polysiloxane

Mechanical Recycling

Nowadays, mechanical reuse, occasionally referred to as bodily waste disposal, is the most prevalent way of reclaiming monomers due to its dependable nature and cost [13]. Cleaning, sanitation, thawing, sanding, melting, and converting the material into a secondary element for a new use are the steps involved. Nevertheless, as previously mentioned sections clarify, thermosets silicones, for example, cannot be melted without disintegrating.

However, a few research still employ actual recovery for silicones. After being reduced to a powder, the rubber is added back to chemically related polymers as a filler [14-17]. The Maximum fluidity and scorching period of time, flex density, and activation force for turbulent flow, for instance, increased when silicone rubber powder was added, according to Ghosh *et al*. (2003). Moreover, the usage of up to 60 phr of powder generated acceptable reductions in tear and tensile strengths relative to the reference rubber [15]. For carpeting applications, Machado *et al*. (2020) combined recycled silicone rubber with styrene-butadiene rubber (SBR) as a filler. When compared to the pure rubbers for the application examined in the research, the virgin compounds of both materials did not significantly change when up to 30 hours of recycled silicone was added [16].

Thermal and Chemical Recycling

The method of thermally recovering silicone substances entails burning the matter to create gas and liberate fillers for other uses. Due to the great temperature strength of silicone for comfort this technique requires a lot of power and releases unwanted greenhouse gases when all of the natural components of the polymer, including -CH3 in PDMS, break down into carbon dioxide.

Despite the fact that siloxanes are structurally and chemically inert polymers up to 350 °C, it has been established that powerful bases or acids as well as specific kinds of enzymes can disrupt the Si-O bonds [17]. One break is sufficient to begin the deterioration process in linear siloxane systems; in contrast, three-dimensional siloxane systems require at least two broken bonds to begin the degradation process. The coupling of the M, D, T, and Q units with the SI-O backbone, which is where the degradation mostly takes place, is extremely important to the breakdown of the polymeric siloxane materials. However, it can also happen on substitute atoms or groups, such as Si-C bonds, both of which lead to lower molecular weight products [18]. One break is sufficient to begin the deterioration process in linear siloxane systems; in contrast, three-dimensional siloxane systems require at least two broken bonds to begin the degradation process. The polymeric siloxane materials' ability to break down is mostly based on the interaction between the M, D, T, and Q units and the Si-O backbone, which is the primary site of degradation. However, it can also happen on the substituent groups or atoms in SI-C bonds, both of which lead to lower molecular weight products.

Some of the processes of breakage of siloxane bonds such as radical scission and calcination, thermal depolymerization and catalytic or non-catalytic depolymerization in different ranges of temperature, are show in below these processes will be further discussed in the following sections.

Depending on the reaction environment and the degradation mechanism, several siloxane degradation products may result. Nevertheless, cyclic monomers like the ones seen in figure D6, D5, D6, octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and hexamethylcyclotrisiloxane (D3) are the typical ones, according to several sources.

