

ENHANCED SUSTAINABILITY FOR SILICONE
BASED MATERIALS

USING PHENOLIC COMPOUNDS AS CROSSLINKERS
FOR AMINOSILICONES: PREPERATION OF SILICONE
ELASTOMERS WITH ENHANCED SUSTAINABILITY

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TITLE: Using Phenolic Compounds as Crosslinkers for Aminosilicones: Preparation of
Silicone Elastomers with Enhanced Sustainability

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Abstract

Silicones (or polysiloxanes) are polymers consisting of an Si-O repeating unit as the backbone of the polymer, and different organic functional groups along the backbone, most commonly two methyl groups. The Si-O bond gives many unique properties to the polymers such as incredible thermal and oxidative stability, low glass transition temperatures, and low surface tensions. These properties, among many others, make silicones unique compared to carbon-based polymers and are used in many applications such as in the automotive, cosmetic, construction and electronics industry. Most silicones are used as thermosetting elastomers and cannot be recycled since thermosets cannot be melted or dissolved in solvents. Thus, they are landfilled once silicone products have met their use and are ready to be replaced. This is further worsened by the fact that most silicone elastomers are cured using metal catalysts such as platinum or tin, which are in very low abundance and typically toxic. Another means of crosslinking silicones must be utilized to meet the sustainable demands of the future.

Non-covalent and covalent dynamic chemistry can offer another means of crosslinking silicones while still maintaining many of their desirable properties but adding the ability to be recycled by thermal reprocessing or specialized reagents. Catechol is an interesting molecule that can exhibit non-covalent and dynamic covalent chemistry and is the perfect candidate to replace metal-catalyzed crosslinking. A library of silicone elastomers is created by mixing catechol, closely related compounds, and amine-functional silicones with properties that are dependent on the ratios of phenol to

amine ([ArOH]:[NH₂]). Elastomers can be reprocessed by heat and can be dissolved by using simple amines, thus, reducing silicone and precious metal waste. Additionally, the silicone elastomers exhibit antioxidant activity that arises due to the radical quenching ability of the catechol.

While catechol can introduce many new properties to silicone elastomers, it is toxic and hinders the sustainability profile and applications of the elastomers. Tannins are a unique class of polyphenolic compounds that are biologically derived and non-toxic, often being added to wine to help with colour and taste. Thus, commercially available tannins used in the winemaking industry are mixed with amine-functional silicones, and a set of materials is created by varying the mass loading of tannins. Up to 10% dilution of the silicone was possible while still retaining the flexibility that silicones are known for. The materials created showed many of the same properties as the catechol crosslinked materials, including recyclability, dissolution, and antioxidant properties. The tannins also impart their properties, such as flame suppression, to the materials.

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Chapter 1. Introduction

1.1 An Overview of the Silicone Lifecycle

1.1.1 Silicone Synthesis

Polysiloxanes (or silicones) are organometallic polymers consisting of repeating Si-O linkages. They are important industrial materials due to their unique properties, such as their thermal and oxidative stability, low glass transition temperature, and low surface energy.¹ This has led to their use in many industrial sectors including construction, transportation, personal care, and electronics. In recent years many polymers have become a topic of controversy due to their massive production but poor disposal after use. In light of this issue, the Government of Canada has gone to the extent of banning the manufacturing and import (2022), sale (2023), and export (2025) of single-use plastics in the form of polyethylene, polypropylene, polystyrene, and polyvinyl chloride.² With silicones being such valuable materials and polymers being a topic of scrutiny, it is important to assess the lifecycle of silicones and to determine whether or not they have the same detrimental effects on the environment as other polymers. If they do have the same detrimental effect, are there any ways to compensate for them at other stages of the lifecycle?

Silicone polymer synthesis starts with elemental silicon, which can be obtained by reducing silicon dioxide in the form of quartzite with carbonaceous materials such as

coke.³ Note the elevated temperature needed for the transformation (Figure 1.1).^{4, 5} This process accounts for one of the steps that require a large amount of energy needed to create silicones, with the added disadvantage that the energy required may be derived from non-renewable feedstocks, including fossil fuels.

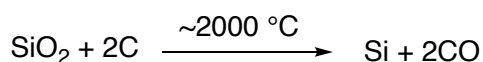


Figure 1.1 Silicon synthesis from silicon dioxide.

Elemental silicon is used to create the monomeric units for silicon synthesis in the Rochow-Müller Process (or Direct Process). The major product of this process is dichlorodimethylsilane, which is necessary for silicone synthesis, with other minor products being created such as the mono- and tri-substituted methyl silanes (Figure 1.2).⁶ Dichlorodimethylsilane can then be used in the production of silicone polymers.

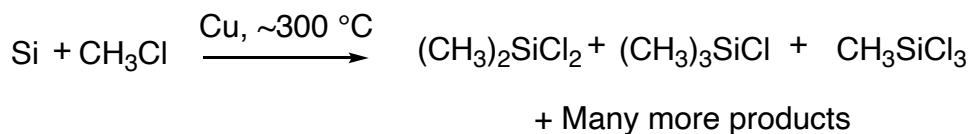


Figure 1.2 Simplified representation of the Rochow-Müller Process

Silicones are industrially produced by the hydrolysis of chlorosilanes to yield hydroxy-terminated siloxane oligomers (2-4 units) and small cyclic oligomers (D₃ and D₄); either of the cyclics can undergo ring-opening polymerization to form high molecular weight polymers in the presence of an acid or base catalyst (Figure 1.3).⁷ Cyclic oligomers can also be used to increase molecular weight by insertion into existing polymer chains. Different temperatures and pressures are typically employed to allow for the removal of

low molar mass products to force the formation of high molar mass linear polymers, adding to the total energy cost in the case of polycondensation.⁸ While the preparation of silicones require a huge energy investment, their place in commercial products and industrial processes arises because of their utility and, in many cases, the small amount required to fulfil an application need. However, the energy toll could be further mitigated if silicone polymers did not have the same end-of-life fate as other polymers. For example, the detriment of the high amount of energy needed to create the polymers could be offset by, for example, more efficient degradation in the environment.

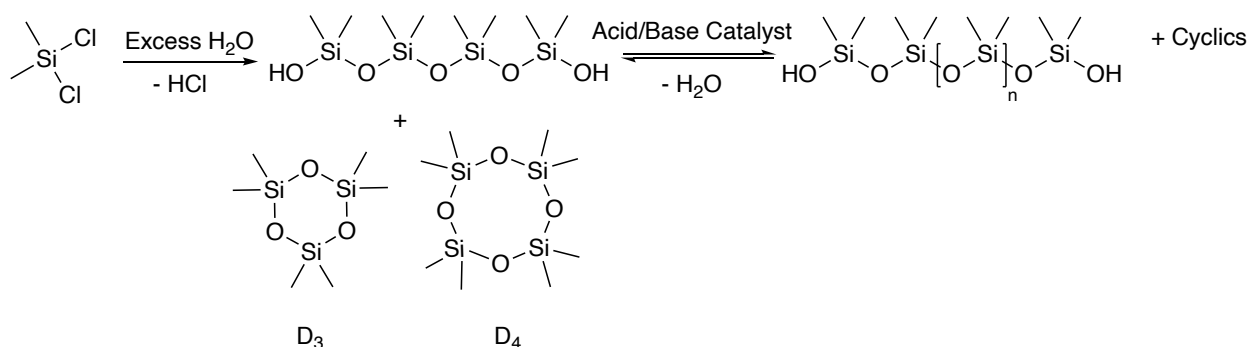


Figure 1.3 Industrial silicone synthesis by polycondensation.

1.1.2 Silicones in the Environment

Unlike most organic polymers, which have been shown to accumulate in the environment and that do not degrade for tens to hundreds of years, silicone fluids are capable of depolymerizing in the environment quite readily. For instance, low molecular weight linear oligomers and cyclic oligomers such as D₄, D₅ and D₆ that are introduced to the environment phase separate from water and evaporate into the atmosphere where they react with hydroxyl radicals through a series of radical processes. Ultimately, the products

are silica, CO₂ and water.⁹ High molecular weight polymers do not evaporate into the atmosphere due to their low volatility, but find their way into wastewater treatment plants and into the eventual solid sludge that is created in the treatment process. The sludge is either landfilled or spread over agricultural plots, where the silicone depolymerizes to lower molar mass linear polymers (and possibly cyclics) due to soil hydrolysis in a matter of days or weeks under appropriate environmental conditions (not, for example, in the Canadian winter).^{10, 11} Further oxidation to sand and water takes a few years. These outcomes are certainly advantageous, and if silicones are disposed of appropriately, they can be considered to have a circular lifecycle.

The ability to undergo environmental degradation is not the same for all silicone products. A large majority of silicones are used as thermoset elastomers, materials that do not melt or dissolve, and which are unlikely to degrade in the environment at a reasonable rate – reliable data is not yet available. Recycling of thermoset silicones elastomers has recently come into commercial practice. For instance, ECO USA (www.ecousarecycling.com) is recycling virgin rubber from silicone manufacturers, which is encouraging, but only at small scale compared to total production. This leads us to the problem: are there ways to change the way silicone elastomers are prepared to encourage their degradation in the environment? An analysis of traditional crosslinking chemistries is required to understand how silicone elastomers are prepared and how one could change the chemistry to create smarter materials.

1.2 Traditional Crosslinking Chemistry

Commercial silicone elastomer formulations typically involve three types of cure chemistries: hydrosilylation, condensation, and radical coupling. Each of these methods involves the formation of covalent linkages. The two methods first mentioned involve the use of a catalyst, platinum in the case of hydrosilylation and tin in the case of condensation. Radical coupling requires the use of a radical initiator, typically a peroxide, and heat, which is required for homolytic cleavage of the peroxide initiator to start the radical chain. A brief discussion of the three crosslinking methods is presented below.

1.2.1 Hydrosilylation (Addition Cure)

Hydrosilylation is one of the most important reactions in the silicone industry. It involves the addition of silicon and hydrogen from a hydrosilane across both double and triple bonds, most commonly C=C and C≡C (Figure 1.4), though many other bonds are reactive as well (C=O, C=N, and more).¹² This reaction can be used for the preparation of important functional precursor chemicals such as γ -propyl silanes, the functionalization of silicone polymers and, most important for this discussion, the crosslinking of silicone polymers.^{13, 14}

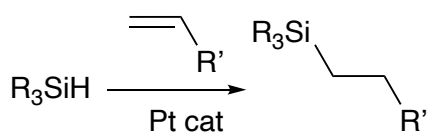


Figure 1.4. Hydrosilylation of a generalized alkene

Silicone polymers and the crosslinker must be functionalized with vinyl and hydride groups for hydrosilylation crosslinking to occur. Typically, crosslinkers are low

molecular weight, highly functionalized oligomers with pendent Si-H bonds while the chain-extending polymer is of varying molecular weight end-capped with vinyl groups (Figure 1.5).¹⁵ One of the major disadvantages associated with hydrosilylation is the use of precious metals for catalysis, which are expensive, fluctuate in price greatly, and are non-renewable. Platinum catalysts are usually employed industrially for their price and efficacy, although, rhodium catalysts can also be seen in specific applications.¹³ While catalysts can be easily recovered and reused in the production of small molecules, they are lost when used for crosslinking polymers to form elastomers. The outcome is that any platinum used for crosslinking elastomers is lost to the environment in dilute form once the silicone is disposed of. Of course, this has led researchers to look for different metals to use for catalysis, such as ruthenium,¹⁶ iridium,¹⁷ and iron.¹⁸ Only the latter is inexpensive, but their efficacy does match the prominent platinum catalysts currently used in the industry.

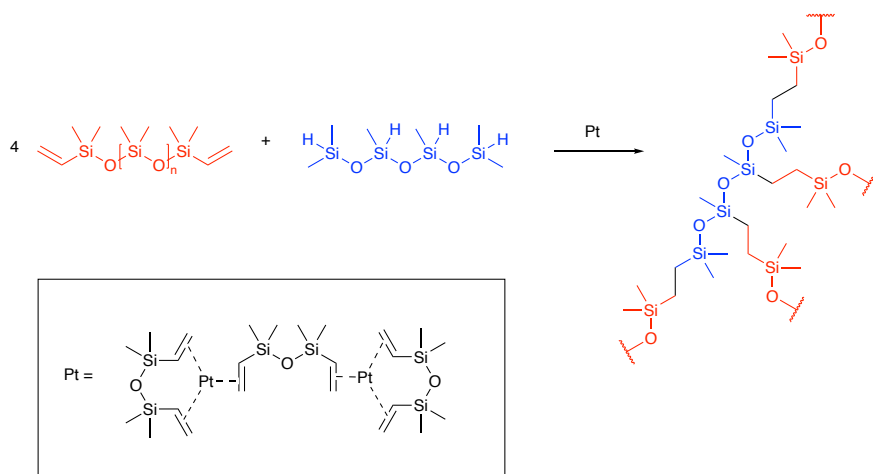


Figure 1.5 Hydrosilylation of a vinyl-terminated silicone and hydride-functionalized crosslinker. The platinum catalyst used most commonly in the silicone industry is Karstedt's catalyst.

1.2.2 Condensation Cure

Most commonly seen in caulk formulations and for application as sealants, condensation cure relies on tri/tetra functionalized silanes (small molecules) and hydroxy-terminated silicones condensing to form a new Si-O-Si bond, typically in the presence of a tin catalyst (Figure 1.6). The silane crosslinker can be alkoxy, acetoxy, or oxime functionalized, all of which react at different rates.⁷ Condensation cure offers many benefits over hydrosilylation, such as better resistance to catalyst poisoning, relatively rapid cure at room temperature, and lower catalyst prices. While tin-catalyzed crosslinking may seem like a perfect alternative to hydrosilylation, it also has many disadvantages.

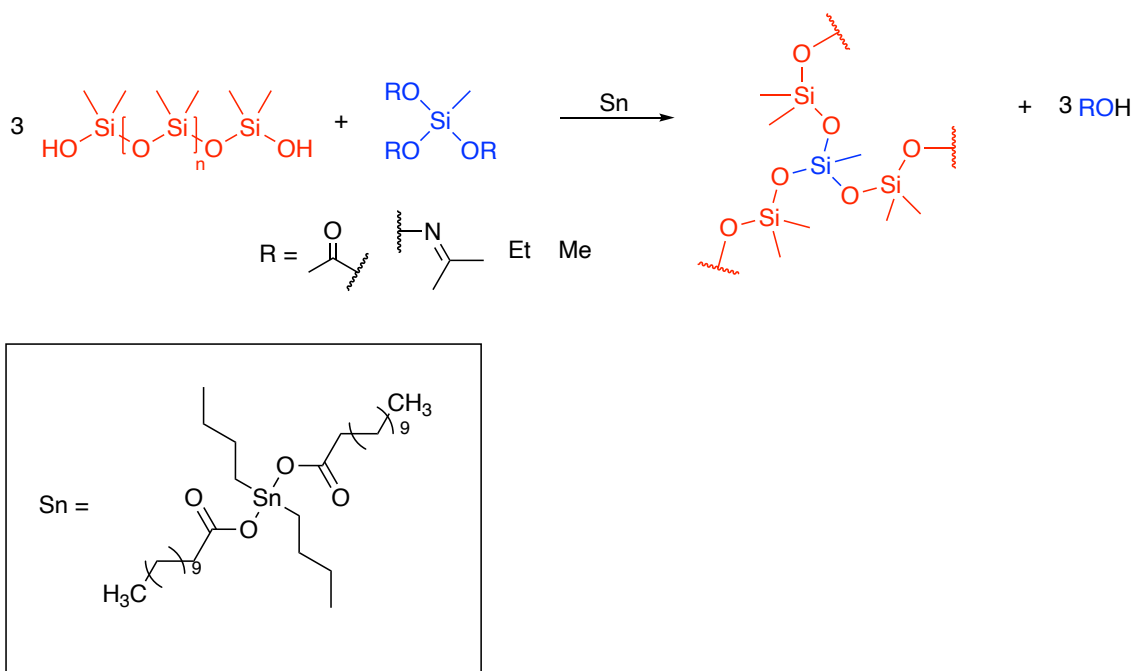


Figure 1.6 Condensation of a hydroxy-terminated silicone and functionalized silane. A tin catalyst that is commonly used is dibutyl tin dilaurate.

Most of the tin catalysts used in formulations are organotin substances, such as dialkyl tin dicarboxylates and tin dicarboxylates.¹⁹ These alkyl tin compounds are known to be toxic to humans and animals and persist in the environment for long periods depending on the alkyl group.^{20, 21} Condensation-cured elastomers can suffer from significant post-curing effects such as hardening over time, which will affect their mechanical properties, potentially leading to failure in the specific applications in which they were intended to be used.²²

1.2.3 Radical Cure

Unlike hydrosilylation and condensation cure, radical cure does not require the use of any metal catalyst. Similar to most organic radical reactions, an initiator is needed – most commonly in the form of a peroxide – the structure of which is dependent on the type of silicone being used. Vinyl-functionalized silicones are typically cured with alkyl peroxides such as di-tert-butyl peroxide, while unfunctionalized methyl silicones generally use peroxy esters or acyl peroxides such as dibenzoyl peroxide for cure (Figure 1.7).²³ Homolytic cleavage of the radical upon heating initiates cross-linking. If only methyl groups are present, H abstraction by the initiator, followed by radical dimerization, is the predominant crosslinking mechanism. If the silicone bears vinyl groups, either the addition of the alkoxy radical across the alkene or H-abstraction can occur leading to *n*-propyl and *i*-propyl carbon bridges respectively (Figure 1.8).²⁴

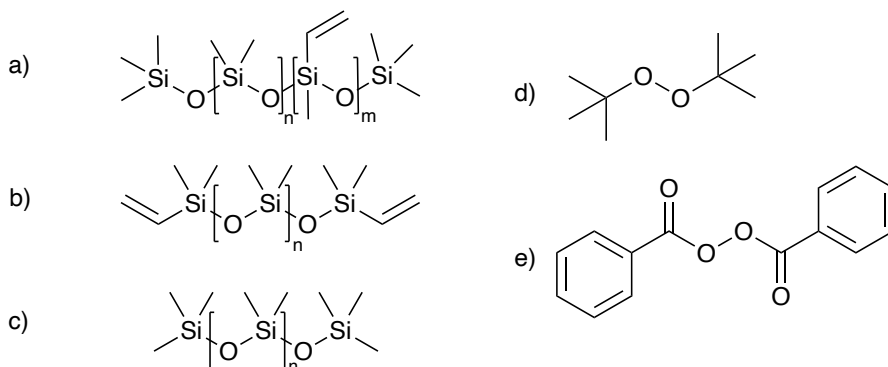


Figure 1.7 a) Pendent vinyl-functionalized silicone, b) terminated vinyl-functionalized silicone, c) methyl-functionalized silicone, d) di-tert-butyl peroxide, e) dibenzoyl peroxide.

One of the major disadvantages of curing silicones with radical methods is the potential loss of control over the location of crosslink sites. Efficient cure requires a large amount of peroxide; radical abstraction and subsequent coupling can occur anywhere along the backbone. This can lead to irreproducible elastomer formation and large amounts of acidic initiator by-products that need to be titrated or heat stripped away so that catalytic depolymerization of the silicone does not take place.^{7, 24} These disadvantages can be alleviated to a degree with the use of vinyl functionalized silicones, where each vinyl groups is a crosslink site, but the partner methyl group is still randomly selected. In addition, the distribution of vinyl groups along a silicone backbone can vary significantly since the polymerization of copolymers does not produce evenly-spaced vinyl groups. This can lead to inefficient crosslinking and variations in crosslinking density which arise from homopolymerization of the vinyl groups.⁷ Neither hydrosilylation nor condensation cure suffer from these issues.

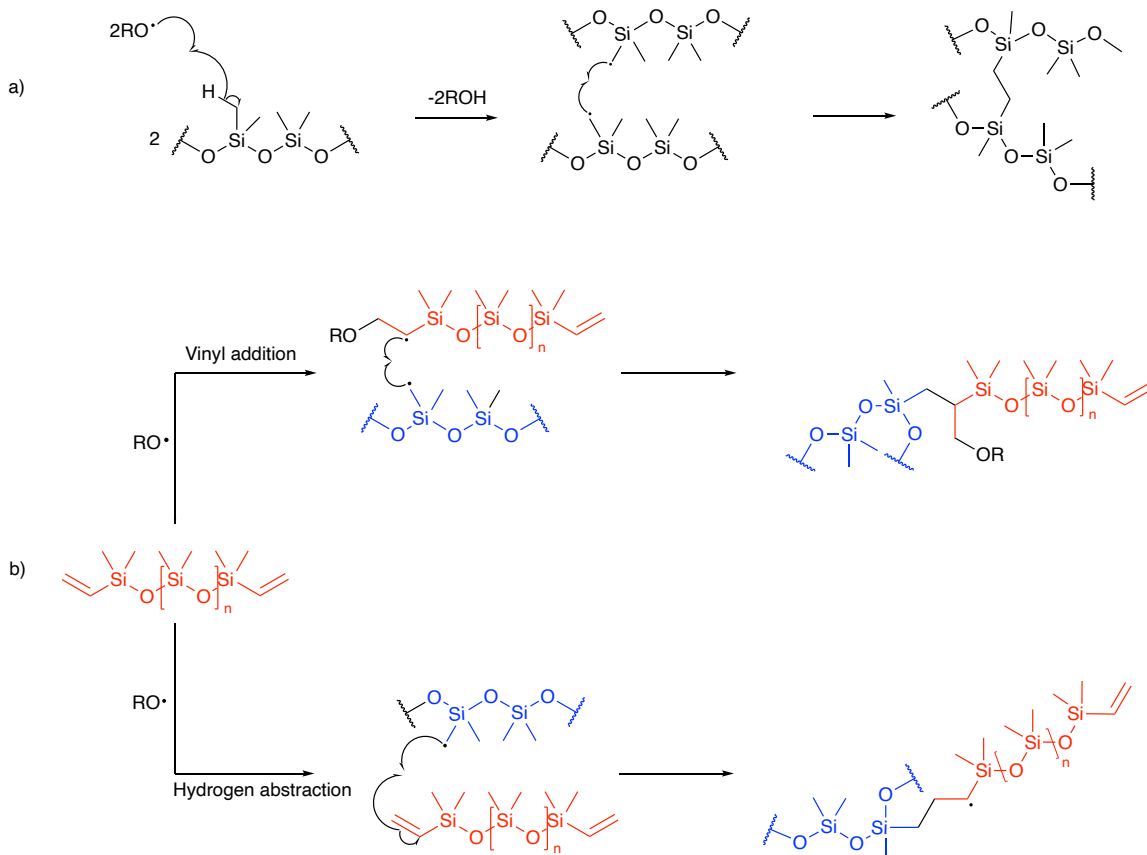


Figure 1.8 a) Hydrogen atom abstraction followed by dimerization of CH_2 radicals resulting in crosslinking of methyl-functionalized silicones, b) two competing mechanisms for crosslinking of vinyl-functionalized silicones

1.3 Modern Crosslinking Chemistry

While covalent crosslinking offers many benefits including robust materials and well-known developed chemistry, it is very clear that there is no need to limit silicone crosslinking to these modes. Tin has issues of toxicity, platinum is expensive due to its limited availability, and radical curing requires the input of additional heat during cure and post-cure, which adds to the total energy cost associated with silicones. Alternative crosslinking processes involving dynamic interactions and/or reversible covalent

chemistry have become a major research topic and many research groups have developed interesting modes of crosslinking that can create durable materials with novel properties without relying on the covalent bonds found in thermosets.

1.3.1 Dynamic Crosslinking: Non-Covalent Chemistry

Dynamic bonding, that is, bonding that can assemble and reassemble depending on the conditions present in the system, encompasses a large group of possible non-covalent interactions.²⁵ Such interactions can range from dipole-dipole, ionic, hydrogen bonding, pi-pi interactions, and so on, all of which differ in their strength of bonding.

These bonds are responsive to external factors such as heat and light, among others, and can access interesting properties such as the ability to be remoulded or self-heal.

Hydrogen bonding and ionic interactions represent some of the most utilized interactions in dynamically crosslinked systems, with several different types of bonding moieties present in the literature. Hydrogen-bound systems can arise from several possible groups including carboxylic acid dimers, amides, ureas, and carbamates, which are commonly used in conjunction with one another (Figure 1.9). Ionically crosslinked systems typically take advantage of acid-base chemistry or metal-ion interactions, such as those seen in Figure 1.9, although there are many other possibilities.

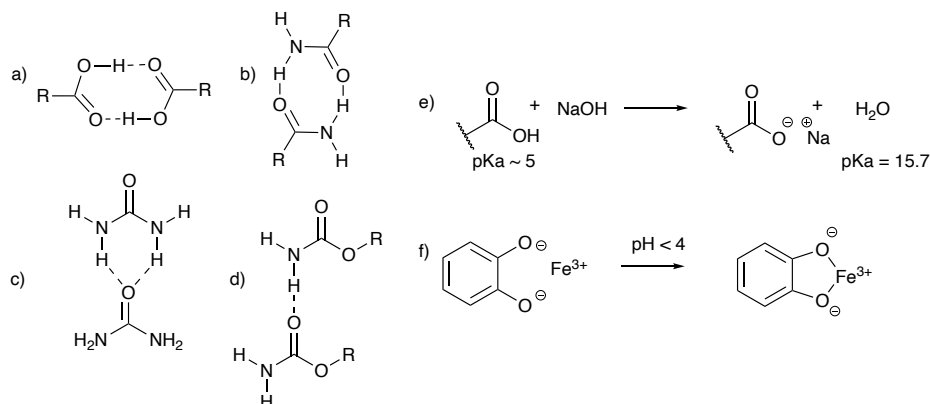


Figure 1.9. Examples of hydrogen bonding motifs: a) carboxylic acids, b) amides, c) ureas, and d) carbamate. Examples of ionic bonding motifs: e) Sodium hydroxide deprotonating a carboxylic acid, f) catecholate dianion coordinated to Fe(III).²⁶

While many research groups are focussing on creating systems that are crosslinked by sophisticated linkages that involve multiple interactions at once, there are many examples of systems that are crosslinked by very simple chemistry, that still deliver materials with interesting properties. For example, silicone polymers can be crosslinked by the incorporation of carbohydrazone onto an isocyanate-terminated polymer, resulting in three urea groups adjacent to one another (Figure 1.10). The tris urea functionality can act as a sextuple H-bonding crosslinker and creates self-healable materials, however, due to the very hard urea segments, the elasticity of the samples is hindered.²⁷ Two very similar ionic interactions can result in completely different modes of crosslinking (Figure 1.10 b) and c)). The first represents taking advantage of acid-base equilibria, with a diamine functionalized silicone deprotonating a di-carboxylic acid functionalized silicone, forming ammonium carboxylate crosslinks. Elastomers produced via this method showed excellent thermoplastic behaviour, illustrated by being crushed into small pieces, placed

into a mould, heated and reforming an elastomer taking the shape of the mould.²⁸ The second example shows a poly(isoprene) polymer functionalized with carboxyl groups, which are neutralized with sodium hydroxide to varying degrees. Crosslinking occurs through the aggregation of the ions forming clusters, which act as physical crosslinks.²⁹ In either case, excellent self-healing capabilities were observed and both materials exhibited time-dependent strain, as shown through mechanical testing at different strain rates; slower strain rates resulted in extensions of up to >1200% and >8000% for silicone and poly(isoprene) elastomers respectively.^{28, 29}

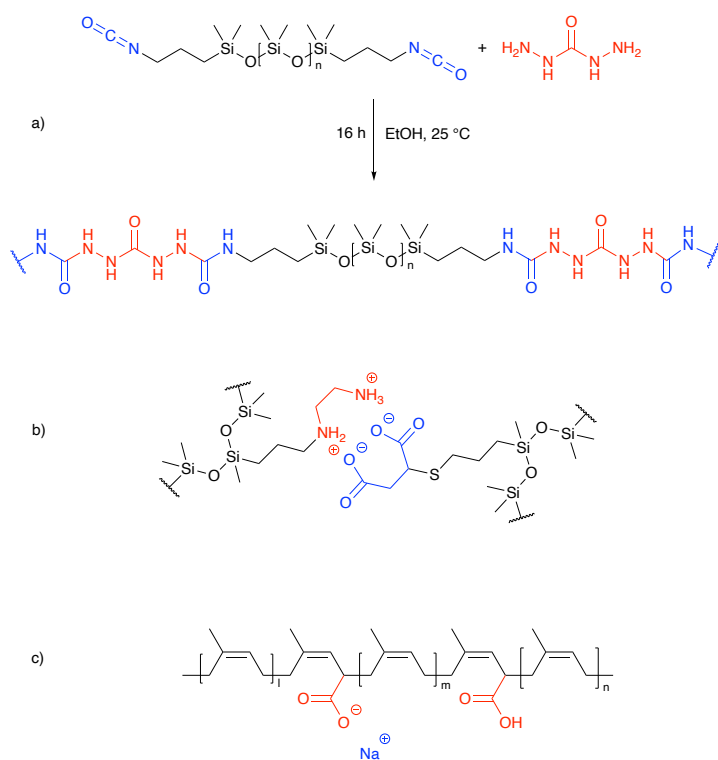


Figure 1.10 a) Silicone polymer functionalized with carbohydrazide yielding a system crosslinked via sextuple hydrogen bonds,²⁷ b) silicones crosslinking via ammonium carboxylates,²⁸ c) poly(isoprene) functionalized with carboxyl groups, a fraction of which neutralized with NaOH.²⁹

In recent years more complex examples of dynamically crosslinked systems have emerged and one of the most common hydrogen bonding groups present in the literature is 2-ureido-4[1H]-pyrimidinone (UPy, Figure 1.11), developed by the Meijer group to act as a directional quadruple hydrogen bonding group.³⁰ This group is capable of dimerizing very rapidly and adds interesting properties to polymers. Since its development, several groups have implemented UPy into different polymeric systems to create elastomers with enhanced mechanical properties and self-healing capabilities. A few examples of the incorporation can be seen in Figure 1.11. When incorporated onto a poly(isoprene) and poly(tetrahydrofuran) backbone, significant improvements in the tensile strength and toughness of the materials were reported (13, 44 MPa and 40 and 354 MJ/m³ respectively), which illustrates dynamic crosslinking can add additional support to covalently crosslinked systems or can serve to be as effective or more effective than covalent crosslinking.^{31, 32} The incorporation of UPy into a silicone environment is also possible and the resulting crosslinked elastomers have interesting properties (Figure 1.11). Remarkable extensions of 2000% can be seen without fracturing of the elastomer, and the elastomer was capable of self-healing very efficiently (92.5% at 70 °C after 12 h). These elastomers could be applied as electric sensors in a three-layer structure with carbon nanotubes and copper wire sandwiched in between pieces of elastomer, and when cut and allowed to self-heal, were still capable of illuminating an LED.³³

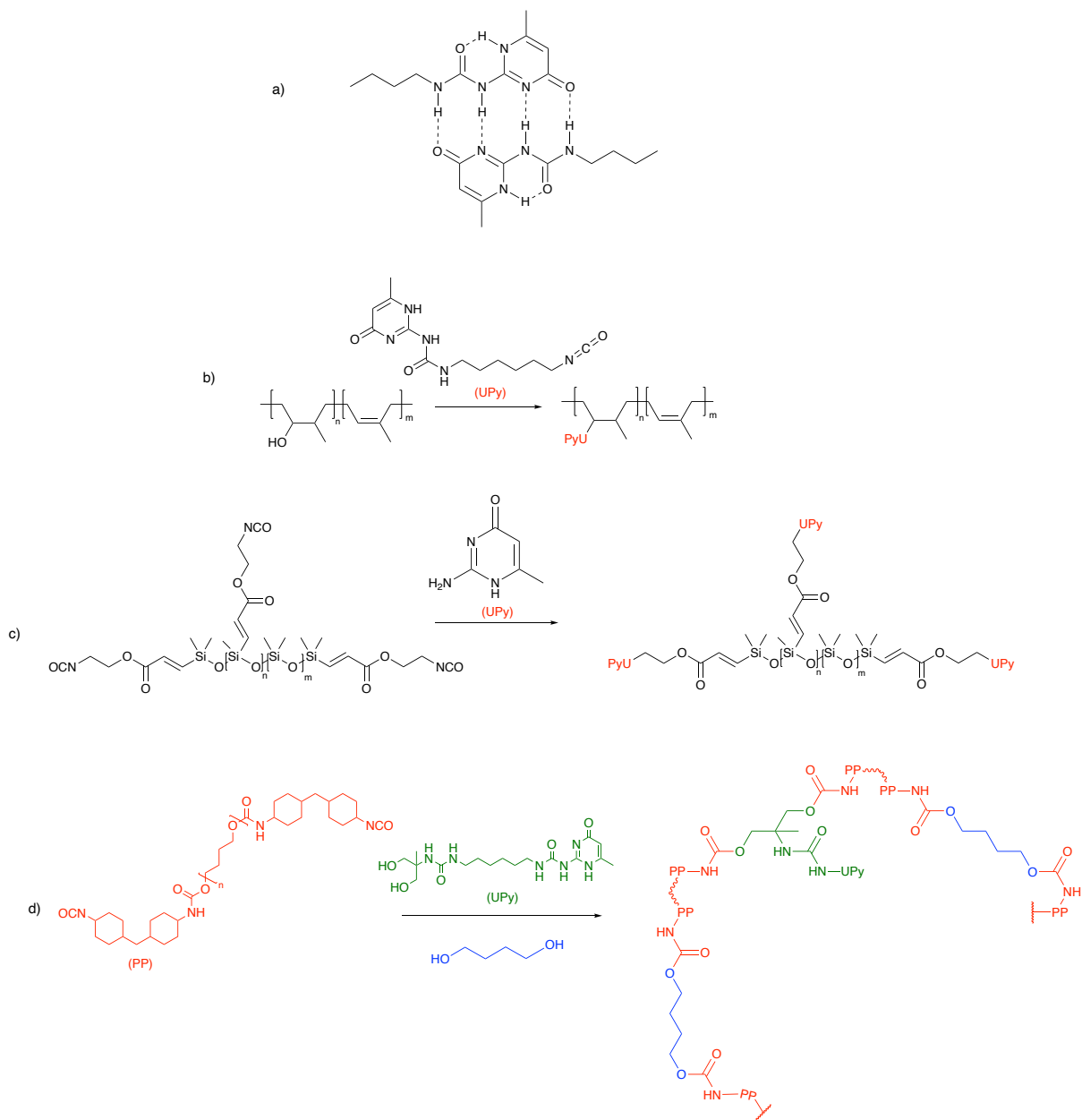


Figure 1.11 a) Structure of UPy,³⁴ b) UPy incorporated through isocyanate condensation on a poly(isoprene) backbone,³¹ c) UPy incorporated via isocyanate condensation on an isocyanate PDMS copolymer,³³ d) UPy incorporated via isocyanate condensation on a poly(tetrahydrofuran) backbone.³²

1.3.2 Covalent Adaptable Networks

While many different crosslinking interactions can form dynamically crosslinked elastomers, those presented above represent interesting examples that aim for very similar properties, i.e., thermoplastic behaviour and recycling. It should be noted that dynamically crosslinked elastomers suffer from one major flaw: the typical temperatures at which they are reprocessed are too low to be practically implemented as a replacement for thermosets where the intended application requires thermal stability. An intersection between thermosets and thermoplastics would be an ideal material that can be recycled yet has excellent thermal stability. This is where covalent adaptable networks (CANs) excel; they represent a very popular and promising research area. While CANs represent a unique category of materials, their mention is still worthwhile, and examples are briefly mentioned.

Covalent adaptable networks can be separated into two categories, dissociative and associative. Dissociative CANs can be reversibly broken by stimuli such as heat or light, and a change in crosslinking density within the network is observed; bonds are broken and only upon removal of the external stimulus will crosslinking density go back to its original state. The Diels-Alder cycloaddition reaction is commonly used when preparing dissociative CANs (Figure 1.12). This reaction is well known to occur at moderate temperatures to favour the products, but upon the addition of elevated temperatures, the retro Diels-Alder reaction takes place due to the dominant entropic effect rather than enthalpic. A common combination of diene and dienophile are furan and maleimide,

respectively, and their derivatives (Figure 1.12). The Diels-Alder reaction has been used to crosslink a variety of different polymeric systems such as poly(isoprene), poly(butadiene), and more recently silicones, each system showing thermoplastic behaviour, but at different temperatures.^{35, 36}

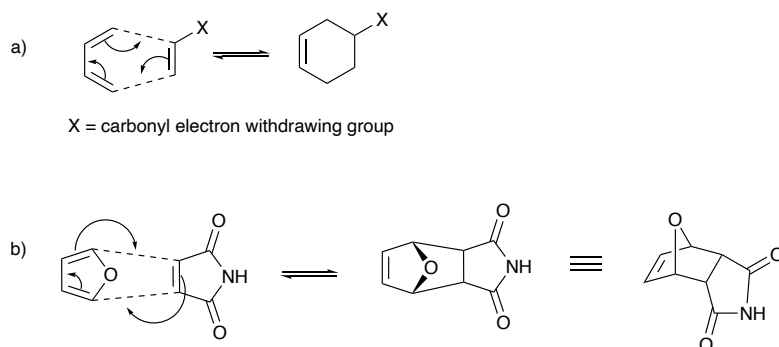


Figure 1.12. a) Generalized Diels-Alder reaction, b) furan and maleimide-based Diels-Alder reaction.

Associative CANs (or vitrimers) are different from dissociative CANs in that, rather than having crosslinked systems that are completely reversible to form the depolymerized monomers (association and dissociation), they instead exchange in one discrete step (Figure 1.13). As a result, the dynamic exchange of functional groups can occur while keeping crosslinking density essentially the same, offering the benefit of keeping the network topology constant after reprocessing. Common examples seen throughout the literature include transesterifications, metathesis reactions, silyl ether exchange, and imine exchange.^{35, 37} Recent examples applied to silicone polymers include aminosilicones crosslinked by di-vanillin forming Schiff base linkages, epoxy-functional silicones ring opened using tri- and di-functional carboxylic acids forming crosslinked networks held together by esters, and thiol-modified silicones crosslinked using a

Meldrum's acid derivative via addition/elimination equilibria (Figure 1.14).³⁸⁻⁴⁰ Each elastomer was reprocessed at significantly higher temperatures than a typical dynamically crosslinked elastomer, ranging from 130 °C to 180 °C with the addition of compression, illustrating their excellent stability.

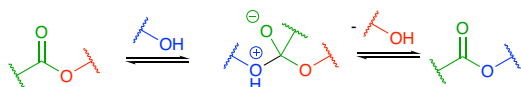


Figure 1.13. Exchange of alcohols during transesterification.

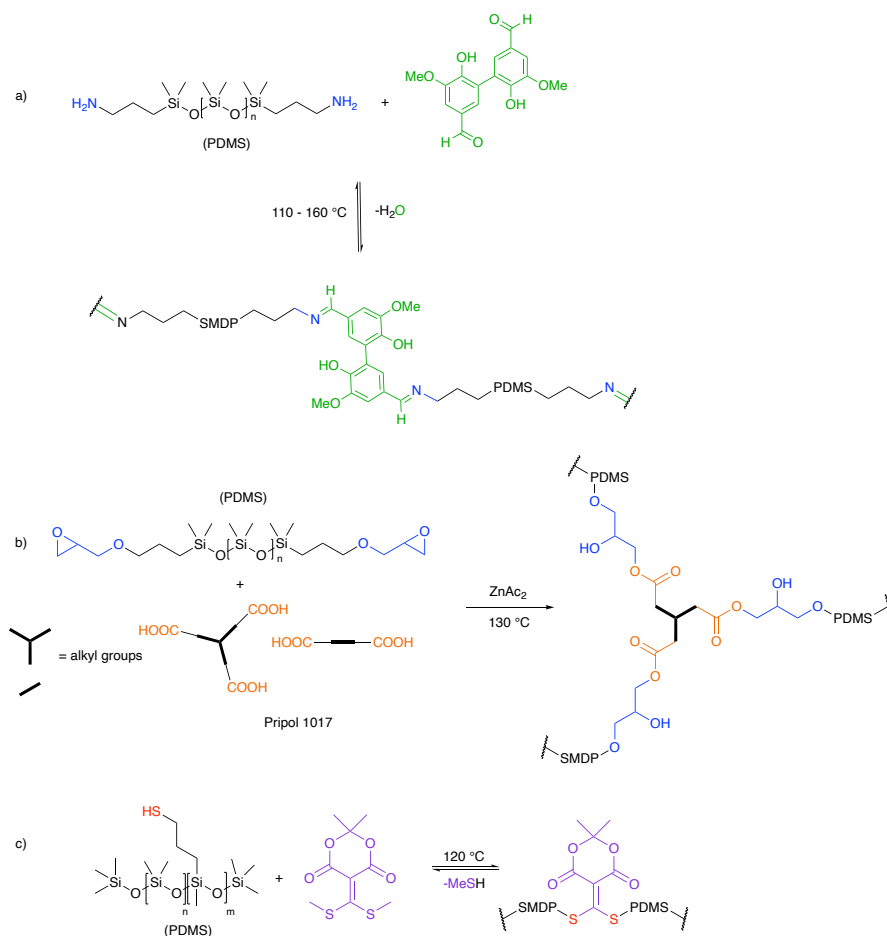


Figure 1.14 a) Crosslinking via imine condensation and phenol hydrogen bonding,³⁸ b) crosslinking via epoxide ring opening forming esters,³⁹ c) crosslinking via addition to a Meldrum's acid derivative.⁴⁰

1.4 Thesis Objectives

Dynamically crosslinked systems offer many advantages over traditionally crosslinked systems and introduce novel properties to silicone elastomers. Most silicone manufacturers, e.g., Dow Corning, Shin-Etsu, and Elkem, focus on thermoset silicone elastomers and offer no thermoplastic silicone elastomer products. Their primary foci have been trying to optimize their existing processes by improving turnover frequencies and turnover numbers through the use of promoters, reducing catalysts loadings while still achieving the same product, or using alternative catalysts that are based on platinum or other late transition metals.¹³ These practices are with good reason from an economic standpoint, as most of the crosslinking methods previously mentioned require significant synthetic work to modify polymers, elastomers that do not have the same properties as commercially available products, or unfavourable reaction conditions in comparison to commercial processes. It would be particularly advantageous if, in addition to the beneficial properties already possessed by silicone elastomers, a process could be developed to permit polymers and crosslinkers that are already synthesized industrially at a large scale and use them to create materials that have properties that are similar to commercial products and also can be recycled.

1.4.1 Silicones Crosslinked using Catechol Chemistry

Catechol is a simple phenolic compound that is industrially synthesized from phenol and has two phenolic hydroxyl groups attached to a benzene ring in an *ortho* pattern (Figure 1.15).⁴¹ In spite of their simple structure, catechols are rich and diverse in

both covalent and non-covalent interactions. Hydrogen bonding and pi-pi interactions are among the most obvious that catechol can participate in and these are important interactions in protein folding, and surface interactions, such as those found with the adhesives mussels use to adhere to various surfaces.^{42, 43} Having two phenol groups makes catechol slightly more acidic than a typical phenol (pKa ~9 compared to 10) making it more prone to deprotonation by weak bases such as amines (pKa of ammonium ~10), thus allowing for acid-base equilibria.⁴⁴ Another interesting non-covalent interaction that catechols can exhibit is cation-pi interactions, the interaction of the quadrupole of the pi system with a cation, which is an additional important interaction present during the adhesion of aquatic species such as mussels and barnacles to different substrates.⁴⁵ Thus, several non-covalent interactions can arise from a very simple molecule, with hydrogen bonding and ionic interactions being the most relevant for this discussion.