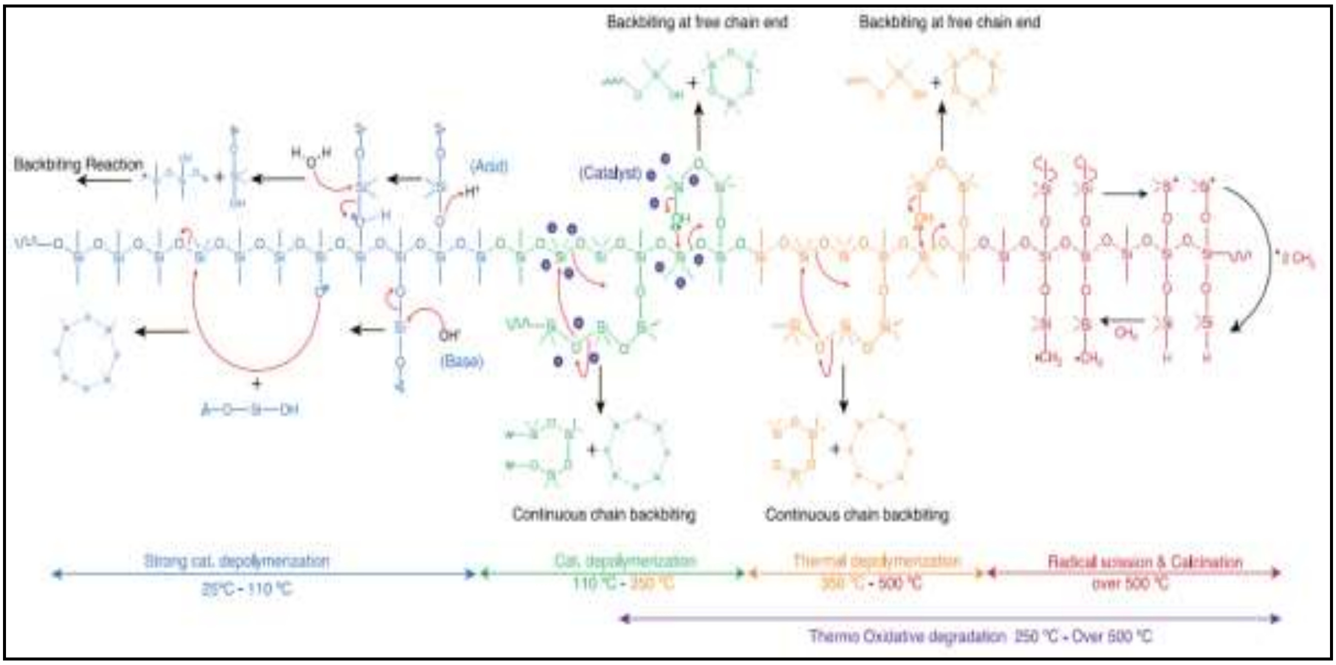


Fig 4: Siloxane bonds breakdown processes by various mechanisms

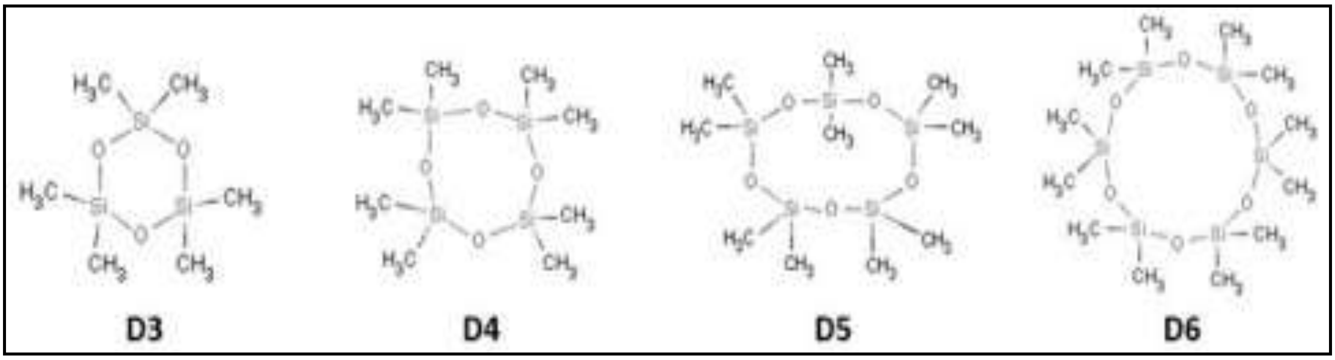


Fig 5: Typical products of the siloxane degradation

Thermal Degradation and Radical Scission Reaction Over 350 °C

Since heat is decline the oldest, it has been studied the most when it comes to depolymerizing polysiloxanes. At temperatures above 350 °C, this phenomenon occurs, and it can be explained by two opposing mechanisms. A radical and molecular mechanism.

The first one creates cyclic siloxanes by a catalytic depolymerization process. The second one is the scission of Si-C bonds through homolytic cleavage, which is seen at higher temperatures and rapid heating and results in the creation of oligomers and methane through hydrogen absorption. Both mechanisms can be seen in the figures 5 & 6 below.