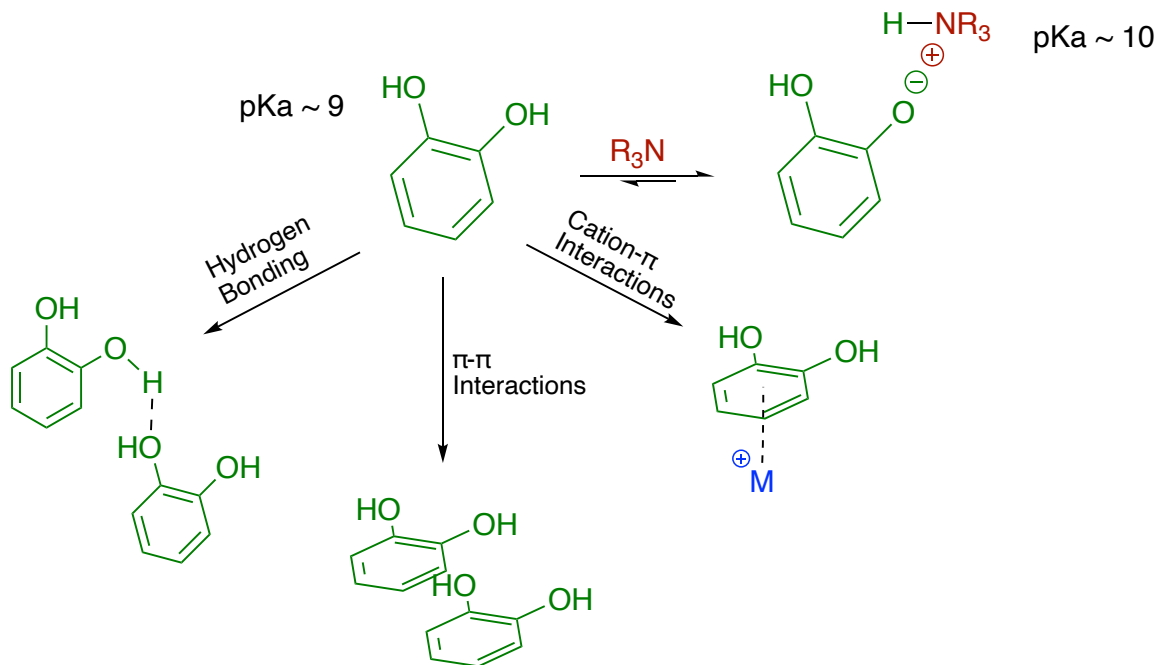


Figure 1.15 Structure of catechol and non-covalent interactions it can participate in. R = hydrogen or alkyl groups, and M = a cationic species, most commonly a metal, but other possibilities exist such as ammonium cations.

Catechol is capable of being oxidized to the respective orthoquinone, and once oxidized can exhibit unique reactivity (Figure 1.16). Orthoquinone can react with a molecule of catechol to create two phenoxy-radicals, which can then couple to form a C-C linkage.⁴⁶ Amines can react with the ortho-quinones in 2 ways that are relevant: via Schiff base condensation; and, aza-Michael addition.⁴⁶ The formation of Schiff bases is particularly interesting since many CANs are already based on this type of reactivity.⁴⁷ It should become readily apparent that catechol while appearing to be a simple molecule on the surface, is versatile in its chemistry.

Since catechol is capable of both dynamic non-covalent interactions, and dynamic covalent interactions, it would be particularly interesting if it could be incorporated into a

siloxane network. To meet our requirements of not modifying any polymers or crosslinkers, we can use readily available, industrially synthesized amine-functional silicones and catechol as a crosslinker, to create a system held together by dynamic linkages. Pyrogallol, similar to catechol but bearing an additional phenol, would also be interesting to investigate. An added benefit of this system could be the novel properties that catechol and pyrogallol have as antioxidants, which may be relevant in silicone products.⁴⁸ Thus, the properties that these phenolic compounds can impart into silicone elastomer products could be valuable, and applications may include adhesives, thin film coatings to protect oxidation-prone substances or antibacterial coatings. An examination of processes that allow catechol and related compounds to crosslink silicones is presented in Chapter 2. The properties of the resulting elastomers are also discussed.

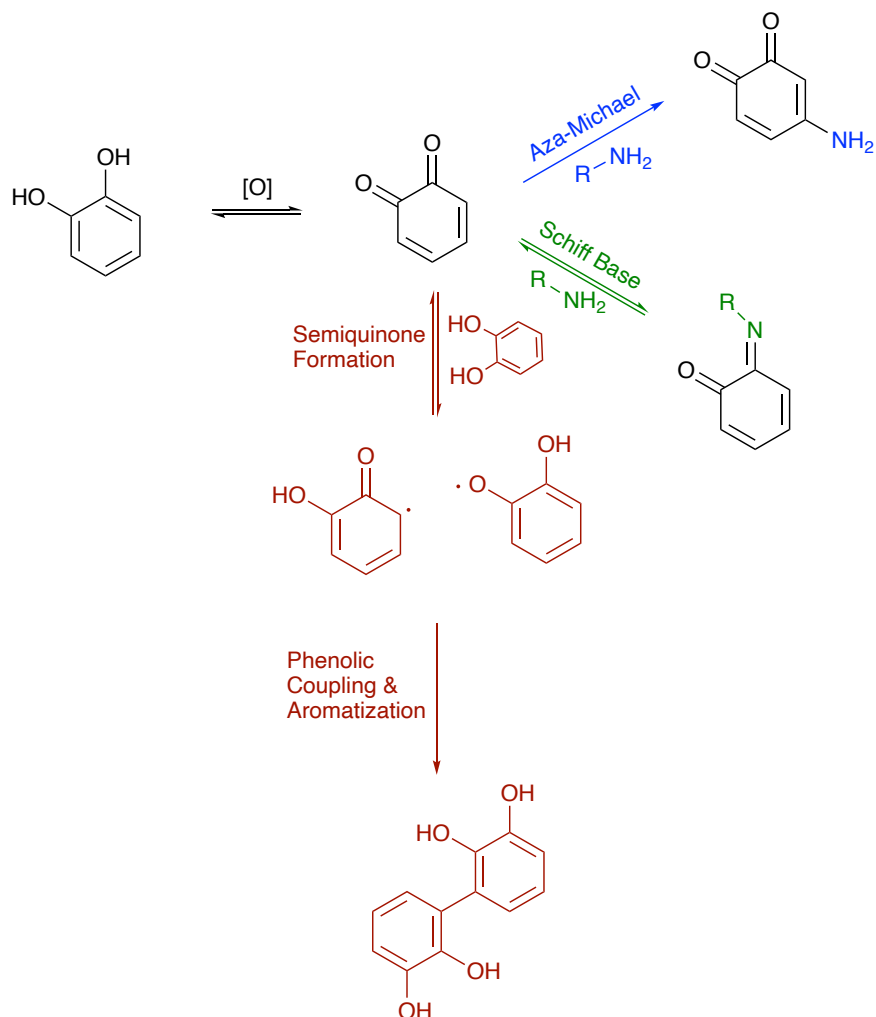


Figure 1.16 Reactivity of orthoquinone with an amine, leading to a Schiff base or aza-Michael product. Coupling of the orthoquinone and catechol is also possible, leading to a di-catechol species. Pyrogallol can also exhibit similar reactivity.

1.4.2 Green Alternatives to Catechol: Tannins

While catechol has many interesting properties and can bring new properties to silicone elastomers, it suffers from being rather toxic. Catechol can undergo a variety of redox properties and can act as a pro-oxidant, leading to damage of biological macromolecules including DNA and proteins.⁴⁴ For this reason, finding an safer

alternative compound/material that has many of the same advantages as catechol is important to create less hazardous materials. Catechol and pyrogallol units are naturally occurring in various biological systems, including fruits, trees, and our brains, where they play important roles. These compounds are known as polyphenols, having multiple different types of phenolic rings present in their structures. A particular class of polyphenols, known as tannins, have found significant industrial use historically, from being used to tan leather, as wood adhesives, being added to alcoholic beverages such as beer and wine, and used to make biobased foams.⁴⁹

Tannins are produced on a commercial scale, and most tannins do not have disadvantageous toxic properties. They could therefore be a fantastic alternative to the simple phenolic compounds mentioned above. Condensed and hydrolysable tannins are categories of tannins based on their chemical structures. Hydrolysable tannins can be classified by their characteristic sugar core, usually D-glucose, and are linked by an ester bond, which is hydrolysable, between the alcohols of the glucose and phenolic fragment of the molecule.^{50, 51} Condensed (or proanthocyanidins) tannins are typically oligomers of catechin and epicatechin and their molecular weight can range from 500 to more than 20,000 g/mol (Figure 1.17).⁵² The synthesis of tannin-based silicone elastomers would keep most of the promising characteristics of the catechol/pyrogallol-based elastomers but build upon them by offering a crosslinker that is already commercially available while being derived from renewable resources. Additionally, tannins are capable of bringing their unique properties to the materials, such as the ability to act as flame retardants.⁴⁹ A

comparison between silicones crosslinked with small molecules and with tannins is the focus of Chapter 3.

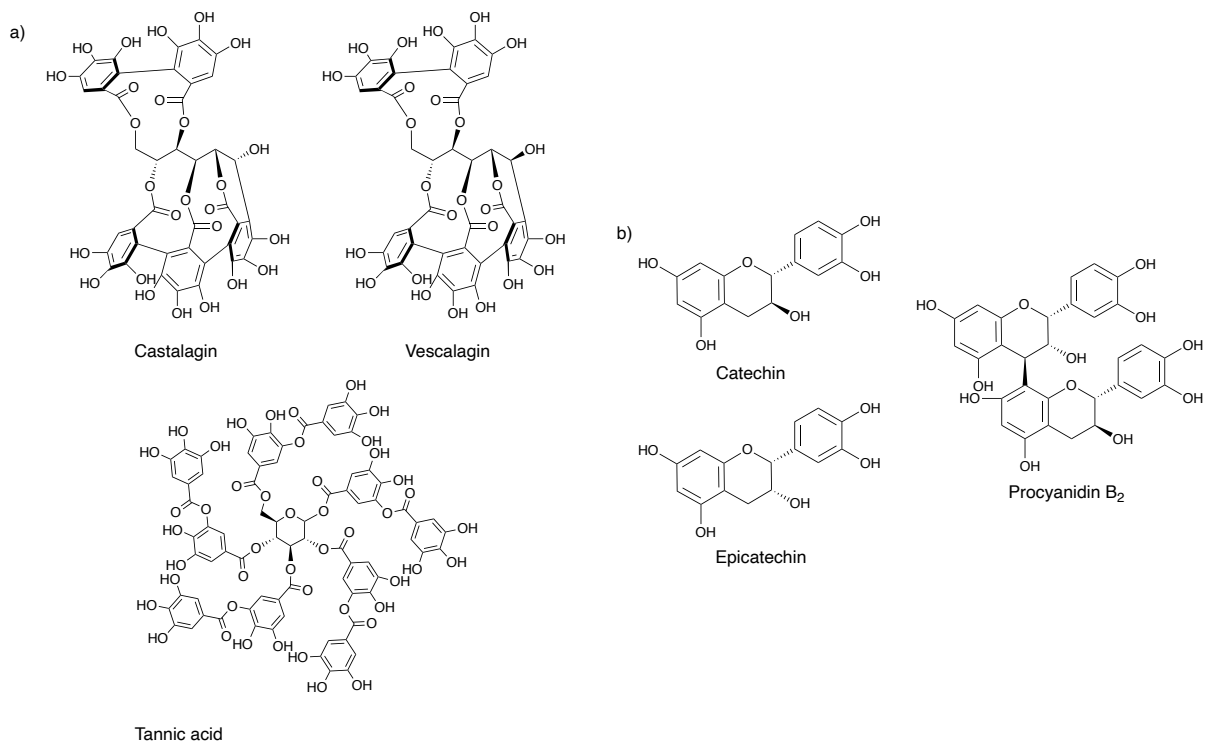


Figure 1.17 Structures of selected tannins: a) ellagitannins castalagin and vescalagin, and gallotannin tannic acid, b) condensed tannins based on monomeric catechin and epicatechin, procyanidin B₂ as an example.

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Chapter 2. Antioxidant Silicone Elastomers without Covalent

Cross-Links

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2.1 ABSTRACT

Improved sustainability is associated with elastomers that readily break down in the environment at end of life and, as importantly, that can be reprocessed/reused long before end of life arises. We report the preparation of silicone elastomers that possess both thermoplasticity – reprocessability – and antioxidant activity. A combination of ionic and H-bonding links natural phenolic antioxidants, including catechol, pyrogallol, tannic acid and others to telechelic aminoalkylsilicones. The mechanical properties of the elastomers, including their processability, is intimately linked to the ratio of [ArOH]:[H₂NR] that was found to be optimal when the ratio exceeded 1:1.

2.2 INTRODUCTION

Polysiloxanes or silicones are an economically important class of polymers widely used due to their excellent thermal and oxidative stability, low T_g and biocompatibility.¹ Recently, the rise in plastic pollution and its associated impacts on wildlife and human health have brought into the spotlight the end fate of all polymer materials, including silicones. Compared to other widely used linear industrial polymers, such as poly(ethylene terephthalate), polystyrene and polyethylene, silicone oils have a favorable end-of-life fate; they are degraded through natural environmental processes to eventually form carbon dioxide, silica, and water.^{2,3} A large fraction of silicones are sold as elastomers or resins. As with other solid, crosslinked polymers, these are thermosets and challenging to recycle, although both academic^{4,5} and commercial processes (e.g., EcoUSA www.ecousaind.com) are beginning to tackle this problem. Inevitably, the rates of degradation of silicone elastomers in the environment will be much lower than for the highly mobile silicone oils.

The sustainability of a polymer must, of course, be determined by examining the entire lifecycle from production to disposal, not simply the end-of-life considerations. The necessary monomers for all silicone polymers are produced using the Direct Process that uses silicon metal as a starting material. Silicon is first prepared from sand in a very energy intensive process⁶ that significantly reduces the degree to which silicones can be considered sustainable. Several strategies can be imagined for improving silicone sustainability. In the first, the amount of silicone needed for a given application is diluted

by incorporating natural materials, including proteins,⁷⁻⁹ cellulose,¹⁰ lignin,^{11, 12} antioxidants¹³ and others; the inclusion of such materials should also facilitate degradation at end of life. In the second, non-covalent linkages including hydrogen bonding, pi-pi association, and ionic linkages or dynamic bonding interactions are used, such that the materials are thermally (re)processable – thermoplastic elastomers – to facilitate reuse, repurposing and finally recycling. These types of bonds should be much easier to be break than covalent bonds at end-of-life, promoting environmental degradation.

A variety of strategies to prepare non-covalently linked silicone elastomers have been reported. Fawcett et al. incorporated coumarin groups into the backbone of linear silicones,¹⁴ which formed elastomers through association of the aromatic coumarin groups and could be recycled thermally. The use of ionic bonds to synthesize silicone elastomers has also received significant attention. Gemini interactions between silicone dicarboxylic acids and silicone diamines led to robust materials, until about 80 °C was reached, at which point they became processable fluids that upon cooling regained their elastomeric properties.¹⁵ An alternative strategy exploits dynamic imine bonds that, in the presence of small quantities of amine or aldehyde, lead to elastomers that are thermoplastic and self-healing at room temperature but completely dissolve in the presence of excess monoamines.^{16, 17} Most of these examples take advantage of the wide availability of aminoalkylsilicones (the terminology ‘aminosilicones’ will be used to reflect telechelic or pendent aminoalkylsilicones).

An alternative strategy to create re-processable silicone elastomers without covalent bonds hinges on hydrogen bonding, which may be transient. Recently, Huang et al. demonstrated that polymer and material properties could be precisely tuned by changing the number of hydrogen bond donors and acceptors in the system.¹⁸ In another example, sugar silicones were shown to exhibit different elastomeric properties ranging from a glass to soft gel simply by modifying the ratio of sugar to silicone.¹⁹ Kong et al. demonstrated that aminosilicones would combine with tannic acid (Figure 2.1) using hydrogen bonding in a simple manner to achieve silicone elastomers linked via hydrogen bonds.²⁰

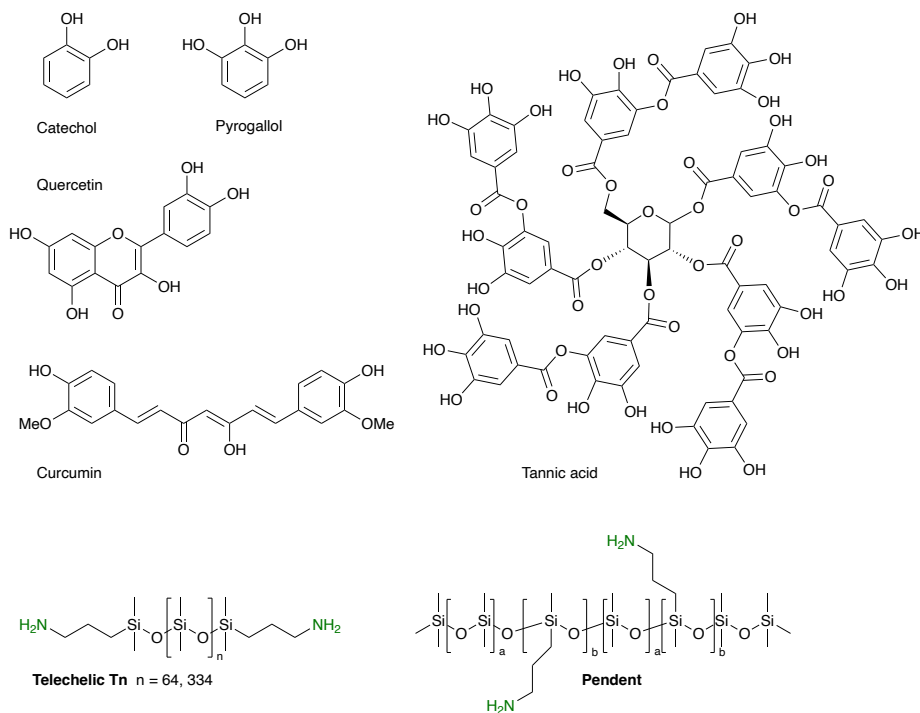


Figure 2.1 Natural phenolic antioxidants and aminoalkylsilicones.

We wished to understand if phenolic hydrogen donors²¹ – functional groups that are also antioxidants – could be used to make (re)processable silicone elastomers. Such materials would be more sustainable both because of facile reprocessing and the incorporation of natural materials. We describe the systematic examination of reactions between simple phenols, diphenols and more complex natural antioxidants with aminoalkylsilicones to prepare supramolecular silicone elastomers through a green, one pot process. The antioxidant capabilities of the resulting elastomers are reported, along with strategies to permit thermal recycling/reprocessing or the complete degradation of the elastomer under mild conditions.

2.3 RESULTS

2.3.1 Preparation of Antioxidant Silicone Elastomers

Preliminary studies were used to map out the types of interactions that could occur between phenols and aminoalkylsilicones. The latter compounds are commercially available in both telechelic and pendent formats (Figure 2.1). It soon became clear that materials derived from pendent silicones, with the possibility of both intra- and intermolecular crosslinking were, at a practical level, unmanageable. It was particularly challenging to create homogenous materials before the mixtures ‘set’ and, even when efficient mixing was possible, it was difficult to avoid brittle products. In addition, the pendent-derived elastomers (or resins), once formed, proved extremely resistant to further modification, including by degradation (see below). Therefore, only telechelic silicone polymers were examined as the key structural elements for antioxidant elastomers (note:

nomenclature $\mathbf{T}_n = \text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OSiMe}_2)_n\text{OSiMe}_2(\text{CH}_2)_3\text{NH}_2$, where $n = 64, 334$).

Note, while it was possible to make elastomers from shorter telechelic polymers (3000 g mol⁻¹ or less) the products varied in moduli ranging from very stiff to brittle glasses that were impractical for many uses, similar to pendent silicone-derived examples.

Initially, studies were undertaken between a series of telechelic silicones and (monofunctional) phenol. It was discovered that there were only subtle increases to the viscosities of the formulations; elastomers did not form. The monofunctional phenol is expected to cap the telechelic monoaminosilicones but has no additional mechanism for crosslinking; any pi stacking/aromatic associations interactions that do exist are not strong enough to create elastomers.¹⁴

The natural antioxidants chosen for this study have a very broad range of structural motifs (Figure 2.1). Therefore, for purposes of comparison it was decided to use the ratio [ArOH]:[NH₂] of aromatic phenol to primary amine functional groups as the basis of comparison for all formulations. For example, in the case of pyrogallol that carries three phenolic groups, a 1:1 [ArOH]:[NH₂] correlates to [pyrogallol]/3:[NH₂].

Unlike simple phenol, the use of phenolic antioxidants with more than one phenol group, such as difunctional catechol, gave elastomers over a wide range of [ArOH]:[NH₂] ratios. A library of elastomers was therefore created, derived from telechelic aminosilicones of various molar masses and antioxidants with both different architectures and numbers of phenol groups in ratios of [ArOH]:[NH₂] 4:1 → 1:4 with catechol and

pyrogallol derivatives (Table S1, Table S2, Supporting Information, SI) and, in less detail, with curcumin, quercetin and tannic acid derivatives (Table S3). The physical properties and appearance of the elastomers were tied to $[\text{ArOH}]:[\text{NH}_2]$; increasing the fraction of ArOH groups resulted in the materials moving from yellow/orange to brown in color with decreased transparency (Figure 2.2) and to stiffer, stronger materials (Figure 2.3).