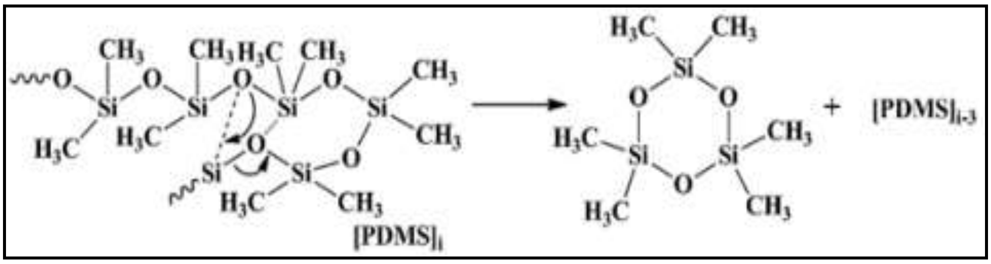


Fig 6: Mechanism for the formation of cyclic oligomers through catalytic depolymerisation

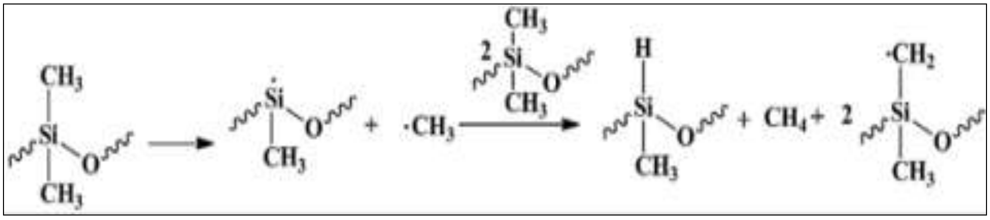


Fig 7: Si-C bonds scission mechanism resulting in oligomers and methane

The products that are produced will also be influenced by the surroundings in which the reaction occurs. In an inert atmosphere, PDMS completely depolymerizes into cyclic-siloxane at temperatures below 600 °C, favoring smaller cycles; at temperatures above 300 °C, silica and CO_2 are seen to be the main products in the air [19].

Although it has been demonstrated that thermal deterioration and radical scission are feasible, they necessitate high temperatures and are energy-intensive processes, which make them unfeasible for large-scale applications from an economic or environmental standpoint.

Some investigator investigated a number of heated deterioration tests of PDMS, PMPS, and polydiphenylsiloxane, in a cloud of nitrogen under temperature-programmed settings (10 °C min−1 under vacuum), in order to determine how heat depolymerization occurs (Since there are two primary viewpoints) [44-45].

They discovered that the degradation products are cyclic compounds, mostly trimers to decamers, and that the reaction rate is maximum at 443 °C. They saw increased heat stability but no modifications to the product when they substituted trimethylsilyl for the hydroxy chain end groups.

KOH was also used to speed up the degradation process, with methane being a major by product. Molecular weight determinations and TGA revealed that polymers containing hydroxy end groups broken down gradually, beginning with the hydroxy end groups. They concluded from their initial investigation that oxygen plays a significant role in the depolymerization reaction. They contend that the oxidation of the methyl group must be the main reaction; if hydrogen peroxide is the main product, it will break down quickly at 200 °C, resulting in a radical reaction. Furthermore, they discovered in their follow-up investigation that PMPS still produces cyclic products while being more thermally stable than PDMS. One of the main products found in PMPS was benzene, whose percentage can be raised by reducing the molecular weight and boosting the temperature

Catalytic depolymerisation from 25 °C to 350 °C

The temperature range in which the catalytic depolymerization can occur is 25 °C to 350 °C. Protons can readily protonate the Si-O bond at lower temperatures in the presence of a strong nucleophile, such as sulfuric acid, trifilic acid, hydrofluoric acid, alcohols, halides, amines, octanoate catalysts, and amines, or electrophile, such as sulfuric acid, trifilic acid, and alcohols & the siloxane bonds' profound polarity Consequently, two silanols are produced if water or the nucleophile attacks the silicon atom nucleophilically [31-40].

Subsequently, they can generate free silanols or cyclic siloxanes via the mechanism of backbiting reactions, which will be elucidated further below. Higher temperatures, up to 350 °C, cause the depolymerization due to Si-O scissions throughout the main chain, and backbiting reactions also create the majority of the products at these temperatures. This kind of depolymerization also involves the use of electrophiles and nucleophiles; for the former, the most popular ones are trimethylaluminium and AlCl3, while for the latter, alkali metal hydroxides and halides, ammonium or phosphonium bases, and alcohols are employed. By using catalysts, temperatures can be lowered in comparison to the thermal degradation process.