Generally, it was necessary to use minimal amounts of the greener solvent 2-propanol (IPA)^{22, 23} to dissolve the pre-elastomer mixture of aminopropylsilicone and phenolic antioxidant, which gave homogeneous elastomeric mixtures after solvent evaporation (mixing was performed using a magnetic stir plate); no catalysts were required. Note that the use of other solvents, such as dichloromethane or toluene, were unsuccessful, as the elastomers formed were not uniform. Some of the phenolic antioxidants, particularly tannic acid and curcumin, were poorly soluble in IPA such that methanol (co)solvents were required. Pre-elastomer solutions led to transparent elastomers while alcoholic dispersions led to opaque elastomers. In all cases the degree of coloration correlated with the phenolic content (Figure 2.2B→D). Uniform elastomers could be created, in some cases, without any solvent at all by mixing at high shear provided one was prepared to use extended preparation times (~1 hour, Figure 2.2A); the use of solvent was more practical.

The rate of cure, using Shore OO hardness as a surrogate for cure, was dependent on a variety of factors, including the presence of alcohol solvents, temperature and the net concentration of phenols and amines; the [ArOH]:[NH₂] ratio played only a subservient role. In the absence of solvents, faster cure was associated with higher phenol concentrations; only with trifunctional pyrogallol at the 4:1 [ArOH]:[NH₂] ratio was cure complete within 3 days, which is inconsistent with H-bonding as the primary chemical crosslinking process; the establishment of H-bonding networks is typically very rapid.²⁴

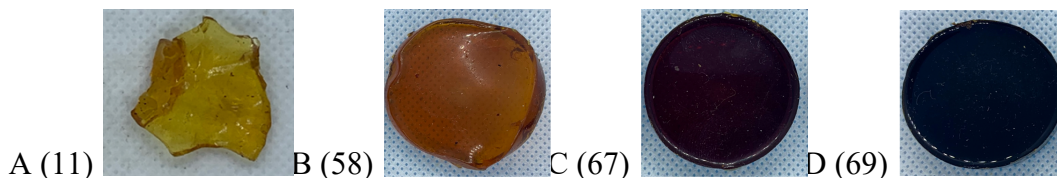
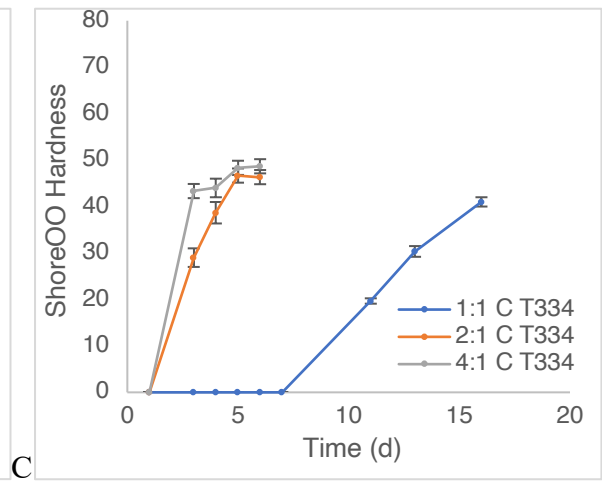
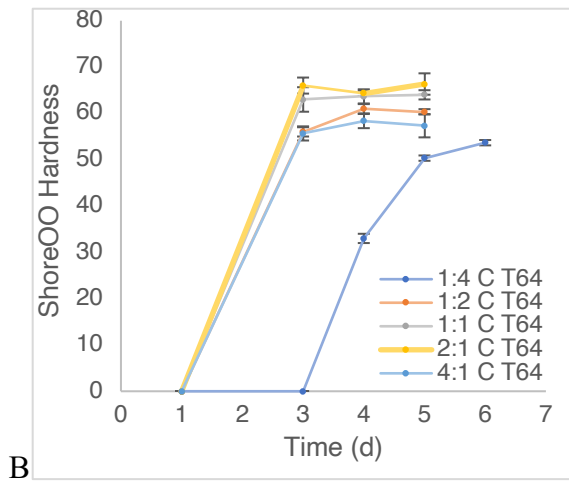
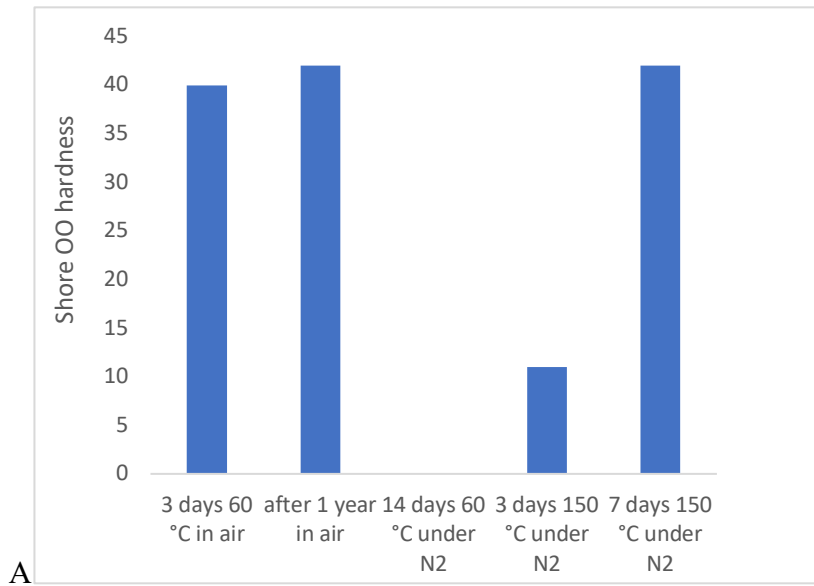


Figure 2.2. A: 1:1 [ArOH]:[NH₂] Catechol elastomers prepared from **T334** without solvent after mixing for 1 hour at 1200 rpm and curing for 15 days (degree of cure not established). Pyrogallol/**T334** elastomers B: 1:2, C: 1:1, D: 4:1 [ArOH]:[NH₂] after curing for 11, 3 and 2 days, respectively, at 60 °C (Figure 2.3B-E). Values in parentheses (Shore OO hardness).



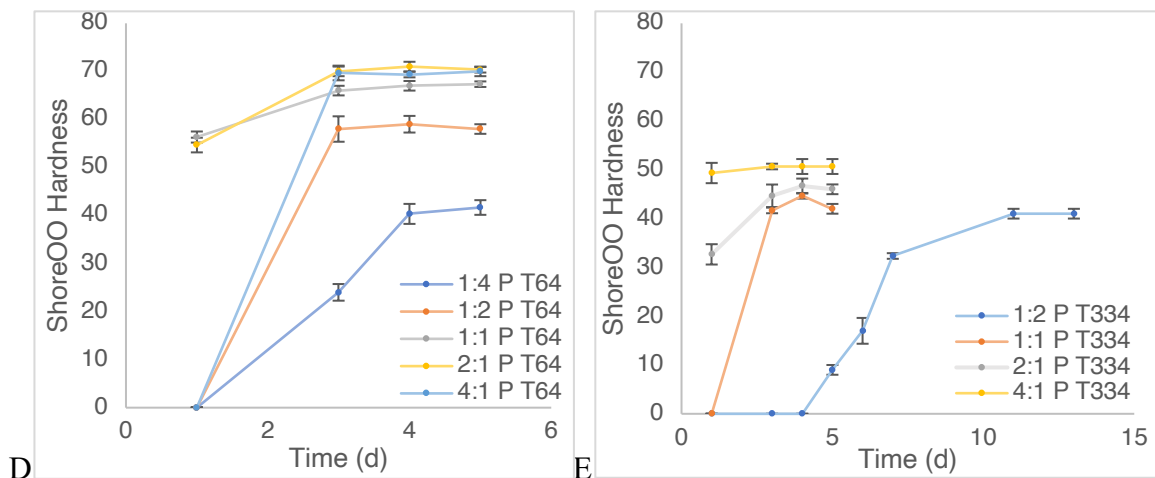


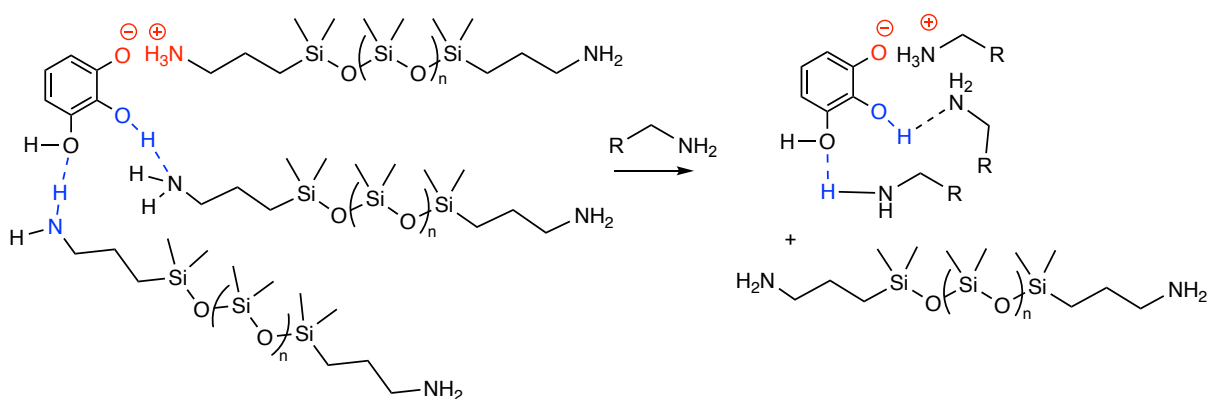
Figure 2.3. A: Differences in Shore hardness for elastomer pyrogallol/**T334** 1:1 cured in air or N₂ at various times and temperatures (the 14 days, 60 °C, N₂ sample was too soft to measure). Cure time tracked by Shore OO hardness as a function of [ArOH]:[NH₂] ratio. Catechol (C) and B: **T64** and C: **T334**. Pyrogallol (P) and D: **T64** and E: **T334**.

Other phenolic compounds cured more slowly. Cure at room temperature typically took 2-4 weeks, but was accelerated by heating (Figure 2.3). Unless kept under nitrogen, the samples slightly darkened in air. Elastomers prepared from more viscous materials typically cured more slowly.

Infrared spectroscopy data of elastomers synthesized from catechol and **T334** showed that O-H and N-H stretching frequencies (3321, 3348 cm⁻¹ and 3281, 3358 cm⁻¹, respectively), normally associated with the phenolic hydroxyl and amine groups, had disappeared after 14 days of curing (Figure S5.1, SI). The sensitivity of our IR instrument was insufficient to detect the putative (ammonium) phenoxide anion that should accompany OH/NH losses in elastomers with low amine content. Therefore, a small

molecule model study was undertaken with 1,3-bis(aminopropyl)tetramethyldisiloxane **T2** in combination with catechol after 24 hours. The IR spectra (Figure S5.2) indicated that the phenolic hydroxyl groups were absent and a new signal at 1487 cm^{-1} can be attributed to the C-O stretching frequency in the ammonium phenoxide product (Figure 2.4A).²⁵ In this case, the amine N-H stretching frequency was still present but had broadened, which can be attributed to hydrogen bonding interactions between the phenolic molecule and the aminosilicone (Figure 2.4A, blue). The chemical shift in the ^1H NMR associated with the aromatic hydroxyl groups of catechol also shifted from 8.76 ppm in the spectrum of catechol, to 4.4 ppm in the product spectrum (Figure S5.3).²⁶ These data are consistent with both H- and ionic bonding in these materials, with the latter more important.

A



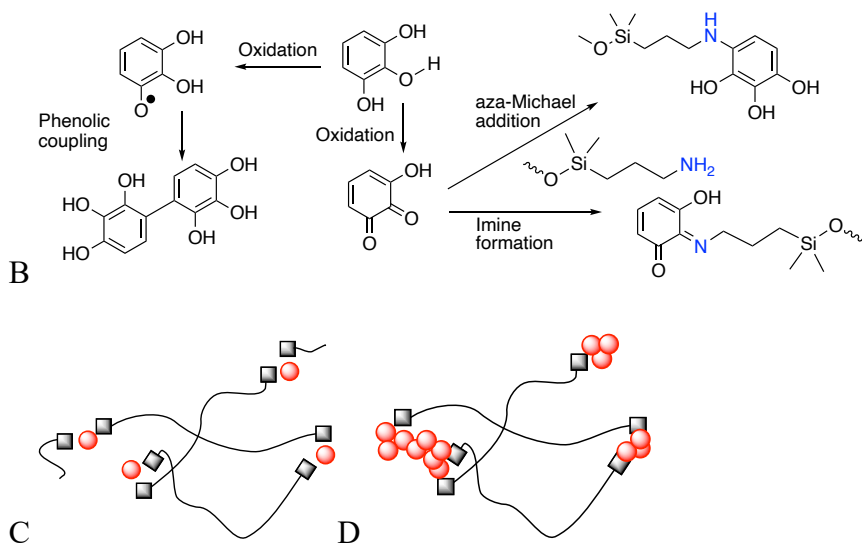


Figure 2.4. Putative bonding motifs between aminoalkylsilicones, e.g., **T64**, and antioxidant phenols. A: ionic and H-bonding, and exchange with small amines; B: Michael addition, imine formation and phenolic coupling; C: 1:1 HO---NH₂ binding vs D: clustering of phenols ● of different densities capped by aminopropylsilicones ■.

Note that cure of these elastomers at higher temperatures 60 - 150 °C under air – was faster, but was also associated with darker coloration and harder elastomers. The oxidation of phenols can be accompanied by phenolic coupling to give new crosslinkable phenolic molecules and, concomitantly, darker colors, particularly at higher temperatures (Figure 2.4B).^{15, 17, 27-30} To examine the impact of phenolic coupling, a comparison was made between samples cured in air or under a nitrogen blanket. Under N₂, elastomers formed, but much more slowly even when elevated temperatures, i.e., 150 °C; the compounds cured under nitrogen, were yellow, not brown or black. Differences in cure can be seen with pyrogallol/**T334** 1:1 cured in air or nitrogen (Figure 2.3A). Thus, the

materials cured under N₂ can develop cure to a similar degree as those prepared under air, but take longer to do so and higher temperatures are required. These data are consistent with oxidative coupling providing secondary crosslinking in air, but only to a minor degree.

The IR spectrum also provides evidence of either imine formation or Michael additions at very low levels arising from oxidation products of 1:1 [ArOH]:[NH₂] pyrogallol crosslinked elastomers. This was more clearly seen by exchanging the aminosilicones with benzylamine, which provided other signatures in the IR (see also below). The solid materials recovered exhibited some evidence of aza-Michael/imine reactions (Figure S5.4). However, as noted below, either type of secondary crosslinking is a minor contributor to the properties of the elastomer; ionic and H-bonding interactions dominate.

2.3.2 Physical Properties

Naively, it was anticipated that optimal crosslinking, as judged by Shore OO hardness, would arise at a ratio of [ArOH]:[NH₂] = 1:1, where all of the possible bonding interactions should be at a maximum (Figure 2.4C). Clearly, this was not the case either for the shorter **T64** or longer **T334** telechelic silicones. With only subtle variation, the Shore OO hardnesses were set predominately by the silicone chain length rather than the quantity of phenol present: Shore OO for **T64**-derived compounds ~60 and for **T334**-derived compounds ~45 (Figure 2.5). This was true for the ‘simple’ di- and tri-phenols,

but also the much more complicated structures of curcumin, quercetin and tannic acid (Figure 2.1, Table S5.2); Young's moduli showed similar correlations. These data are consistent, at higher phenol concentrations, with the linking of amines to clusters of phenols – the sizes of which are related to concentration of phenols in the matrix – rather than simple 1:1 ArOH:NH₂ interactions (Figure 2.4A-C). This conclusion, and the possible presence of antioxidant clusters (Figure 2.4C), is supported by DSC (differential scanning calorimetry) that, in one case, showed a crystalline transition in the as-formed elastomer that, on a second heating had disappeared (this effect was not observed in a different sample of the same material, Figure S5.5, SI). Extension at break with elastomers containing longer silicones chains were much higher with the longer **T334** elastomers.

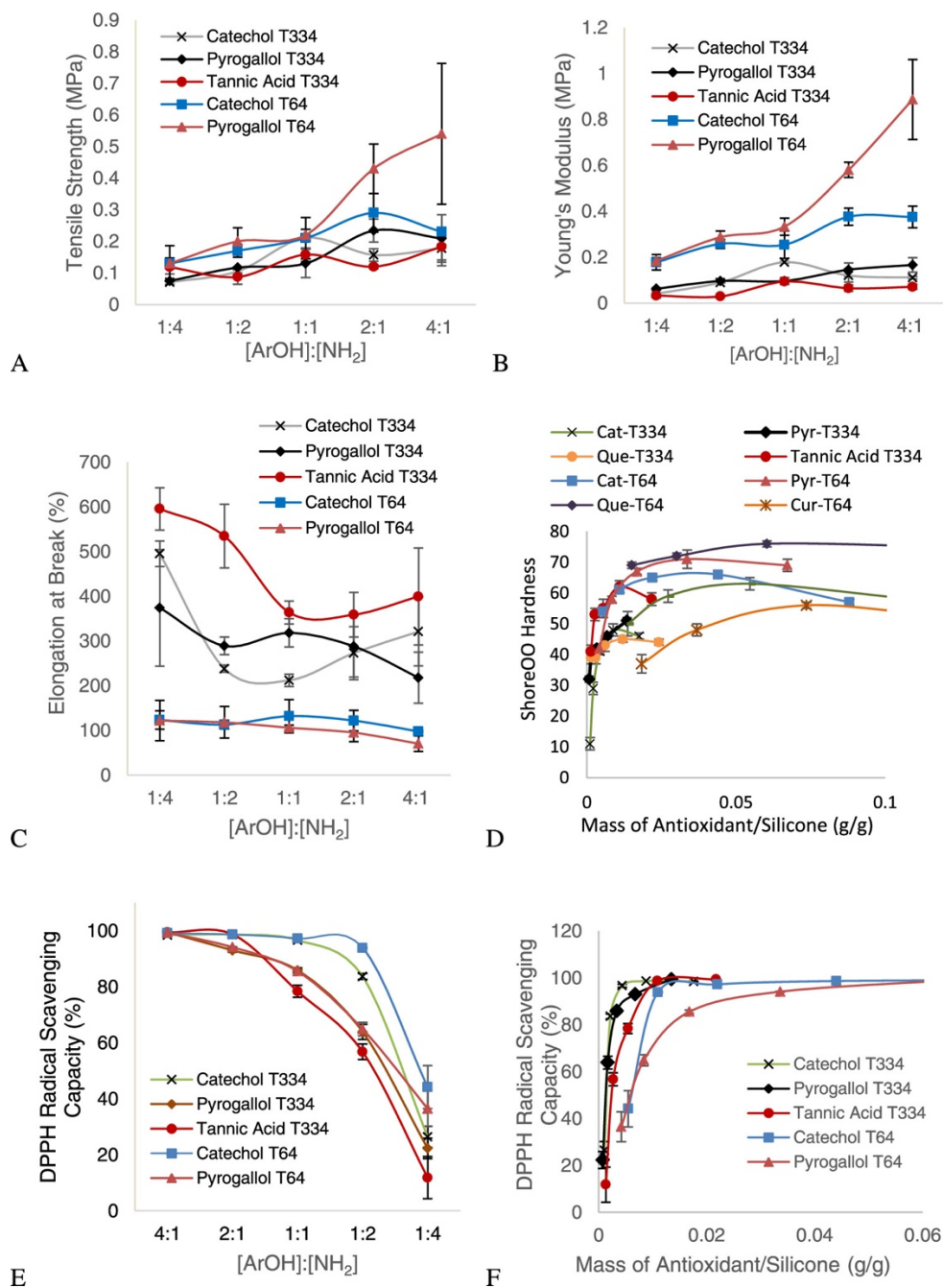


Figure 2.5. A: Tensile strength; B: Young's modulus; C: Elongation at break of elastomers as a function of [ArOH]:[NH₂] ratio. D: Shore OO hardness as a function of wt%

antioxidant in the elastomer. Antioxidant capacity of catechol and pyrogallol elastomers created with **T334** based on E: [ArOH]:[NH₂] ratio and F: wt% antioxidant in the elastomer. Measurements shown are the mean of 9 replicates. Cat = catechol, Pyr = pyrogallol, Que = quercetin, Cur = curcumin.

Samples became significantly darker if heated in air or allowed to age for up to two years at room temperature (Figure 2.2). While this is indicative of oxidative coupling (Figure 2.4B), it was not accompanied by measurable changes in hardness – it is not an efficient crosslinking process compared to the ionic/H-bonding processes (Figure S5.4). This was confirmed during the degradation studies (see below) in which the elastomers completely broke down in the presence of simple amines and the black materials associated with oxidative coupling or other covalent interactions were found at only very low levels (Figure 2.4A). Thermogravimetric analysis (TGA) of a catechol/silicone elastomer showed excellent thermal stability (Figure S5.5, SI).

2.3.3 Elastomer Reprocessing/Recycling

Thermoplasticity was observed at elevated temperatures with the phenol/aminosilicone elastomers. The materials could be broken/cut into pieces or ground at low temperature and then reassembled into elastomeric slabs simply by heating. In our hands, this was most efficiently achieved using a heat press at 180 °C. After heating samples for 40 minutes at 180 °C, all samples had recovered over 90% of the original properties (at 20 minutes heating, between 50-90% recovery was observed, suggesting insufficient time for annealing, Table S5.2). Thus, one must decide if complete recovery

of properties or time of recovery is more important. Note that thermal (re)processing could be practiced multiple times. A 2 year-old sample was cut into pieces, heat processed under pressure, sequentially five times with only a nominal change in Shore hardness from 42 to 36 (Figure S5.6). Thermal processing led to darker elastomers, presumably due to oxidative processes.^{15, 17, 27-30}

Solvation of the phenol/aminosilicone elastomers was slow and inefficient in non-polar organic solvents and was not observed in water regardless of pH from 3-9 (silicones are known to depolymerize outside of this pH range). For example, **T334** combined with catechol or pyrogallol, respectively, exhibited 0% swelling in water; about 129% swelling in IPA and 420-920% swelling in toluene over 2 days (Table S5.4, Figure S5.7). The corresponding mass losses of the elastomer after drying were: <1% (H₂O); 5-9% (IPA) and 9-16% (toluene); in the latter 2 cases the extracts were slightly yellow. The extractables show only silicone oil (Figure S5.8). Solvation could only be induced if elastomers were kept in an excellent polar solvent, THF, over very extended time periods (~ 30 days). Much faster degradation was observed when a chaotropic solution containing tetramethylguanidine, trifluoroacetic acid and THF was used.¹⁵ These data demonstrate the challenges of overcoming multiple bonding modes simultaneously; the combination of ionic and H-bonding to crosslink the materials is very effective.

It was also possible – and much more convenient – to overwhelm ionic/H-bonding interactions and dissolve the elastomer simply by dissolution in a molar excess of a

monoamine; butylamine was chosen because of its convenient boiling point. It took 1-3 days for complete dissolution to occur depending on the [ArOH]:[NH₂] ratio; materials formed at lower [ArOH]:[NH₂] ratios dissolve faster. This is not, of course, a solvation but instead a chemical exchange of one amine by another leading to elastomeric breakdown (Figure 2.4A). Once the amine was removed by evaporation, the elastomer reformed as either a film or bulk material (Figure S5.9).

2.3.4 Antioxidant properties

It has previously been shown that reactions of DPPH (2,2-diphenyl-1-picrylhydrazyl) – a redox indicator that antioxidants cause to convert from a purple to yellow color – can be performed in a silicone environment.³¹ All the natural phenols shown in Figure 2.1 exhibit antioxidant activity on their own to differing degrees; pyrogallol is a more efficient antioxidant in comparison to catechol.^{32, 33} Once within a silicone matrix, the differences between antioxidants were more subtle. Silicone elastomers containing higher phenolic crosslinker loadings showed higher antioxidant activities, as indicated by the lower absorbance at 520 nm (Figure 2.5D,E). As noted above, IR data shows, essentially, the absence of free phenol peaks. Thus, the antioxidant activity in these elastomer is proposed to be delivered from the phenolate, as is well known to occur³⁴.

2.4 DISCUSSION

Silicone elastomers are frequently utilized because of what they don't do, including not degrading: under high electric voltage/currents, high/low temperatures, or in the presence of water. One would like to maintain those beneficial properties, where needed, but add additional functionality, including better sustainability. The combination of natural phenolic materials with aminosilicones achieves both these objectives.

2.4.1 Bonding Motifs

Kong et al. suggested that tannic acid interacts with aminosilicones via H-bonding.²⁰ With efficient mixing, H-bonding is normally a rapid, facile process²⁴ and formation of elastomers from such bonding alone is inconsistent with the slow cure times observed (Figure 2.3). Several other bonding motifs are possible between phenols and amines in addition to H-bonding between the amine and phenol. The pKas of phenols and ammonium ions are very similar,³⁵ suggesting ionic linkages are also viable. The slow cure is also consistent with previous studies that suggest ionically crosslinked elastomers require elevated temperatures to achieve full cure.^{15,30} In addition, the oxidation of phenols, particularly polyphenols, to ketones leads to a variety of binding motifs including imines, and derivatives of aza-Michael addition products (Figure 2.4A,B).³⁶

The binding motifs that hold the elastomers together include hydrogen bonds²⁰ but, based on IR data, ionic bonding is more important (Figure 2.4). The observation that optimal bonding occurs between the natural and synthetic materials at $[\text{ArOH}]:[\text{NH}_2]$

ratios $> 1:1$ is consistent, in addition to H/ionic bonding, to phase separation of the antioxidant into separate phenol-rich domains, which act as secondary types of crosslinking.

We were concerned that oxidative phenolic coupling (Figure 2.4B) could be an important bonding motif leading to crosslinking of the elastomers. This suggestion was supported by the darker colors that accompanied heating, particularly in air, or leaving the samples for extended periods of time (up to two years). However, it was not supported by the outcome of the degradation experiments. The reaction with butylamine leads to brown or black solutions, but not to retained elastomers or gels; the mass fractions recovered of the brown/black materials were insignificant. Thus, color did not correlate with crosslink density (unfortunately – it would have been a convenient way to monitor cure) and oxidative coupling is only a very minor process occurring in these elastomers.

Data measured on the library of elastomers shows that mechanical properties correlate well with, and can be simply tuned by, the length of the telechelic silicone polymer with longer silicone chains leading to softer, more extensible materials, due to lower crosslink densities. However, at a given $[\text{ArOH}]:[\text{NH}_2]$ ratio there was little impact of the specific antioxidant structure on physical properties, as shown by comparing Shore OO hardness or Young's modulus (Figure 2.5A-D, Table S5.2, Table S5.3); pyrogallol was an outlier at $[\text{ArOH}]:[\text{NH}_2]$ ratios. The antioxidant silicone elastomers are robust

elastomers with properties that are very similar at room temperature to pure, commercial silicones.

The ability to thermally reprocess/reuse the elastomers simply by heating, or completely de-crosslink the elastomers under mild conditions, for example using butylamine, further increases the inherent sustainability of the elastomers (we note that the amine-promoted decrosslinking of even highly colored elastomers was very efficient, leading to solutions with no residual gels or elastomers; thus, the phenolic coupling that is likely responsible for the intense color^{27, 28} remains a very minor process in the cure profile). Clearly, these benefits will also act to limit the use of these materials to applications that will not take place at elevated temperatures or under basic conditions. In addition, the elastomers take on colors not everyone will find attractive, and they are not transparent at higher antioxidant loadings. It is our opinion that these possible detriments are far outweighed by their improved sustainability.

The elastomers also exhibit antioxidant activity due the presence of phenols and phenolates. Although the structures of the phenolic compounds contained: tannic acid; pyrogallol; and catechol are very different, there was surprisingly little difference in the degree to which the elastomers acted as antioxidants (Figure 2.5E); tannic acid was less effective than the other two on the basis of [ArOH]:[NH₂] ratios, but in the middle of the pack based on wt% loading. These data suggest that self-association between the phenolic compounds themselves – which will be different depending on antioxidant structure –

acts to moderate both antioxidant activity and binding to aminosilicones. The self-association of the aromatic constituents in such domains will be facilitated by phenolic hydrogen bonding, but may rely even more on low(er) levels of solubility of phenolic compounds in the silicone medium and favorable interactions between the aromatic groups, including pi-pi or related interactions.¹⁴ Regardless of the specific bonding motifs, it is straightforward to select mixtures to generate elastomers with both appropriate physical and antioxidant properties. That is, an appropriate formulation can be selected depending on the desired outcome, including: physical; antioxidant properties; cost using a wide variety of di- or oligophenolic antioxidants and commercial aminosilicones.

Commercial silicone elastomers are thermosets that rely on cure catalysis by radical, metal ester or transition metal complexes that may be expensive (Pt) and or toxic (Sn); removal of the catalyst and by products is typically impractical except for radical processes with which the elastomers are usually baked post cure. Metal catalysts can leach from the body of the elastomer to the local environment, which could be problematic. Antioxidant elastomers prepared from antioxidants and aminosilicones, unlike other processes that require covalent bonds for crosslinking,¹³ are thermoplastic and need no cure catalyst whatsoever, obviating any concerns about catalysts or their release. When the elastomer eventually undergoes degradation, it will do so releasing antioxidants that are already well dealt with in the environment. Thus, on this basis alone, one can consider these elastomers more sustainable.

The presence of the natural materials within the silicone elastomer dilutes the amount of silicone one needs for a given application. Since the synthesis of silicones starts with a very high energy process to make silicone metal,⁶ any dilution of the silicone by natural materials reduces the net energy content in the product. For the moment, we can only hypothesize that the presence of these materials will facilitate degradation of these antioxidant silicones in the environment; work is underway to attempt biological degradation. These factors too increase the sustainability of the elastomers.

Until recently, the incorporation of natural products into synthetic polymers was frequently seen to be a compromise, for example, to reduce costs. However, natural products can also deliver utility. The antioxidants described here have been shown to have interesting biological properties, including anticancer³⁷ or antibacterial/antifungal properties.³⁸ While we have only demonstrated to date the application of antioxidant properties within the silicone elastomers, the use of the phenolic natural materials enables additional sustainability based on many different metrics, including absence of catalysts, thermal reprocessing, and facile recycling.

2.5 EXPERIMENTAL SECTION

2.5.1 Materials

Aminopropyl terminated polydimethylsiloxanes, **T37** (DMS-A15, 50-60 cSt, $M_n=3000 \text{ g mol}^{-1}$), **T64** (DMS-A21, 100-120 cSt, $M_n=5000 \text{ g mol}^{-1}$), **T334** (DMS-A31, 900-1100 cSt, $M_n=25,000 \text{ g mol}^{-1}$) and 1,3-bis(3-aminopropyl)tetramethyldisiloxane **T2** were

purchased from Gelest. Catechol (99%), phenol (99%), 2,2-diphenyl-1-picrylhydrazyl (DPPH), dimethyl sulfoxide-*d*₆ (99%), curcumin, quercetin (95%), tannic acid, 1,1,3,3-tetramethylguanidine (99%), butyl amine (99%), benzyl amine (99%) and trifluoroacetic acid (99%), were obtained from Sigma-Aldrich. Pyrogallol (99%) was obtained from EMD-Millipore Corporation. Solvents were obtained from Fisher Scientific. All reagents and solvents were used without further purification.

2.5.2 Methods

An ASTM D412 Type D cutting dye was purchased from Universal Grip Co. Tensile measurements were performed using an Instron 5900 series Universal Mechanical Tester. Young's Modulus were taken at 10% strain. UV-Vis measurements were performed using a BioTek Synergy LX multi-mode plate reader. ¹H-NMR spectra were obtained using a Bruker NEO 600. IR spectra were obtained using a Nicolet 6700 FT-IR Spectrometer. Dynamic scanning calorimetry was measured on a TA-instruments DSC Q20 calorimeter with a heating ramp of 10 °C·min⁻¹ under an N₂ atmosphere.

2.5.3 General Procedure for Synthesis of Elastomers

The appropriate mass of **T334**, **T64**, or **T37**, phenolic compound, and solvent (Table S5.1) were added to a 100 mL Flacktek cup. The mixture was stirred using a magnetic stirrer set to 500 rpm until a homogenous solution was obtained. Solutions were placed in an oven at 60 °C for 2-15 days to cure in the case of catechol and pyrogallol. Cured samples were placed on Teflon sheets and processed using a 12-ton Dabpress heat

press at 180 °C to provide samples ~ 1 mm thick for ~ 20 min, or 40 min in the case of catechol 1:1 and 2:1 **T64** and 4:1 **T334** (Table S2). Samples were then cut using an ASTM D412 Type D cutting dye to provide samples for tensile tests or a 1.5 cm diameter metal punch to provide samples for antioxidant assays. Dynamic scanning calorimetry (DSC) was measured on a TA-instruments DSC Q20 calorimeter with a heating ramp of 10 °C·min⁻¹. Thermogravimetric analyses were done using a Mettler Toledo TGA-DSC 3+ using 70 µL alumina pans (2 to 5 mg of sample). A 30 cm³ min⁻¹ nitrogen purge was applied and the furnace was heated from 25 °C to 500 °C at 10 °C min⁻¹ (Figure S5.5).

2.5.4 Role of Phenol

Samples prepared with phenol were formulated identical to those seen in the general synthesis of elastomers, however, elastomers were never obtained even after curing for >30 days at 60 °C (Table S5.1).

2.5.5 General Procedure for the Synthesis of Elastomers with No Solvent

The appropriate mass of catechol and either **T64** and **T334** were weighed out according to a 1:1 [ArOH]:[NH₂] (Table S5.1). The catechol was placed in a mortar and pestle lined with weighing paper and the aminosilicone was placed in a 10 mL FlackTek cup. The catechol was crushed into a fine powder, added to the 10 mL Flacktek cup containing the aminosilicone, and the two were stirred for 1 h at 1200 rpm on a magnetic stirrer. After a homogenous solution was obtained, the sample was speed mixed at 3500 rpm for 10 s to ensure even dispersion using a FlackTek speedmixer (Dual Asymmetric

Centrifuge [DAC] Model DAC 150.1 FV7-K). Samples were then placed into an oven to cure at 60 °C for 4 days in the case of the **T64** sample, or 15 days in the case of the **T334** sample. In practice, the use of a solvent was more practical.

2.5.6 General Procedure for the Synthesis of Tannic Acid-based Elastomers

The appropriate mass of tannic acid and either **T334** or **T64** were placed into a round-bottomed flask and an Erlenmeyer flask, respectively. The aminosilicone was dissolved in 2-propanol while the tannic acid was dissolved in ethanol (Table S5.3), after which the tannic acid solution was added to the round-bottomed flask. The solution was stirred for ~20 min (until homogenous), and the solvent was removed using a rotary evaporator. Samples were poured into a 100 mL Flacktek cup and put into an oven to cure at 60 °C for 1-4 days for **T64** samples and 3-7 days for **T334** samples.

2.5.7 General Procedure for the Synthesis of Curcumin/Quercetin Elastomers

Either **T334** or **T64** was dissolved in 10 mL of IPA via stirring on a magnetic stirrer (Table S5.3). The appropriate phenolic compound was weighed, placed into an Erlenmeyer flask, and dissolved using the appropriate solvent. The phenolic solution was poured into the round-bottomed flask containing the aminosilicone, and the solution was stirred rapidly for 60 min. The solvent was then removed using a rotary evaporator, samples were poured into a 100 mL Flacktek cup, and put into an oven to cure at 60 °C. Cure times varied from 1-4 days for quercetin, **T64**, 1-2 weeks for curcumin **T64**, and 3-7 days for quercetin **T334**.

2.5.8 Curing under Nitrogen

The same formulations as those indicated in the previous section were used for cure under nitrogen (Table S5.1). To cure under nitrogen, the aminosilicone was weighed in a two-neck flask which was capped with two rubber stoppers. The flask was purged with nitrogen for 1 min, followed by a 20 min sparge. The phenolic compound was quickly added, and the reaction was done under a positive pressure of nitrogen (Figure 2.3A).

2.5.9 Model Siloxane Studies

T2 and catechol were weighed in a 1:1 [ArOH]/[NH₂] ratio. The siloxane was dissolved in toluene in a round-bottomed flask, and catechol was dissolved in the minimal amount of 2-propanol (~1mL) in an Erlenmeyer flask. The catechol solution was added to the siloxane solution, and the mixture was stirred at 500 rpm for 24 h. An IR spectrum was collected after 24 h.

2.5.10 Swelling Behavior and Extraction of Unbound Sol

Elastomer pieces ranging from 0.10 to 0.13 g (Table S4) were weighed and placed in a 20mL vial. To the vial 1mL of solvent (toluene, IPA, or water) was added and the vial was capped. The elastomer was allowed to sit in the solvent for 24 hours and was weighed afterwards. The solvents were collected and analyzed via NMR and the elastomers were dried for 6 d in an oven at 60 °C (Figure S5.7 and Figure S5.8).

2.5.11 Thermoplasticity: Repeated Thermal Processing of the Elastomer

A 2-year old sample of 1:1 [ArOH]:[NH₂] pyrogallol **T-334** was cut into several pieces and heat pressed at 180°C for 20 minutes to obtain a flat piece of elastomer. The elastomer was cut into two pieces, were stacked on top of one another and the ShoreOO hardness was measured. This was done 4 more times, and the ShoreOO hardness was measured each time.

2.5.12 Antioxidant Activity

Note that DPPH is a very convenient, colorimetric reagent for antioxidant detection. However, assays based on it are prone to a variety of subtleties in reaction efficiency based on solvent, pH, type and location of aromatic OH groups, etc.³³ The assay was selected initially to facilitate qualitative determination of antioxidant activity (elastomers make a purple DPPH solution turn yellow), and then followed by proper measurement using a UV–vis spectrophotometer. The controls catechol (positive—82% efficacy) and T334 (negative—3% efficacy) in the assay described below show that the reactivity correlating DPPH to ArOH is less than 1:1 (Table S5.5).

DPPH was dissolved in IPA (50 mL) to provide a stock solution of 0.5 mM. Elastomers were placed in the bottom of 24-well plates and 1 mL of DPPH stock solution was pipetted onto the surface of the elastomers. Samples were placed in the dark for 15 min, removed from the wells after 15 min, and 200 µL of DPPH solution was transferred to a 96-well plate and the absorbance at 520 nm was read.

These conditions were initially chosen so that all elastomers prepared, with their wide-ranging ratios of phenol/aminosilicone, would mostly be captured with a single assay type and a fixed aliquot of DPPH (Figure 2.5E,F). However, one consequence is that some samples will have higher phenol loadings than available DPPH. That is, the experimental limit of 100% underestimates the antioxidant polymer of some samples.

2.5.13 Chaotropic Reagent Elastomer Degradation

The chaotropic reagent was prepared by creating a stock solution of tetramethyl guanidine, trifluoroacetic acid, and THF followed by dilution following the procedure given by Zheng et al.¹⁵ The elastomers, ~0.1g, were placed in vials containing the chaotropic reagent, and were stirred until dissolution was observed, typically 1-2 days.

2.5.14 Simple Amine Elastomer Degradation

For elastomer degradation using simple amines, benzyl- or butylamine (5 mL) was dissolved in toluene (5mL) in a 20 mL vial. Either pyrogallol or catechol-derived elastomers (~0.1 g) was ground in a mortar and pestle with liquid nitrogen into a coarse powder. The elastomer crumb was added to the vial, and then alternately sonicated for 1 h then stirring on a magnetic stirrer for 24 h until full dissolution of the elastomer was observed, typically occurring between 1-3 days. After evaporation of butylamine, the elastomer reformed (Figure S5.9). By contrast, with benzyl amine an orange/yellow crystalline solid formed at the bottom of the flask after air drying that showed evidence of reactions between the amine and oxidized phenol (Figure S5.4).

2.6 ASSOCIATED CONTENT

Supporting Information. Tables of recipes for elastomers and their physical properties; IR and NMR spectra of selected elastomers as prepared and after degradation; photographs of elastomers; DSC of two elastomers and TGA of one elastomer based on **T334**.

2.7 AUTHOR INFORMATION

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Chapter 3. ‘Oaked’ Silicones: Natural Tannins as Crosslinkers for More Sustainable Silicones

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3.1 Abstract

Improved circularity in elastomers requires better opportunities for reusing/repurposing before ultimate disposal, and better degradability once placed in the environment. Silicone oils degrade in the environment, and aminoalkylsilicone oils will crosslink with ionic/hydrogen bonding with small phenols to form robust elastomers. We report that tannins – commonly used for enhancing flavors in wines – are excellent crosslinkers for aminosilicones. Simply mixing a solution of the tannin in alcohol/water with aminosilicones provided an elastomer after evaporation. Physical properties could be tuned simply by varying the quantity of food grade tannin and the molar mass of the telechelic aminosilicones. The products were thermoplastic and could be processed at 140 °C, or completely depolymerized by the addition of butylamine to regenerate the aminosilicone consistent with an enhanced life cycle for these elastomers.

3.2 Introduction

Polyphenolic compounds have gained wide recognition due to their abundance in nature, diverse structures, and interesting properties. One class of these compounds, tannins, finds many applications.¹ In addition to their historical utilization in the leather tanning industry, and their antibacterial and antioxidant properties,²⁻⁴ tannins are often utilized to modify the character of wines.⁵ They are naturally found particularly in red wines, they may be added to wine during fermentation, or may leach from oak barrels used for fermentation into the wine (Figure 3.1).^{6,7} They are, thus, widely accepted as food grade materials.

Tannins, both condensed and non-condensed, are phenolic compounds. The source of their antioxidant activity is typically associated with the ability of phenols to react with reactive oxygen species, including a variety of radicals, to create much less reactive phenoxy radicals.^{8,9}

Silicones are important industrial polymers with unique properties, including a low glass transition temperature and excellent oxidative and thermal stability. Linear dimethylsilicone polymers of low to high molecular weight degrade in the environment relatively quickly to low molecular weight monomers and cyclic monomers; longer times are required for their eventual breakdown into silica, carbon dioxide and water either in soil or in the atmosphere.¹⁰⁻¹² Typically, silicone oils are crosslinked to form thermoset elastomers using metal or, less frequently, radical catalysts.¹³ While details on rates of degradation of thermoset silicone elastomers are scarce, rates will inevitably be much slower than for mobile, linear

oils. That is, the desirable resilience of silicone elastomers in use is likely to be a detriment to their ability to undergo degradation once placed in the environment. It is encouraging to note that silicone elastomer recycling is increasingly the focus of research studies,¹⁴⁻¹⁶ and some processes have been commercialized on more than one continent (e.g., EcoUSA www.ecousaind.com).¹⁷ However, the bulk of silicone elastomers are handled in a similar manner to other thermosets; they are deposited into landfills.