The backbiting reaction is the primary mechanism for the generation of the lower molecular weight products at both lower and higher temperatures for the catalytic depolymerization as well as for the thermal degradation. It can occur by two different methods. The backbiting in the first mechanism starts near the end of the hydroxyl chain. It targets the polymer's backbone, causing cyclization, the removal of cyclic oligomers-whose sizes vary based on the point of attack-and the creation of a shorter silanol termination, as above in figure. But the polymer chain itself might potentially provide the source of this chain transfer mechanism. Linear sequence in a cyclic intermediate step where rearrangement occurs, the backbone folds back on itself. As seen in figure 4.6, the backbone folds back on itself on a cyclic intermediate step when a rearrangement occurs, producing a new Si-O bond and a cyclic siloxane oligomer.

Different studies about catalytic depolymerization using Lewis acids, strong acids or strong bases, fluoride and metallic catalysts, for example, can be found in the literature

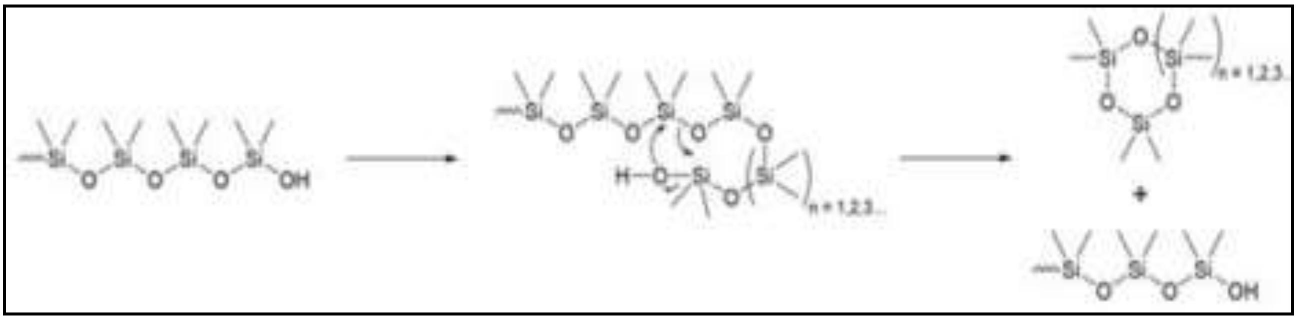


Fig 8: Backbiting reaction at the free silanol chain end

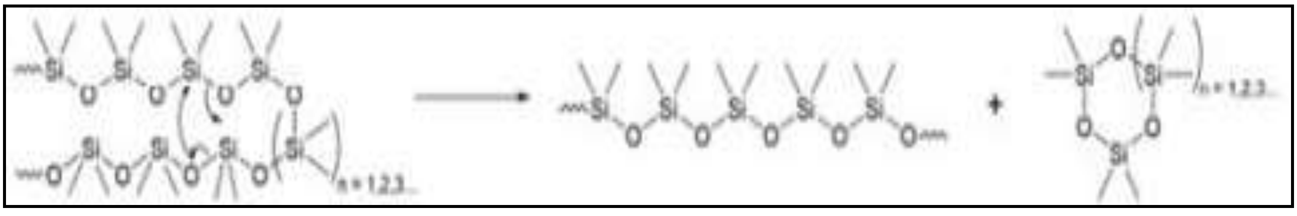


Fig 9: Backbiting reaction within the polymer chain

For instance, Enthaler *et al*. have worked in different strategies to depolymerize linear, branched and cured silicones. They used boron at lower temperatures and iron or zinc catalysts at temperatures higher than 100 °C to activate the silicone backbone and trigger the attack by either chloride or fluoride fed by different organic sourced and transfer agents like benzoyl fluoride, benzoyl chloride and acetic anhydride, resulting in the polymer degradation and acid by-products with low yield. The silicon monomers obtained were mostly dimethyldichlorosilanes or dimethyldifluorsilanes with up to 86% yields. After being isolated, these monomers can be repolymerized forming a new product.

Even though different authors have used different reagents to achieve the depolymerization of silicone polymers through a catalytic process, their application in an industrial scale is not trivial because some of the catalysts and reagents used, along with several by-products generated, are not environmentally benign, going against the current trend to establish a greener chemistry. Some studies are also conducted at temperatures that, while not as high as those used for thermal depolymerization, still result in a high energy cost.

Reversion

Eversion is a sealed environment degradation technique that breaks down RTV silicone network chains into low molecular weight products through thermal activation.

In a study examining the role of tin catalysts in the condensation of cured RTV silicone rubbers, van der Weij proposed this mechanism. Initially, in order to fully comprehend the reversion mechanism, it is imperative to have a solid understanding of both the catalyst utilized and the condensation process that cures the silicone elastomer. As a result, this procedure will be reviewed in full below [35].