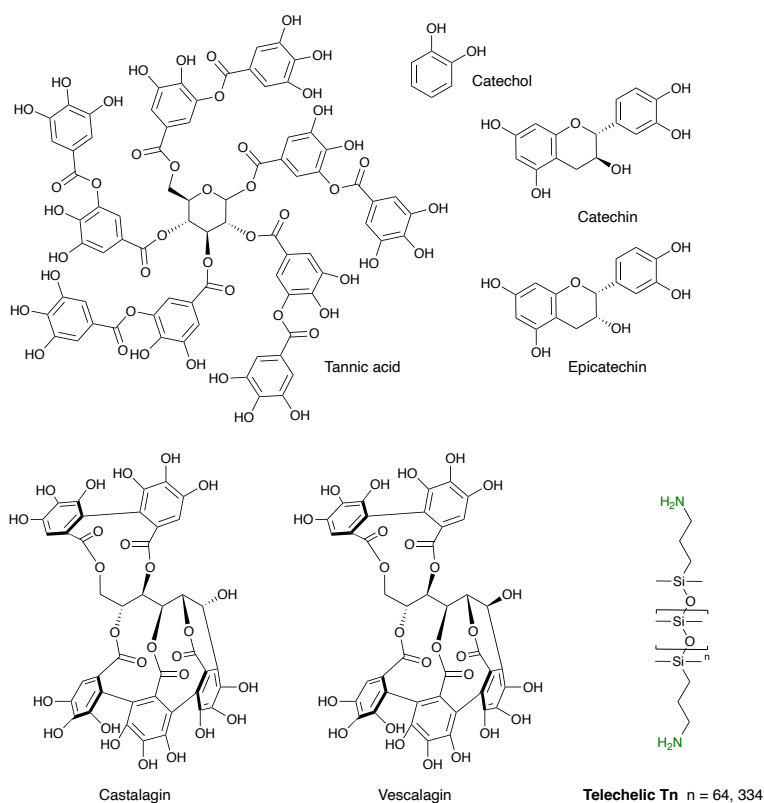


Figure 3.1. Structures of ellagitannins (castalagin, vescalagin) predominantly found in oakheart wood, grape tannins/proanthocyanidins, which are typically repeating units of catechin and epicatechin^{18, 19} and telechelic aminosilicone

A variety of strategies have been adopted to create useful silicone elastomers that do not rely on Si-C or Si-O bonds for crosslinking and that are, therefore, more susceptible to reuse and environmental degradation. These can include dynamic bonds, including imines^{20, 21} and aromatic association (possibly pi-pi interactions, Figure 3.2).²²

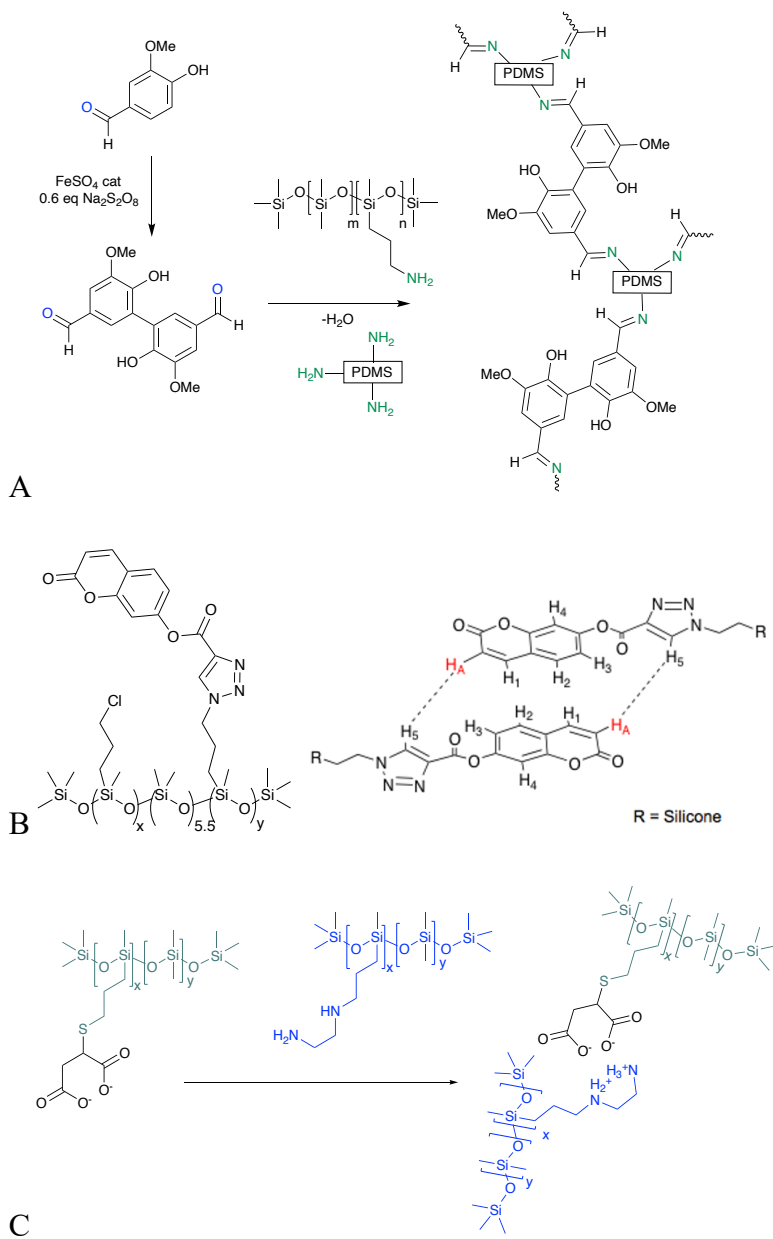


Figure 3.2. Atypical silicone crosslinks. A) Dynamic imine bonds,²¹ B) aromatic association,²² and C) ionic bonding.²³

Hydrogen bonding – another class of weak bonds – also provides an important crosslinking motif in biology, e.g., DNA, and also in polymers/materials.²⁴

Different H-bonding motifs used in polymer synthesis include urea,²⁵ urethane,²⁶ and 2-ureido-4[1H]-pyrimidinone (Upy),²⁷ including in silicone polymers.²⁸

Polymer properties can be tuned simply by changing the number and location of hydrogen bond donors and acceptors in the system.²⁹ This is particularly true when H-bonding occurs with low surface energy silicones. Less than 0.1 wt% sugar on a telechelic silicone is sufficient to induce transitory crosslink sites upon the application of force;³⁰ the crosslinking efficiency was found to be directly linked to the HO/silicone monomer ratio.³¹ Complementary H-bonding interactions between silicones bearing thymine residues on the backbone were also shown to form viable crosslinks.³²

Ionic bonding is also highly effective in forming silicone elastomers,³³ as shown in the combination of silicone dicarboxylic acids and silicone diamines.²³ Simply mixing aminopropylsilicones with hemin – a dicarboxylic acid – also led to robust elastomers.³⁴ Kong et al. reported that aminosilicones would combine with tannic acid (Figure 3.2) to form crosslinks using hydrogen bonding to create silicone elastomers.³⁵ Subsequent research demonstrated that crosslinking processes in this case involved both H-bond and ionic bonds; the pKas of ammonium salts and phenols are very similar.^{36, 37}

Many advantages can accrue from elastomers that are crosslinked with bonding motifs other than covalent bonds. The products are typically thermoplastic, easy to repurpose and can be normally induced to undergo complete degradation on demand. It was of interest to add functionality to this type of silicone elastomers. Although silicones themselves are highly resistant to oxidation, the incorporation of antioxidant properties could be beneficial to substrates with which the silicones are in contact. Few examples of rubbers exist that possess intrinsic antioxidant activity; typically, small molecule antioxidants are added during cure. Some reports have described the incorporation of larger antioxidant molecules, such as lignin and betanin, into an elastomeric matrix.^{38,39}

We have previously demonstrated that viable silicone elastomers can be made simply by mixing aminosilicone and small to medium sized molecules bearing at least two phenolic groups, such as catechol.³⁶ As part of an effort to broaden the utility of these materials it was of interest to use antioxidants that, compared to catechol, are fundamentally less toxic. We report on the use of natural tannins as silicone crosslinkers to give silicone elastomers and foams that are more biocompatible and which, because of the greater complexity of the phenols found in tannins for wine, should lead to a higher ability to tune the properties of the resulting foams.

3.3 Results

3.3.1 Synthesis of Elastomers

As a first step, it was decided to directly compare the behavior of lignin, a high molar mass, highly aromatic polymer that has previously been examined as a filler in silicones⁴⁰⁻⁴² with commercially available aromatic tannins normally used in the wine industry (in this case, Tan'cor Grand Cru and Quertanin). The two tannin mixtures differ in composition in that the former – designed as a stabilizer after fermentation – contains catechin, grape tannins and ellagic tannins from oak, while the latter – designed for use during fermentation – contains ellagitannins, which have been found to be predominantly vescalagin and castalagin (Figure 3.1),⁴³ and possess “a strong capacity for complex formation.”

The Piers-Rubinsztajn (PR) reaction between silanes and various alcohols, phenols or alkoxy silanes generates new disiloxane structures with concomitant generation of hydrogen gas and/or small volatile alkanes that operate as blowing agents (Figure 3.3A).⁴⁴ The $B(C_6F_5)_3$ -catalyzed reaction between PHMS ($Me_3Si(OSiMeH)_nOSiMe_3$), telechelic hydrosilicones and lignin led efficiently to silicone foams that, surprisingly since lignin burns so well, have excellent flame resistance (Figure 3.3B).^{41, 42}

The PR process similarly worked very well with tannins (Figure 3.3B). It was a possible to make foams with excellent physical properties. Foams containing up to 50wt% tannin were closed cell, low density (< 0.5 g/mL) elastomeric materials with better performance and higher capacity for the aromatic constituent than

lignin foams. There was a general trend of higher density and lower Young's modulus for the foams as the filler loading (wt%) increased within the matrix (Table 3.1, Table 3.2); foams prepared with high loadings of tannin ~70wt% crumbled under pressure. The foams were less attractive in terms of their flammability, which was notably higher than analogous lignin foams (a larger fraction of lower molar mass organic materials burned, than was the case with lignin, ESI†).

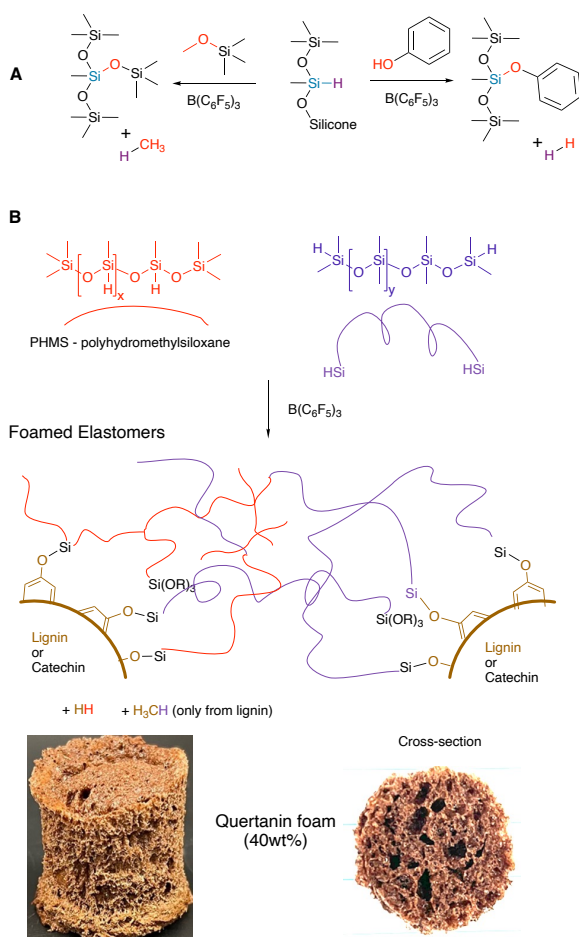


Figure 3.3. A) Piers-Rubinsztajn reaction with alkoxy-silanes and phenols. B) Foamed elastomers prepared by the PR reaction with hydrosilicones and lignin or catechin.

These foam experiments were only designed to allow familiarization with the chemical behavior of the tannins. They behave like more soluble analogues of the high molar mass lignin polymer. As small molecules, they possess a much narrower range of properties than lignin, a polymer that shows a much higher degree of variability, as it is affected both by its biological source and, particularly, by how it was processed.^{45, 46}

The main focus of this work was to attempt to exploit tannins utilizing processes that much better fit the principles of Green Chemistry. The PR reaction is very powerful. However, the need to utilize $B(C_6F_5)_3$ as a catalyst is problematic in that it is a powerful (reactive) Lewis acid (and in the presence of water, a Brønsted acid), its high cost and the perfluorocarbon residues it contains; what is the final fate of $B(C_6F_5)_3$ in the environment? We wished to learn if the polyphenols in lignin and in tannins could be used to reversibly crosslink aminosilicones ('aminosilicones' refers to aminopropylsilicones) utilizing ionic and hydrogen bonds rather than generating thermosets using covalent bonds.

Simply mixing aminosilicones in isopropanol with small molecules like catechol leads to robust elastomers.³⁶ Initial tests using the same protocol but with lignin as a substrate were disappointing. Elastomeric materials were not formed when lignin was mixed with aminosilicones regardless of the type of lignin used. In most cases, the lignin sedimented out of a more viscous fluid. Unlike the PR reaction with

lignin in which both ArOMe⁴⁷ and ArOH⁴⁸ groups will react with SiH groups, ionic bonds can only form between ArOH groups in lignin and NH₂ groups on the silicone. We reasoned that perhaps the inability to form elastomers from lignin indicates an insufficient number of phenol groups on lignin are present.

One strategy to improve ionic bonding in lignin would be to increase the number of available OH groups that could interact with amines. A procedure adapted from Sawamura et al.⁴⁹ was effective in converting OMe groups to OH groups. Following this modification, sufficient OH groups were present such that elastomers formed from the demethylated lignin product when reacted with aminosilicones, which had Shore OO durometer of 43 (< 50 kPa Young's modulus,

Figure 3.4A,B).

However, on reflection, this process too fails many of the green chemistry principles, as stoichiometric quantities of the strong acid HI and use of DMF, a problematic solvent, were required, and the alkylating agent MeI was generated. So, while the process works we were, so to speak, barking up the wrong tree with respect to sustainability.

Unmodified lignin was insufficiently able to form ionic bonds with aminosilicones to give elastomers. Small phenols like catechol, pyrogallol, etc., do form ionic elastomers, but their toxicity profiles leave something to be desired. Could food grade tannins destined for wine offer a better outcome?

Tannins are, in essence, low molar mass analogues of lignin but the aromatic oxygen substituents are free phenols (Figure 3.1). Two different tannin mixtures were separately dissolved in appropriate solvents, methanol in the case of Tan'cor

Grand Cru and water for Quertanin, and then mixed with aminosilicones dissolved in isopropanol, all solvents that can be considered green.⁵⁰ Combining the solvents proved to be an effective way of introducing the tannins to the silicones. If not stirred vigorously and continuously, both tannin/silicones solutions phase separated. After dispersing for 30 minutes at room temperature, the solvents could be removed under vacuum and final cure at 60 °C for 1-4 days led to opaque, red/brown elastomers. Note that homogeneous solutions in water/alcohol could be realized at low tannin loadings. When high loadings of tannins were used, particularly for Quertanin formulations, precipitation of a brown solid occurred rapidly upon addition of the tannin solution to the silicone, which can be attributed to the rapid formation of hydrogen bonds and ionic linkages from the plentiful phenols available in the ellagitannins (Figure 3.1).

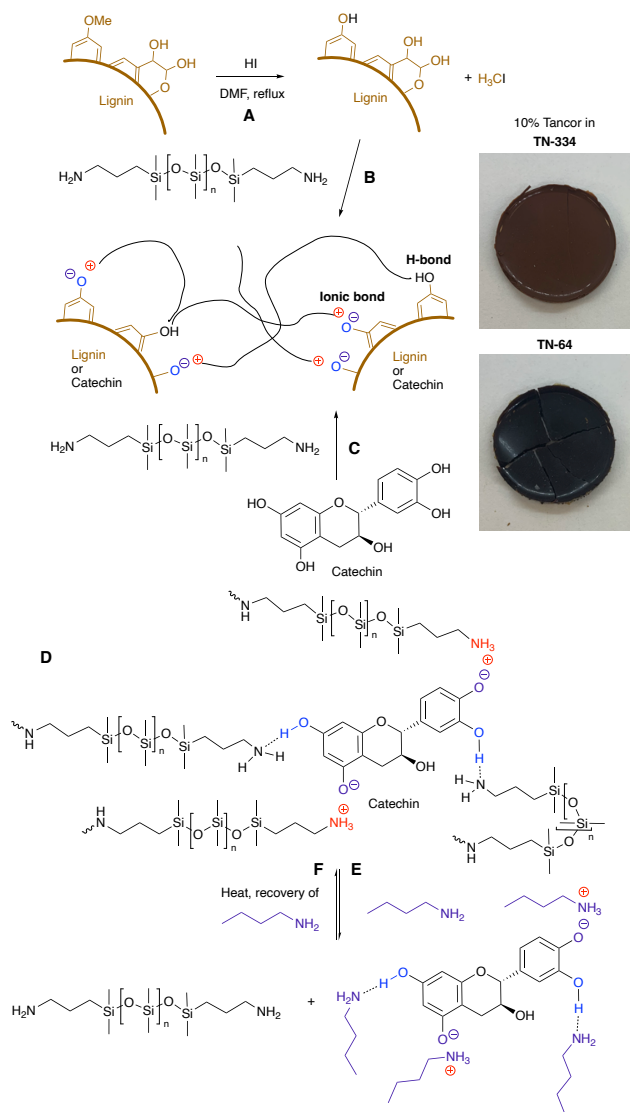


Figure 3.4. A) Demethylation of lignin. Forming ionically bound elastomers from B) demethylated lignin or C) catechin. D) Model showing crosslinks formed from ionic and H-bonding with catechin. E) Degradation of elastomers using butylamine. F) Recovery of butylamine and reforming the elastomer by heating.

3.3.2 Physical Properties

Tannin loadings from 1 – 20wt% were investigated (Table 3.3). Materials made from 1 to 10wt% tannin loading were uniform and smooth. Elastomers created with ≥ 20 wt% tannin loading typically exhibited both surface and internal defects (e.g., pores, rough surfaces) due to their very high viscosities and formed poor elastomers as judged by non-uniform dispersion of the tannin, leading to differing crosslinking densities across a given piece of rubber. More detailed physical characterization was carried out with the materials containing up to 10wt% tannin.

The products were nicely behaving elastomers that, as expected, were softer when made with longer telechelic silicones; the lower crosslink densities in these cases were reflected in the Young's moduli. Within each of the series of elastomers the physical properties followed different trends. The materials made from lower molar mass silicone **TN-64** showed a correlation between elongation at break and loading of tannin. The longer chain analogues derived from **TN-334** exhibited poorer correlation between tannin content and physical properties.

3.3.3 Antioxidant Properties

Phenols are powerful antioxidants. This is one of the key reasons that tannins are used in winemaking.⁵⁻⁷ The elastomers produced here readily decolorized DPPH (Table 3.5), a traditional colorimetric marker for antioxidant activity (AO).^{51, 52} The trend of higher AO with higher tannin loadings was expected. Of interest is the continued AO activity over time.

3.3.4 Repurposing/Recycling

Most thermosets are very difficult to recycle, as it is typically necessary to break covalent bonds along the backbone or at a crosslink site. The materials reported here are crosslinked mostly through ionic and H-bonds. Heating at 140 °C, with additional pressure, allows the elastomers to take on new shapes. Nominally the materials are melting at this temperature, but the very, very high viscosity they possess dictates the use of external pressures that, inevitably, will limit secondary applications. We demonstrated the ability to create thin films. A more practical way to repurpose or recycle the elastomer involves temporary removal of crosslinks. It is straightforward to completely degrade the elastomers by adding butylamine. The elastomer is recovered (in a new shape if desired) simply by evaporating/recycling the butylamine (Figure 3.4E,F). Alternatively, the silicone oil can be isolated from the butylamine solution, for example, by use of non-polar solvents that will dissolve the silicone but not the tannin.

3.4 Discussion

This work was motivated by the desire to benefit from the properties of silicone elastomers, but to improve their reusability, controlled degradation at end of life and use of food grade materials, all of which fit with the principles of Green Chemistry and would improve the sustainability of the materials.

The initial experiments to teach us about the chemical properties and resulting material properties of tannin-containing silicones explored the preparation of foam materials from tannins using covalent bond crosslinks. On one hand, any dilution

of silicone polymers with natural materials is beneficial. There is a high energy content in silicones due – in an upstream process – to the need to convert sand to silicone. Utilizing the PR reaction, it was possible to displace up to 50% of a silicone polymer with tannins to make foams. The performance of the foams was excellent with, mostly, closed cell structures, excellent and reproducible flexibility, much better than the lignin analogues.⁴² Their performance with respect to flame stability did not quite match that of lignin-filled foams in that more organic combustion occurred. Nevertheless, these are potentially useful materials for insulation applications in addition to the benefit that comes from the high content of natural materials.

On the other hand, the foam products are linked by covalent bonds and it is as yet unclear whether the materials will undergo accelerated degradation when compared with pure silicone foams/elastomers in the environment. While the foaming process that is catalyzed by $B(C_6F_5)_3$ is very efficient, the environmental credentials of this catalyst, particularly with its perfluoro ligands, are unclear. If sustainability is the goal, alternative crosslinking chemistry is required.

Aminosilicones can form both hydrogen³⁵ and ionic bonds³⁶ with phenolic structures like tannic acid; the pKa of ammonium salts and phenols is very similar. Good control over elastomer formation was reported when small molecules with precise structures, for example, catechol and pyrogallol, were used as crosslinkers. It was of interest to take commercial tannins (Figure 3.1), mixtures of condensed (oligomers frequently of catechin) and free polyphenol small molecules, as

crosslinkers for silicones. Could one obtain properties similar to commercial silicone thermosets, while delivering antioxidant activity, and reusability/recyclability and while working with food grade materials?

Up to about 10wt% tannin content, it was straightforward to create elastomers with moduli that increased in proportion to the amount of contained tannin and therefore, crosslink density (Table 3.4). Only a fraction of available phenols participated in crosslinking in these systems. At higher concentrations of tannin, the materials were too brittle because, we infer, the phenolic groups of the tannin self-associate into domains because insufficient silicone is present to bridge small molecules or clusters of phenols. With high tannin concentrations, the brittleness is ascribed to cohesive failure of the phenolic clusters.

The two tannin samples are comprised of very different mixtures of natural phenols. These differences manifest in the differences in physical properties of the resulting elastomers and were also affected by the chain length of the telechelic silicones used as chain extenders. The relationship between physical properties and the nominal crosslink density (number of linking bonds per unit volume) was not linear, which we ascribe to the many different phenol types found in the tannin mixtures; different network structures will arise depending on which phenols become pinned first with amines to generate a crosslink. We have not examined in detail the fraction of crosslinks arising from H-bonds³⁵ vs from ionic bonds.³⁶ However, the trends suggest that the desired physical properties can be targeted

using the 3 variables: tannin type; and quantity; and chain length of silicone chain extender

Telechelic silicones are available in many other lengths than those reported; the lowest molar mass silicones are disiloxanes. A broad range of elastomers with desired properties – beyond those reported – can thus be prepared from readily available starting materials. The behavior that relates to the high value in the tannins, particularly in the wine industry – their antioxidant activity – remains in the silicone elastomers. Within error, the antioxidant capacity correlates directly with mass fraction of tannin, regardless of the tannin used (Table 3.5).

Silicones are entirely synthetic and have a high energy toll associated with their synthesis. One objective of this research is the development of strategies that, at the same time, dilute the fraction of silicon needed for a give application, and deliver new functionality. More broadly, do these materials follow the principles of Green Chemistry? The use of tannins, in addition to diluting the amount of silicone used for a given process, fulfils the requirement to use natural feedstocks (principle 7). The process is simple and practicable, and utilizes green solvents water, methanol and IPA (principle 12). Perhaps most important of all, particularly for elastomers, they have robust properties under normal conditions, but are thermoplastic so that they can be thermally reprocessed and, when desired, completely dissolved/recycled by the use of butylamine as a solvent (principle 10, note: we are currently looking for more biocompatible amines for this process.).

We recognize that certain aspects of these materials will not be perceived as attractive to traditional users of silicones, for example, longer cure times and the color. But the benefits in terms of utility for many applications, as in sealants or protective antioxidant films, natural content, the lower silicone (and therefore energy content) outweigh those disadvantages. An assessment of this statement for use in the wine industry is underway.

3.5 Experimental

3.5.1 Materials

Telechelic 3-(aminopropyl)-terminated polydimethylsiloxanes: TN-64 DMS-A21 (100-120 cSt, $M_n = 5000 \text{ g mol}^{-1}$), and **TN-334** DMS-A31 (900-1100 cSt, $M_n = 25,000 \text{ g mol}^{-1}$), and **TH-64** DMS-H21 (100 cSt, $M_n = 4,000 - 5000 \text{ g mol}^{-1}$), PDMS (poly dimethyl siloxane) DMS-T21 (100 cSt, $M_n = 5970 \text{ g/mol}$) were purchased from Gelest. 2,2-Diphenyl-1-picrylhydrazyl (DPPH), butylamine, and hydroiodic acid (55% in water) were purchased from Sigma-Aldrich. Sodium metabisulfite was purchased from VWR. Tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$, BCF) was purchased from Alfa Aesar. PHMS - methyl hydrogen siloxane homopolymer ($\text{Me}_3\text{SiO}(\text{HMeSiO})_m\text{SiMe}_3$, DC1107), was a gift from Dow Corning (now Dow, Midland, MI). Quertanin and Tan'cor Grand Cru were purchased from Laffort. Lignin was obtained from FPInnovations and, separately, Weyerhaeuser; the Weyerhaeuser material had much higher molar mass and lower solubility than the FPInnovations product. Solvents were purchased from Fisher Scientific. All reagents and solvents were used without further purification.

3.5.2 Synthetic procedures

General preparation of tannin-based foams

An appropriate mass of tannin (Table 3.1) was added to a 30 mL syringe that had its top cut off (at the Luer lock end). BCF stock solution (5mg/mL, 9.77 mM) was prepared by adding BCF (40 mg) to a 20 mL vial and dissolving it in dry toluene (0.5 mL) and PDMS (7.5 mL). Depending on the sample, different quantities of the stock solution (0.2 - 0.5 mL) were added to the 30 mL syringe containing the tannin, which was mixed with a glass stir rod for ~20 s. **TH-21** and **PHMS** were first transferred into a 20 mL vial and mixed, after which were added to the 30 mL syringe. The mixture was stirred vigorously for 3 s and allowed to foam for 30 – 60 s. After the foam had solidified, it was ejected from the syringe by pushing it out with the plunger and allowed to cure for 24 h at room temperature.

Attempted preparation of lignin crosslinked elastomers

Lignin from either Weyerhaeuser or FPInnovations, was weighed (0.01 g) into a 20mL vial and dispersed in methanol (~10 mL). **TN-64** was weighed (4.99g) in a round-bottomed flask and dissolved in 2-propanol (10 mL). The lignin dispersion was added to the round bottom flask containing the **TN-64** solution and was mixed for 30 min at 1500 rpm. After mixing, the solvent was removed using a rotary

evaporator and the sample was transferred to a Flacktek cup. The cup was then transferred to a 60 °C oven and allowed to cure for 120 h. Upon removal from the oven, a viscous solution with precipitated lignin at the bottom of the cup was observed. No elastomer was obtained with either type of lignin.

Lignin modification

Lignin was modified using a procedure adapted from Sawamura *et al.* with slight modifications.⁴⁹ Lignin (110 mg) was refluxed in hydroiodic acid (420 mL (@1.7 g/mL), 3.18 mmol) and DMF (3 mL) for 8 h. The reaction was allowed to cool to room temperature and the mixture was washed with hexanes. The solution was then poured into a concentrated solution of Na₂S₂O₅, where a precipitate was formed that was collected by vacuum filtration and washed with minimal water. The final product was oven dried and weighed (82 mg). The modified lignin was then dispersed via sonication in methanol (10 mL) and was mixed with a solution of 2-propanol (10 mL) and **TN-64** (4 mL, 1.6 mmol amine) for 30 min on a magnetic stirrer. The solution was placed in an oven at 60 °C for 120 h to cure, after which an elastomer formed. The average ShoreOO value (n=4) was 43, SD = 2 considerably lower than elastomers derived from tannins (see below).⁵³

General method for the preparation of tannin crosslinked elastomers

The appropriate mass of **TN-334** or **TN-64**, was added to a 100 mL round-bottomed flask (Table 3.3). The appropriate mass and volume of tannin and solvent, respectively, were added to a vial and sonicated until dissolution was observed, and the resulting tannin solution was poured into the 100 mL round-

bottomed flask. The mixture was stirred using a magnetic stirrer set to 1500 rpm for 30 min. The solvent was removed using a rotary evaporator and the resulting oil or solid, depending on tannin content, was poured/scraped into 100 mL Flacktek cups. The cups were placed in an oven at 60 °C for 24-120 h to cure.

3.5.3 Physical property testing of elastomers

Elastomer remoulding

Cured silicone/tannin samples were placed on Teflon sheets and processed using a 12-ton Dabpress heat press at 140 °C to provide samples ~ 1 mm thick (6 tons of pressure was applied to the sample set between 1 mm stainless steel spacers). Samples were then cut using an ASTM D412 Type D cutting dye to provide dogbone samples for tensile tests.

Tensile Testing

Tensile measurements were performed using an Instron 5900 series Universal Mechanical Tester. Young's Moduli were measured at 10% strain

Elastomer dissolution

An elastomer sample (~0.1g) was placed in a 20 mL glass vial. To the same vial, toluene (10 mL) was added followed by butylamine (5 mL). The solution was then sonicated for 1 h, followed by stirring on a mechanical stirrer for 24 h; the solution was sonicated for 1 h and allowed to stir once again. These steps were repeated until the elastomer was completely dissolved, typically 1-3 d. Once dissolved, the solvents / residual amine were removed in vacuo.

Young's Moduli of Foams

Young's modulus values were measured using a MACH-1 micromechanical testing instrument (Biomomentum Instruments) equipped with a 17 N multi-axis load cell and 0.5 mm hemispherical indenter using a Poisson ratio of 0.5 and a constant indentation depth of 1.0 mm with a 1 s dwell time; all measurements were conducted at 22 °C and obtained in triplicate measurements.

Foam Density Measurements

Foam density was measured by water displacement. A 100 mL graduated cylinder was filled with ~70 mL of water and the volume was recorded. The foam was weighed using an analytical balance and then submerged in the water within the graduated cylinder. After submerging, the volume was recorded once again. Displacement was calculated by taking the difference between the submerged volume and the original volume, and foam density was calculated by dividing the recorded mass by the difference in volume calculated.

Table 3.1. Foam Formulations.

Sample	Wt% in silicone (%)	Mass of TH-64 ^a (g)	Mass of PHMS (g)	Mass of Tannin (g)	Weight % BCF Catalyst
Tancor	20	1.000	0.300	0.325	0.05
	30	1.000	0.300	0.560	0.05
	40	1.000	0.300	0.870	0.05
	50	1.000	0.300	1.300	0.13
Quertanin	20	1.000	0.300	0.325	0.05
	30	1.000	0.300	0.560	0.05
	40	1.000	0.300	0.870	0.05
	50	1.000	0.300	1.300	0.05

^a Nomenclature for telechelic hydrogen functional polymers: **TH-n** =

$\text{HMe}_2\text{Si}(\text{OSiMe}_2)_n\text{OSiMe}_2\text{H}$, where n is the number of siloxane repeating units.

Table 3.2. Mechanical properties and densities of foams.

Sample	Wt% in silicone (%)	Density (g/mL)	Young's Modulus (kPa)
Foams			
Tancor	20	0.377	2.58 ± 0.4
	30	0.392	8.82 ± 1
	40	0.428	10.6 ± 2
	50	0.469	30.0 ± 2
Quertanin	20	0.358	7.29 ± 2
	30	0.476	10.0 ± 1
	40	0.511	23.8 ± 3
	50	0.480	10.4 ± 2

Antioxidant assays

DPPH (0.01 g, 0.025 mmol) was dissolved in 2-propanol (50 mL) to provide a stock solution of 0.5 mM. A 1.5 cm diameter metal punch was used to cut samples (~0.1g, circular coupon, 1 mm thickness x 15 mm diameter) from films prepared by heat pressing. Elastomers were placed in the bottom of 24 well plates and DPPH stock solution (1 mL) was pipetted onto the surface of the elastomers.

Samples were placed in the dark for 15 min, and then removed from the wells.

DPPH solution (200 μ L) was transferred to a 96-well plate, and the absorbance at 520 nm was read using a BioTek Synergy LX multi-mode plate reader (Table 3.5).

This was repeated 3 more times in 15-min intervals (30, 45, 60 min).

Flame test

The test sample (~13 mm diameter, 3 mm thick) was clamped in the vertical position, the top of a gentle blue flame (natural gas combustion) was held at a 45° angle for 10 s to initiate fire from the bottom end of the test sample, then removed and the sample allowed to burn or spontaneously self-extinguish (the process was recorded as a video on iPhone. Selected photos over time and videos recorded on an iPhone can be found in the ESI†).

Table 3.3. Tannin crosslinked silicone elastomer formulations

Sample	Wt% in silicone (%)	Mass of tannin (g)	Mass of silicone (g)	Volume of MeOH/H ₂ O/2-propanol (mL)
TN-64^a				
Tancor	1	0.103	10.004	5/0/10
	5	0.528	10.086	10/0/10
	10	1.102	10.009	20/0/10
	20	2.555	10.059	30/0/10
Quertanin	1	0.102	10.000	0/0.4/10
	5	0.526	10.019	0/0.8/10
	10	1.105	10.016	0/1.6/10
	20	2.542	10.024	0/10/10
TN-334				
Tancor	1	0.1006	10.035	5/0/10
	5	0.524	10.018	10/0/10
	10	1.103	10.028	20/0/10
	20	2.521	10.047	30/0/10
	50	10.034	10.004	50/0/10
Quertanin	1	0.1024	10.117	0/0.4/10
	5	0.528	10.023	0/0.8/10
	10	1.101	10.023	0/1.6/10
	20	2.505	10.099	0/10/10

Nomenclature for telechelic polymers: **TN-n**, where n =

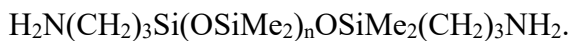


Table 3.4. Mechanical properties of elastomers

Sample	Wt% in silicone (%)	Tensile Strength (MPa)	Young's Modulus ^a (MPa)	Elongation at Break (%)
Elastomers				
TN-64				
Tancor	1	0.210 ± 0.03	0.231 ± 0.02	136 ± 22
	5	0.299 ± 0.04	0.504 ± 0.07	75.5 ± 2
	10	0.219 ± 0.04	0.408 ± 0.1	62.4 ± 9
Quertanin	1	0.128 ± 0.06	0.112 ± 0.02	230 ± 70
	5	0.255 ± 0.007	0.312 ± 0.04	131 ± 20
	10	0.375 ± 0.05	0.457 ± 0.02	103 ± 12
TN-334				
Tancor	1	0.115 ± 0.02	0.0657 ± 0.007	325 ± 27
	5	0.138 ± 0.007	0.0807 ± 0.006	244 ± 6
	10	0.0803 ± 0.02	0.0866 ± 0.02	134 ± 35
Quertanin	1	0.155 ± 0.04	0.0933 ± 0.01	332 ± 72
	5	0.167 ± 0.03	0.0931 ± 0.006	278 ± 53
	10	0.293 ± 0.05	0.104 ± 0.02	333 ± 38

^a Foam Young's modulus values were obtained from compressive methods while elastomer values are obtained from tensile methods. The 20wt% materials contained voids and gave irreproducible results.

Table 3.5. Antioxidant activity (AO)

Sample	15 Minute	30 Minute	45 Minute	60 Minute
	AO	AO	AO	AO
	Quenching	Quenching	Quenching	Quenching
	Ability	Ability	Ability	Ability
	(%)	(%)	(%)	(%)
Tancor TN-334				
1%	8.0 ± 3	22 ± 10	43 ± 7	53 ± 9
5%	14 ± 6	49 ± 7	81 ± 3	88 ± 0.4
10%	21 ± 6	71 ± 6	88 ± 0.3	88 ± 0.3
Quertanin TN-334				
1%	6.0 ± 5	14 ± 4	30 ± 3	43 ± 4
5%	21 ± 10	35 ± 7	62 ± 9	77 ± 8
10%	20 ± 7	54 ± 2	75 ± 3	89 ± 0.4

3.6 Conclusions

Commercially available tannins serve as ionic and H-bonding crosslinkers for amine-functional silicones. Elastomers are created through a one pot process that simply involves mixing the tannins and silicones in the presence of small quantities of green solvents; up to 10% of silicone can be replaced by natural tannin. The antioxidant properties of the tannins are retained in the final elastomers, which are thermoplastic and can be remolded using both heat and compression. At end of life, simple amines dissolve the elastomers completely and the solution could be evaporated to reform the elastomer in a new shape, or one can recover silicone oil and tannins. These simple ingredients allow the preparation of high-quality elastomers that are readily reused or converted back to starting materials without the need for covalent bond crosslinks.

3.7 Author Contributions

M.A.B. and K.T. developed the hypothesis that drove the project. K.T. did the preparation and characterization of the silicone tannin materials and wrote the first draft of the manuscript. M.A.B. edited and contributed to the final draft, supervised the work and obtained funding.

Conflicts of interest

There are no conflicts to declare

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3.8 Notes and references

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Chapter 4. General Conclusions

Silicones are used extensively in the chemical industry and in the daily lives of the general population for good reason. Their properties make them unique in comparison to other polymers and consequently, there is a heavy reliance on them. The industrial production of silicones has striking flaws, notably the enormous amount of energy needed to reduce silica to silicon and the subsequent conversion of silicon to chlorosilanes using the Direct Process. Traditional crosslinking methods do not allow for simple recycling methods, which has shifted the focus of modern research in materials science to recyclable/compostable plastics and rubbers. Hence, in this research, phenolic compounds are a unique way to impart recyclability and unique features to silicones elastomers.

In Chapter 2 of this thesis, small phenolic compounds could be used to crosslink amine-functional silicones, and the rubbers had mechanical properties similar to unfilled silicone rubber, thus, leading to little compromise between sustainability and function. The materials could be recycled at elevated temperatures with the addition of compression and the phenolic molecules imparted their own properties, such as antioxidant activity, to the materials. If solubilization is desired, the addition of either a chaotropic reagent or butyl amine could completely dissolve the rubber. Further work is being investigated to eliminate the use of the problematic reagents used in depolymerization, such as amino acids.

Additionally, in Chapter 3 the addition of natural products in the form of tannins, were used in replacement for the toxic small molecules used in Chapter 2. These tannins could be used to dilute the amount of silicone present in elastomers by up to 10% while still retaining flexibility and mechanical integrity, which was a huge improvement over the 1-2% incorporated while using small molecules. The tannin crosslinked elastomers had many of the same properties as the small molecules crosslinked elastomers, but could be recycled at 140 degrees Celsius, reducing the energy needed by ~22%, and showed mediocre flame-suppressing properties. Further work being investigated is the tannin crosslinked elastomer's ability to degrade in composting environments, and the results so far are promising. This thesis represents a small portion of the work that could be investigated, as the number of phenolic compounds present in nature and synthetically is endless, and the properties the resulting materials could have could cover a variety of industries. Silicone products will inevitably fall under the regulatory constraints many carbon-based polymers are facing; novel crosslinking methods must be investigated to alleviate the issues surrounding sustainability

Chapter 5. Appendix

5.1 Supporting Information for Chapter 2: Antioxidant Silicone without Covalent

Crosslinks

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Table S5.1. Formulations for elastomers.

[ArOH]:[NH ₂]	Mass of phenolic (g)	Mass of amino silicone (g)	Volume of isopropyl alcohol (mL)
Phenol			
T64			
1:4	0.0281	3.023	5
1:1	0.1227	3.242	5
4:1	0.4736	3.104	5
Catechol			
T37			
1:4	0.094	10.015	1
1:2	0.187	10.029	1
1:1	0.370	10.085	2
2:1	0.743	10.042	5
4:1	1.473	10.051	5
T64			
1:4	0.057	10.010	1
1:2	0.116	10.036	1
1:1	0.2215	10.027	2
2:1	0.4471	10.046	2
4:1	0.8879	10.067	5
T334			
1:4	0.0108	10.073	1
1:2	0.025	10.074	1
1:1	0.0449	10.0184	1
2:1	0.0898	10.0232	1

4:1	0.1785	10.0685	2
Pyrogallol			
T37			
1:4	0.072	10.006	1
1:2	0.141	10.030	1
1:1	0.285	10.039	2
2:1	0.565	10.046	2
4:1	1.129	10.035	5
T64			
1:4	0.045	10.031	1
1:2	0.085	10.012	1
1:1	0.169	10.039	1
2:1	0.333	10.036	2
4:1	0.680	10.057	5
T334			
1:4	0.0089	10.012	1
1:2	0.0162	10.018	1
1:1	0.0332	10.008	1
2:1	0.0678	10.031	1
4:1	0.137	10.070	2

Table S5.2. Mechanical properties of silicone elastomers prepared with catechol and pyrogallol as prepared^a) and after thermal treatment (180 °C for 20 minutes).

[ArOH]:[NH ₂]	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at Break (%)	Shore OO Hardness
AS SYNTHESIZED				
Catechol				
T64				
1:4	0.13 ± 0.02	0.173 ± 0.03	123 ± 21	54 ± 1
1:2	0.17 ± 0.02	0.258 ± 0.02	113 ± 10	61 ± 1
1:1	0.21 ± 0.07	0.245 ± 0.06	132 ± 37	65 ± 1
2:1	0.29 ± 0.06	0.376 ± 0.04	122 ± 23	66 ± 1
4:1	0.23 ± 0.01	0.375 ± 0.05	98 ± 2	57 ± 2
T334				
1:4	0.075 ± 0.002	0.0622 ± 0.004	374 ± 130	11 ± 1
1:2	0.12 ± 0.002	0.0962 ± 0.007	289 ± 20	29 ± 2

1:1	0.21 ± 0.005	0.178 ± 0.003	212 ± 14	41 ± 1
2:1	0.16 ± 0.02	0.120 ± 0.06	273 ± 59	46 ± 2
4:1	0.18 ± 0.04	0.111 ± 0.006	321 ± 77	48 ± 2
<hr/>				
Pyrogallol				
T64				
1:4	0.16 ± 0.04	0.191 ± 0.01	144 ± 34	42 ± 2
1:2	0.20 ± 0.04	0.287 ± 0.03	118 ± 36	58 ± 3
1:1	0.22 ± 0.02	0.333 ± 0.04	106 ± 6	67 ± 1
2:1	0.43 ± 0.08	0.580 ± 0.03	95 ± 20	71 ± 1
4:1	0.52 ± 0.2	0.942 ± 0.2	78 ± 10	69 ± 1
T334				
1:4	0.070 ± 0.006	0.0405 ± 0.006	495 ± 29	32 ± 1
1:2	0.11 ± 0.005	0.0898 ± 0.002	238 ± 8	41 ± 1
1:1	0.15 ± 0.007	0.0960 ± 0.01	318 ± 32	42 ± 1
2:1	0.23 ± 0.04	0.145 ± 0.03	305 ± 66	46 ± 1
4:1	0.21 ± 0.08	0.166 ± 0.03	218 ± 57	51 ± 1
<hr/>				
AFTER THERMAL TREATMENT ^{b)}				
Catechol				
T64			20 min	40 min
1:4	0.058 ± 0.02	0.0875 ± 0.01	105 ± 21	
1:1	0.064 ± 0.04	0.267	50 ± 16	60 ± 1
2:1	0.079 ± 0.02	0.142 ± 0.02	93 ± 45	61 ± 3
T334				
4:1	0.077 ± 0.02	0.050 ± 0.01	287 ± 47	52 ± 2
Pyrogallol				
T334				
2:1	0.047 ± 0.01	0.0487 ± 0.01	150 ± 30	

a) All measurements were obtained in triplicate after curing for 1-15 days depending on the elastomer (see Figure 3). b) Shore OO data was obtained after thermally treating for 40 minutes.