As can be observed, a hydroxy end blocked polymer (PDMS)-that is, the polymer that needs to cure-a silane crosslinker, and a catalyst are required for condensation to occur. Here, the crosslinker and catalyst molecules will be the same as those employed by Weij in his research, resulting in the dicarboxylation of dialkyltin and tetraethoxysilane (TEOS), respectively.

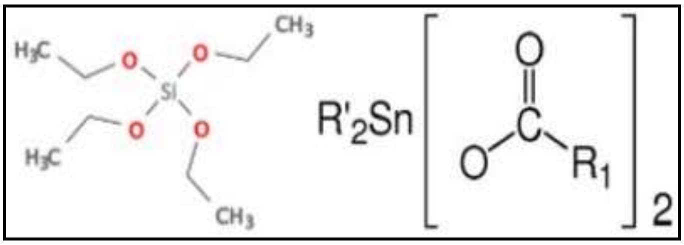


Fig 10: Structures are dicarboxylated by dialkyltin and TEOS, respectively

When producing room temperature vulcanized silicones, organotin compounds are typically the catalyst of choice due to their excellent crosslinking time, selectivity, and network density, which lead to a good reaction efficiency without the requirement for harsh conditions. However, as some investigations have shown, the material may degrade if residual organotin catalyst is present in a given environment [41, 42]. This is crucial knowledge about the mechanism of reversion that will be discussed in more detail later.

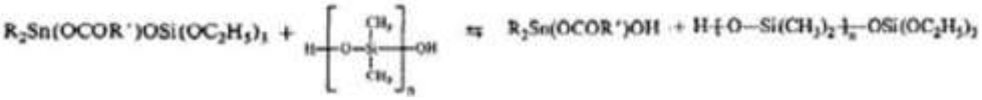
The tin catalyst is only active when there is some water present, as reported by Severnyi *et al*. and verified by Weij. This means that, as shown in equation 4.1, the active catalyst of the reaction is really the hydrolysis product of the organotin complex, the organotin hydroxide [43]. The reaction's by product is carboxylic acid.

$$R_2Sn(OCOR')_2 + H_2O > R_2Sn(OCOR')OH + R'COOH \quad (1)$$

Then, the catalyst that is now active, organotin hydroxide, reacts with the crosslinker alkoxysilane, resulting in an organotin silanolate, an intermediate compound that contains the Sn-O-si moieties and that, according to equation, are well-known to be highly effective catalysts for RTV silicone elastomers and ethanol as a by-product.

$$R_2Sn(OCOR')OH + Si(OC_2H_5)_4 \text{->} R_2Sn(OCOR')OSi(OC_2H_5)_3 + C_2H_5OH \quad (2)$$

Lastly, the hydroxy end blocking PDMS, which is thought to function as these protic agents, reacts with the Sn-O bond from the organotin silanolate, which is easily cleaved by protic agents like water or alcohols. Consequently, the silicone network's distinctive Si-O-Si bonds are formed, and the organotin hydroxide catalyst is renewed.



$$R_2Sn(OCOR')OSi(OC_2H_5)_3 + H\left[O-\overset{CH_3}{\underset{CH_3}{Si}}\right]_n OH \rightleftarrows R_2Sn(OCOR')OH + H\left[O-Si(CH_3)_2\right]_n-OSi(OC_2H_5)_3 \quad (3)$$

The regenerated catalyst is prone to continue to react with the silicone chain as long as accessible alkoxy groups are present. The schema shown in, compiles the relevant reactions that lead to the network formation of the silicone rubber.

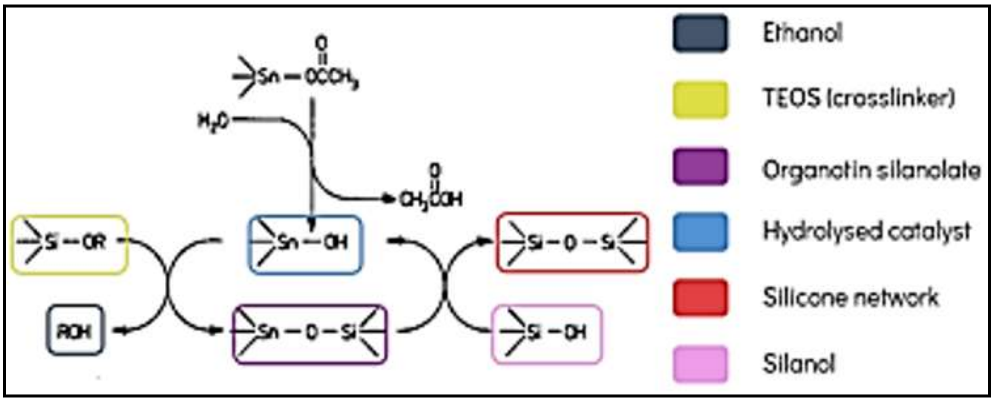


Fig 11: Schema of the relevant reactions of the condensation mechanism of silicone rubber

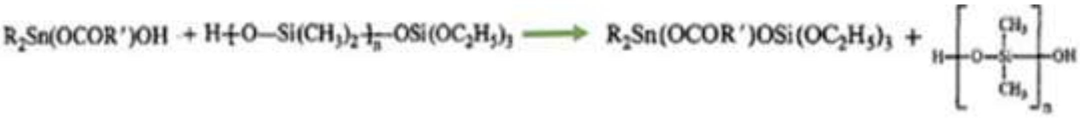
Now that the condensation process has been thoroughly defined, the revision method may be discussed. Simplified, the reversion is the polycondensation process reversed, where the deterioration of the polymer results from the breaking of siloxane linkages. It should be noted that the reactions described below can only occur in a closed, sealed environment. Moreover, the equations shown below are those van der Weij proposed in the 1980s because there haven't been many investigations done on the process [34].

The polycondensation mechanism's equation 1 produces ethanol as a by product.

Given that the reaction took place in a sealed space, alcohol does not evaporate. As the reaction proceeds, the alcohol content rises to the point where equation 2's thermodynamic equilibrium is flipped, reversing the process. Now, the hydrolyzed catalyst and the TEOS are restored when the ethanol produced combines with the organotin silanolate. Cross-linking (equation 4).

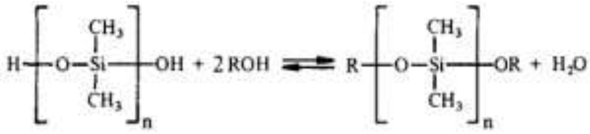
R2Sn(OCOR')OSi(OC2H5)3 + C2H5OH ---------> R2Sn(OCOR')OH + Si(OC2H5)4 (4)

The number of products gradually rises as the constituents of equation 4 react, until the hydrolyzed organotin content becomes so significant that the equation's 3 equilibrium is upset, resulting in the attack on the silicone network. The catalyst breaks the Si-O-Si bonds when it combines with the silicone rubber, producing the hydroxide end of the decrosslinked silicone chains and producing the intermediate product (Sn-O- Si).

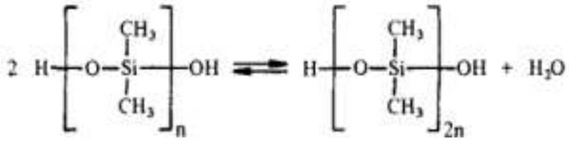


$$R_2Sn(OCOR')OH + H\left[O-Si(CH_3)_2\right]_n-OSi(OC_2H_5)_3 \longrightarrow R_2Sn(OCOR')OSi(OC_2H_5)_3 + H\left[O-\underset{CH_3}{\overset{CH_3}{Si}}\right]_n-OH \quad (5)$$

Equation 4 states that the breakdown of the silicone chain will continue as long as ethanol is present in the solution and the organotin silanolate is still being formed. Additionally, the PDMS-OH chains that are produced by equation 5 can react further with excess ethanol or with another silanol to produce an alkoky ended PDMS or a crosslinked product (equations 6 and 7, respectively).



$$H\left[O-\underset{CH_3}{\overset{CH_3}{Si}}\right]_n-OH + 2ROH \rightleftharpoons R\left[O-\underset{CH_3}{\overset{CH_3}{Si}}\right]_n-OR + H_2O \quad (6)$$



$$2\ H\left[O-\underset{CH_3}{\overset{CH_3}{Si}}\right]_n-OH \rightleftharpoons H\left[O-\underset{CH_3}{\overset{CH_3}{Si}}\right]_{2n}-OH + H_2O \quad (7)$$

However, if the ethanol in the system-which is the outcome of equation 2-is not evaporated, it makes sense that a larger portion of the silanol groups would become blocked by alkoxy groups.

Figure 12 displays the pertinent reversion mechanism reactions.

Van der Weij claims that this kind of breakdown of organotin-catalyzed silicone rubbers can only occur at high temperatures (about 90 °C) and when there is an abundance of alcohol present. The result is a weak jelly-like substance. He said, as follows: an irreversible alcohol blocks a large portion of the silanol groups, which causes deterioration. Additionally, he stated that since silicone rubber that cures by another process does not exhibit this kind of degradation, the degradation is most likely to occur at the crosslinks.

Despite the fact that reversion is a common method of degrading silicone rubber because it doesn't need high temperatures or environmentally hazardous reagents, this material might potentially be recycled by repolymerizing the resulting paste product till.

As of right now, no scholarly articles have thoroughly examined this mechanism. One additional benefit of this process is that, in contrast to previous techniques of degradation and recycling, reversion would permit the silicone product to be reused in its whole, including the fillers, resulting in a more circular system.

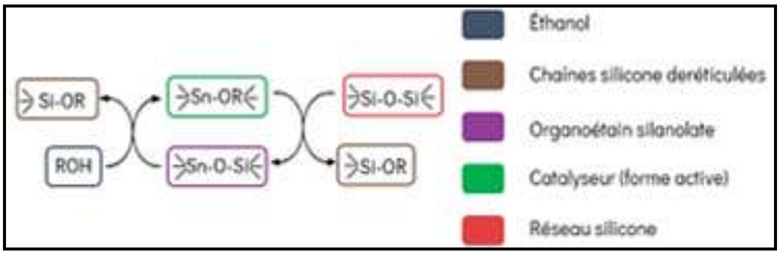
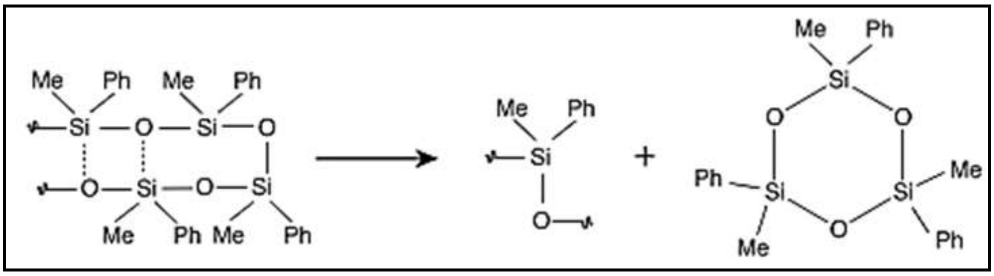


Fig 12: Schema of the relevant reactions of the reversion mechanism

Other Methods of Degradation

There are other special techniques for depolymerization, but the majority of them rely on heat or catalytic reactions involving acids or nucleophiles. Tanny and St Pierre used γ-irradiation to study PDMS deterioration at an ambient temperature of about 30 °C; the dose rate of 60Co was 0.35 Mrad h^{-1}. Based on the findings, they found D4, D5, and a trace quantity of D6. This study is intriguing since it compared the effects of radiation and thermal degradation on the same material. According to their findings, D3 accounts for almost 60% of the total weight of cyclic PDMS systems in thermal degradation, whereas D4 makes for around 30%. D4 is the D5 is around 45% by weight, while γ-irradiation is a key donor, at about 50%. 130 Chinn and colleagues investigated the deterioration of SYLGARD under doses of γ-irradiation varying from 0 to 25 Mrad h^{-1}. Across the whole radiation range and at a rate roughly proportional to the dose, they found that crosslinking was the main contributor. A chain scission mechanism that was thermally aged for two weeks at 70 °C and observed in the radiation range of 5-10 Mrad h^{-1} was also noted. The maximum yield of D6, D7, and D8 was obtained from the generated cyclic products, which ranged from D3 to D8. Furthermore, the cyclic product D3 is not favored [46]. The excitation of phenyls in PDMS and PDPS was theoretically investigated by Kroonblawd *et al.* in 2018 to ascertain its impact on depolymerization associated with consequences of aging. They discovered that water molecules play a major role in chain scission routes when they are energized and that they can react with the chain backbone to release free benzene and produce silanol side groups. In contrast, in conditions devoid of water, phenyl rings typically abstract hydrogens [47].



PMPS thermal depolymerization mixtures contain linear and cyclic products

They discovered that water molecules play a major role in chain scission routes when they are energized and that they can react with the chain backbone to initiate free benzene and create side groups for silanol. In contrast, in conditions devoid of water, phenyl rings typically abstract hydrogens [48]. The literature does not adequately examine the mechanistic processes underlying the irradiation techniques. It is possible for free radical reactions to occur if radiation has reduced the ionic nature of the siloxane skeleton. [49]Increasingly crucially, as thermodynamic factors like enthalpy and entropy grow increasingly significant at higher temperatures, kinetic factors appear to have a small effect in many heteroatom equilibrations. Therefore, statistical considerations are used to elucidate how ring-chain equilibration results in the creation of circular compounds. For instance, the probability of ring closure, or equilibrations considered to be scrambling events, is dependent on the concentration of any cyclic molecule in homeostasis with its open-chain analog signals [50-51]. An alternate theory is that Si-CH3 and H radicals can be produced as a result of high-energy interactions with methyl groups. C-Si bonds are furthermore shattered, producing main chain and methyl radicals [52-53]. In a vacuum, PDMS main chain pyrolysis has an activation energy of 40 kcal mol^{-1}. Si-O-Si bonds can be broken in this procedure by uncoupled electrons from O atoms in PDMS coordinating with 3d empty orbitals of nearby Si atoms [54]. A single bond's bonding electrons are typically localized, however in PDMS, they may be thought of as somewhat delocalized. Si atoms in the Si-O-Si main chain of PDMS have lower electronegativity, and electrons are delocalized by the overlap of 3d empty orbitals, which are the d orbitals of Si atoms and the p orbitals of O atoms. This action contributes to the reduction of the energy of π* orbitals and would increase the prevalence of n to π* at the energy level of excitation. In comparison to larger cyclic forms or straightchain siloxanes, the delocalization degree is higher in the smaller cyclic forms. A greater energy source, like γ-irradiation, results in a decrease in the energy needed to excite the valence electrons. This causes the absorption bands to redshift or become more n to π* character, which increases the proportion of smaller cyclics like D3 [55].

Furthermore, depolymerization has been induced in a few investigations using ultrasonic techniques, which include vibrating the bonds at a resonant frequency to break them apart. Rubber that has been packed with silica was recycled utilizing ultrasonic energy at 170 °C to depolymerize and repolymerize it back into polymers [56]. Additionally, PDMS can be broken down at room temperature using acid catalysts and ultrasonic radiation [57-58].

Conclusion

The current method of disposing of silicone elastomers that have reached the end of their useful lives does not align with the increasing global awareness of environmental issues that is expected for a product with so many uses and rising demand. Recycling thermosets, particularly in an environmentally responsible manner, becomes an increasingly challenging task. As of right now, only one company recycles silicone elastomers, and even then, the process has negative environmental effects because it requires a lot of energy and is costly, which makes it less appealing to businesses than using virgin raw materials, which are less expensive.

Furthermore, during the repolimerization of the revision's silicone product, the use of PDMS-OH chains in addition to the tin catalyst made it possible to recreate a crosslinked network with acceptable features and attributes. Both the mechanical and swelling test findings showed promise when comparing the recycled silicone material to the virgin one.

Taking into account all of the findings from this investigation, it has been shown that recycling this kind of material is possible through the reversion of a tin-catalyzed room-temperature vulcanized silicone elastomer, which results in a depolymerized product. This is then followed by its repolymerization with another tin catalyst and PDMS-OH chains.

Future research could focus on improving the repolymerization conditions to speed up the process and try to enhance the resulting qualities to bring them even closer to the values of virgin silicone. Expanding the use of the reversion process to include other kinds of silicone networks-like those that cure via polyaddition-would also be interesting.

Field Perspective

Studies on the deterioration of materials based on siloxane have been thoroughly examined over the years, as demonstrated above. However, rather than developing techniques for recycling and reuse, the majority of studies have primarily concentrated on learning more about the stability of the siloxane polymers. Our vision is for the field to move further in this direction, allowing for the on-demand reuse of siloxanes and preventing the energy-intensive procedures employed in their production from being wasted on disposable materials. To "green" the catalytic processes, however, more research and development is required. Only then will solvent-free or more environmentally friendly solvents be able to power these processes. Additionally, to catalyze the breakdown of siloxane elastomers and resins used in commercial applications, it would be excellent to provide on-demand depolymerization using light or other alternative energy sources.

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