Table S5.3. Formulations for elastomers created with more complex phenolic compounds

[ArOH]:[NH ₂]	Mass of phenolic (g)	Mass of amino silicone (g)	Volume of EtOH/MeOH/ <i>i</i> -PrOH (mL)	Shore OO/Shore A Hardness
Tannic acid				
T64				
1:2	0.137	10.022	1/0/5	50 ± 4
1:1	0.817	30.015	5/0/25	59 ± 2
2:1	1.640	30.079	5/0/25	63 ± 2
4:1	3.270	30.078	5/0/25	58 ± 2
T334				
1:4	0.0143	10.084	1/0/0	41 ± 2
1:2	0.0275	10.038	1/0/0	53 ± 2
1:1	0.165	30.048	5/0/25	55 ± 3
2:1	0.329	30.083	5/0/25	62 ± 2
4:1	0.653	30.012	5/0/25	58 ± 2
Quercetin				
T64				
1:4	0.075	10	0/20/0	
1:2	0.151	10	0/20/0	69 ± 1
1:1	0.302	10	0/20/0	72 ± 1 / 14 ± 1
2:1	0.604	10	0/10/18	76 ± 1 / 20 ± 1
4:1	1.209	10	0/10/36	75 ± 1 / 20 ± 2
T334				
1:4	0.015	10	0/0/28	39 ± 2
1:2	0.030	10	0/0/28	39 ± 2
1:1	0.061	10	0/0/28	43 ± 2
2:1	0.121	10	0/0/28	45 ± 1
4:1	0.242	10	0/0/28	44 ± 1
Curcumin				
T64				
1:4	0.184	10	0/0/28	37 ± 3
1:2	0.369	10	0/0/28	48 ± 2
1:1	0.737	10	0/0/28	56 ± 1
2:1	1.475	10	0/0/28	53 ± 2
4:1	2.95	10	0/0/46	68 ± 1

Table S5.4. Elastomer swelling and mass loss in different solvents represented as a percentage. **Day 0 = initial mass, day 1 = swelled mass, day 7 = mass after drying for 6 days.**

Catechol T334 Toluene				
[ArOH]/[NH ₂]	Day	Mass (g)	Swelling (%)	Mass loss (%)
1:1	0	0.1244		
	1	0.9473	761.5	9.083
	7	0.1131		
2:1	0	0.129		
	1	0.7413	574.7	10.08
	7	0.116		
4:1	0	0.1295		
	1	1.1912	919.8	15.91
	7	0.1089		
Catechol T334 IPA				
1:1	0	0.1263		
	1	0.1639	129.8	4.751
	7	0.1203		
2:1	0	0.1272		
	1	0.1646	129.4	5.896
	7	0.1197		
4:1	0	0.1292		
	1	0.1678	129.9	8.901
	7	0.1177		
Catechol T334 Water				
1:1	0	0.1062		
	1	0.1064	100.2	0.2825
	7	0.1059		
4:1	0	0.1037		
	1	0.1038	100.1	0.1929
	7	0.1035		
Pyrogallol T334 Toluene				
1:1	0	0.1296		
	1	0.7348	567	8.564
	7	0.1185		

2:1	0	0.1267		
	1	0.6791	536	9.629
	7	0.1145		
4:1	0	0.1288		
	1	0.5433	421.8	12.97
	7	0.1121		
Pyrogallol T334 IPA				
1:1	0	0.1281		
	1	0.1661	129.7	4.996
	7	0.1217		
2:1	0	0.1294		
	1	0.1674	129.4	5.565
	7	0.1222		
4:1	0	0.128		
	1	0.1641	128.2	5.547
	7	0.1209		
Pyrogallol T334 Water				
1:1	0	0.1036		
	1	0.1048	101.2	0.1931
	7	0.1034		
4:1	0	0.0982		
	1	0.0986	100.4	0.7128
	7	0.0975		

Table S5.5. DPPH control masses of phenolic compounds and aminosilicones and radical scavenging capacity (Figure 5E,F).

Sample ([ArOH]:[NH ₂])	Mass g (mmol)	Available antioxidant (μmol)	DPPH Consumed (% of predicted ^a)
Catechol	0.0274 (0.249)	0.25	82 ± 1
T334	0.100 (0.004)	N/A	3 ± 3

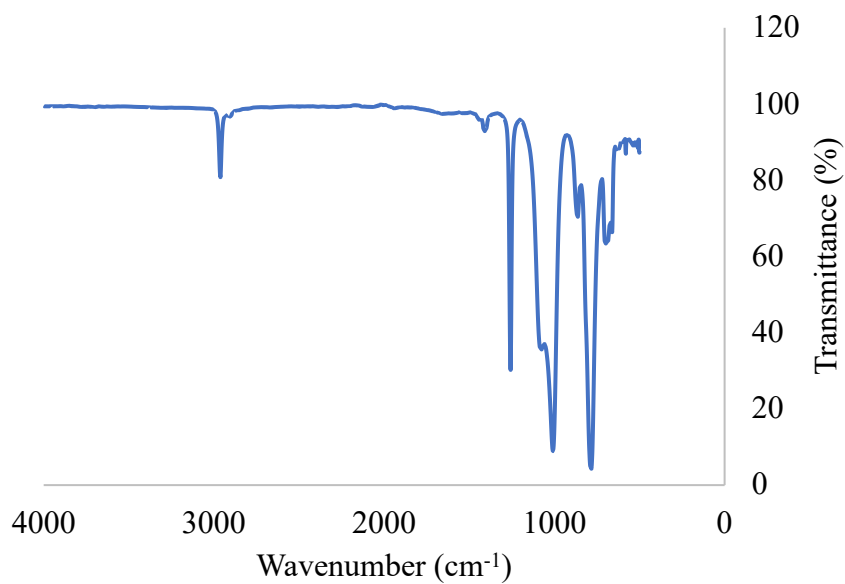


Figure S5.1. IR Spectrum of 1:1 [ArOH]:[NH₂] catechol and **T334** elastomer.

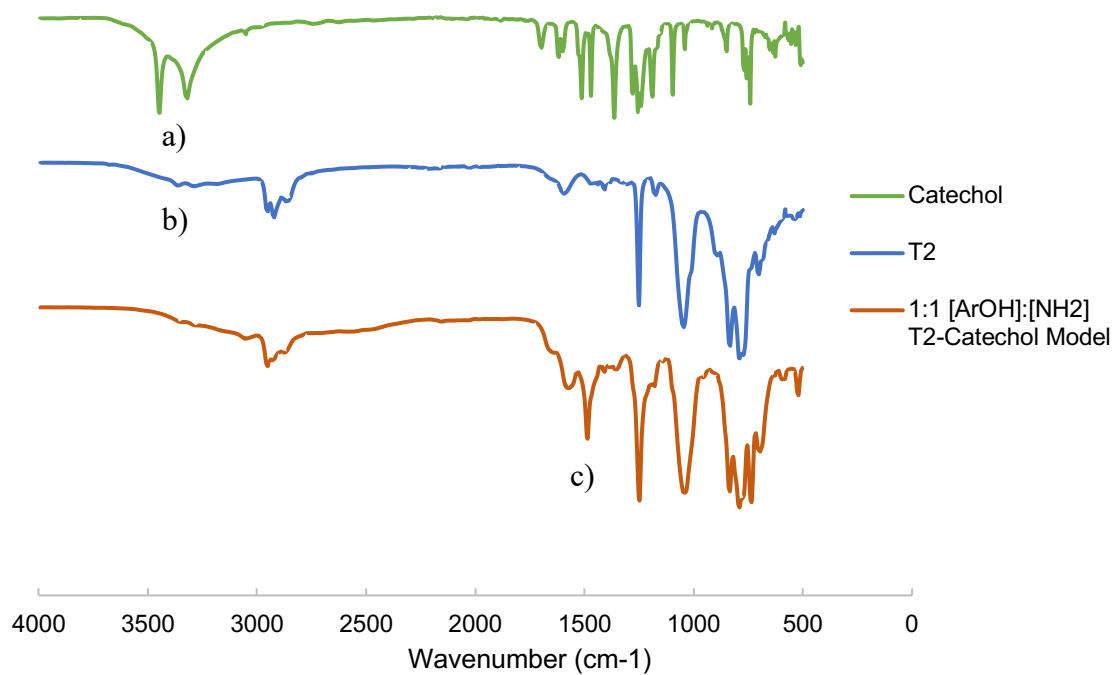


Figure S5.2. The IR spectrum overlay of catechol, 1,3-bis(aminopropyl)tetramethyldisiloxane, and 1:1 [ArOH]:[NH₂] mixture of catechol and **T2** after 24 hours stirring. a) ArOH stretching (3321 and 3348 cm⁻¹). b) NH₂ stretching (3281 and 3358 cm⁻¹). c) ArO⁻ C-O stretching (1487 cm⁻¹).

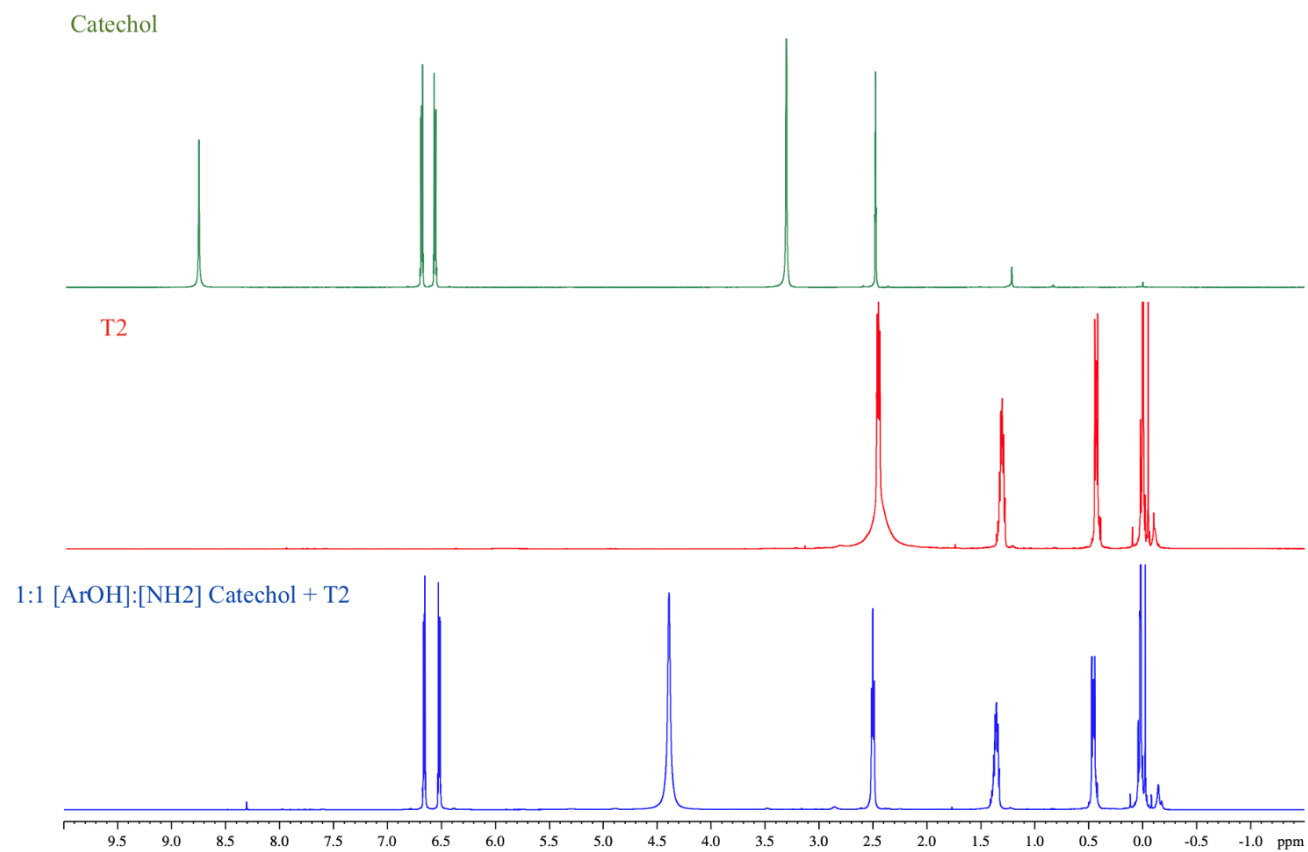


Figure S5.3. ¹H-NMR spectrum overlay of catechol, **T2**, and 1:1 [ArOH]:[NH₂] Catechol

+ **T2** in DMSO-d₆

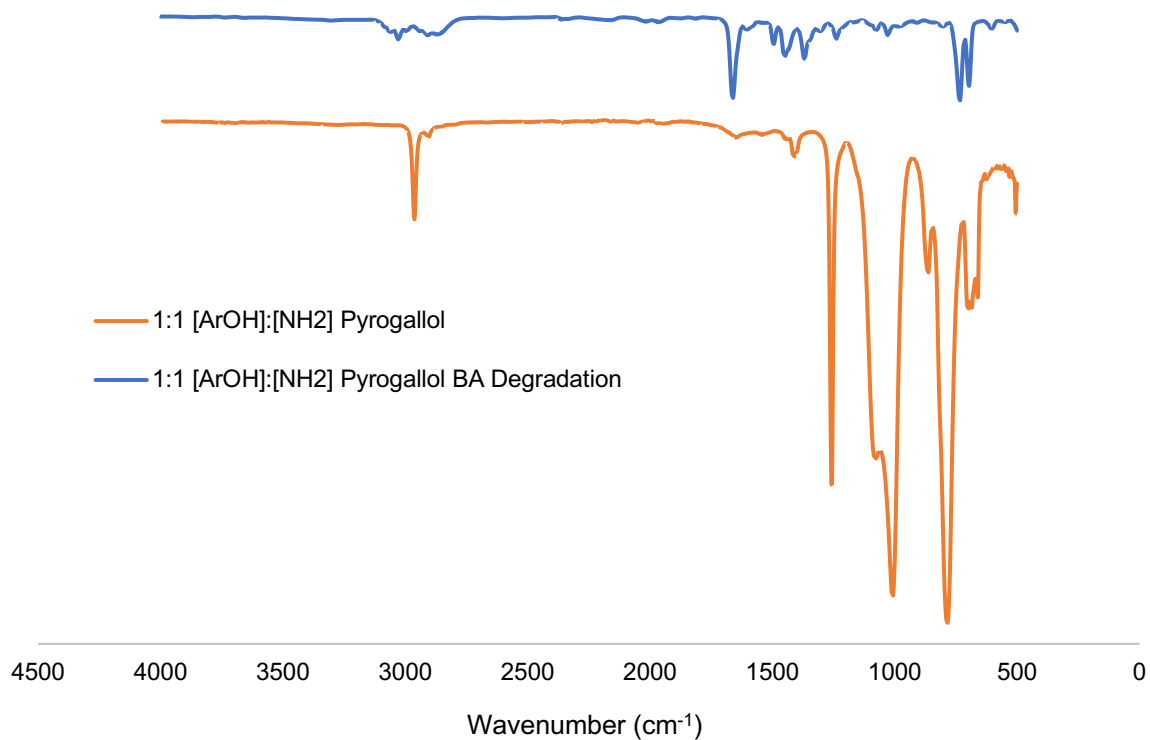


Figure S5.4. IR Overlay of 1:1 [ArOH]:[NH₂] pyrogallol **T334** elastomer and the respective benzylamine (BA) degradation product. a) Either a C=N or C=O weak stretching frequency at 1653 cm^{-1} . b) Either a C=N or C=O medium stretching frequency at 1662 cm^{-1} .

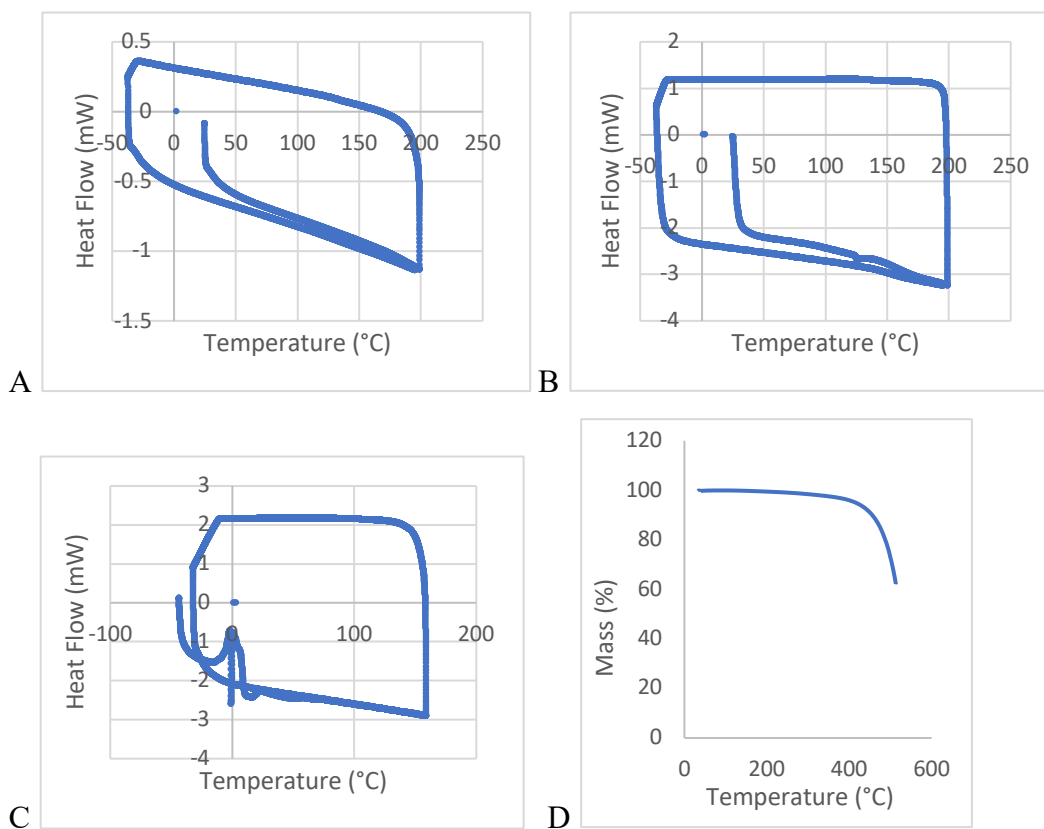


Figure S5.5. DSC of two different **T334** elastomers A) Pyrogallol/1:4 [ArOH]:[H₂NR], B) Pyrogallol/4:1 [ArOH]:[H₂NR], C) Catechol/4:1 [ArOH]/[NH₂R], and D) TGA under nitrogen of catechol/**T334** 1:1 [ArOH]:[H₂NR].

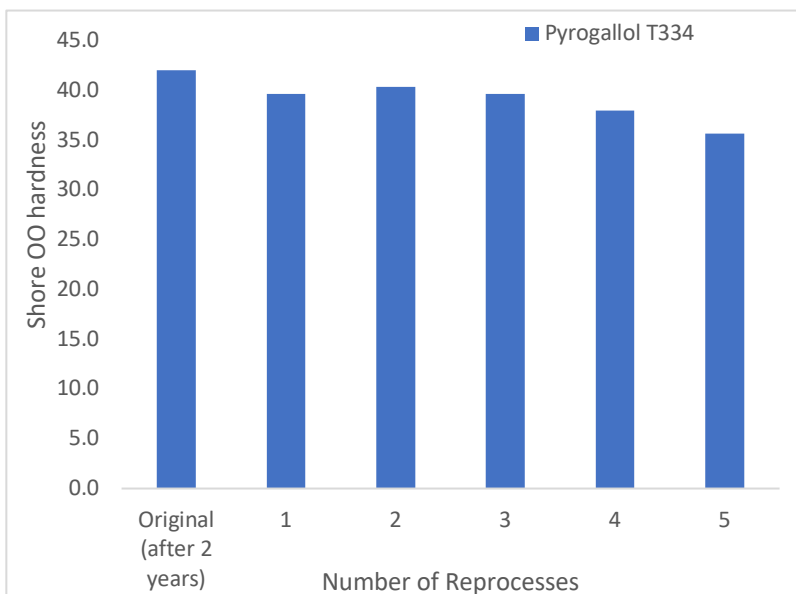


Figure S5.6. Thermal reprocessing of a 2 year old sample that was 5 times cut into small pieces and then remolded under heat pressing for 5 sequential times showing little change in Shore hardness.

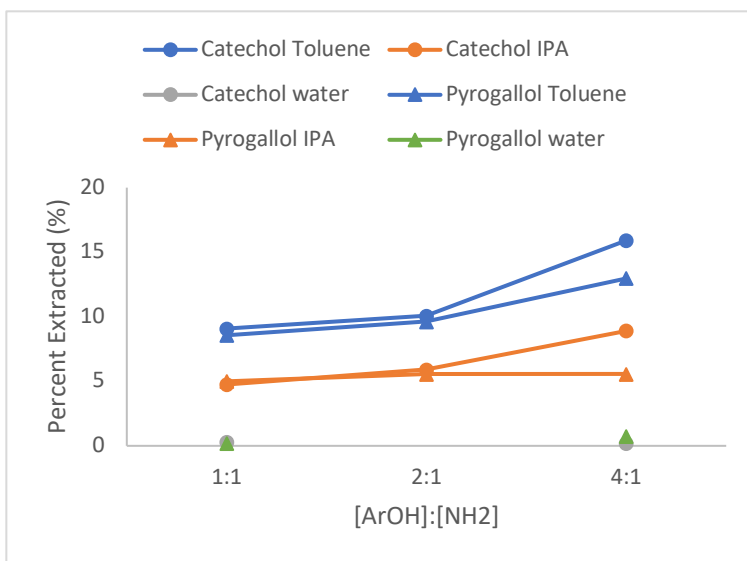


Figure S5.7. Efficiency of extract removal in various solvents.

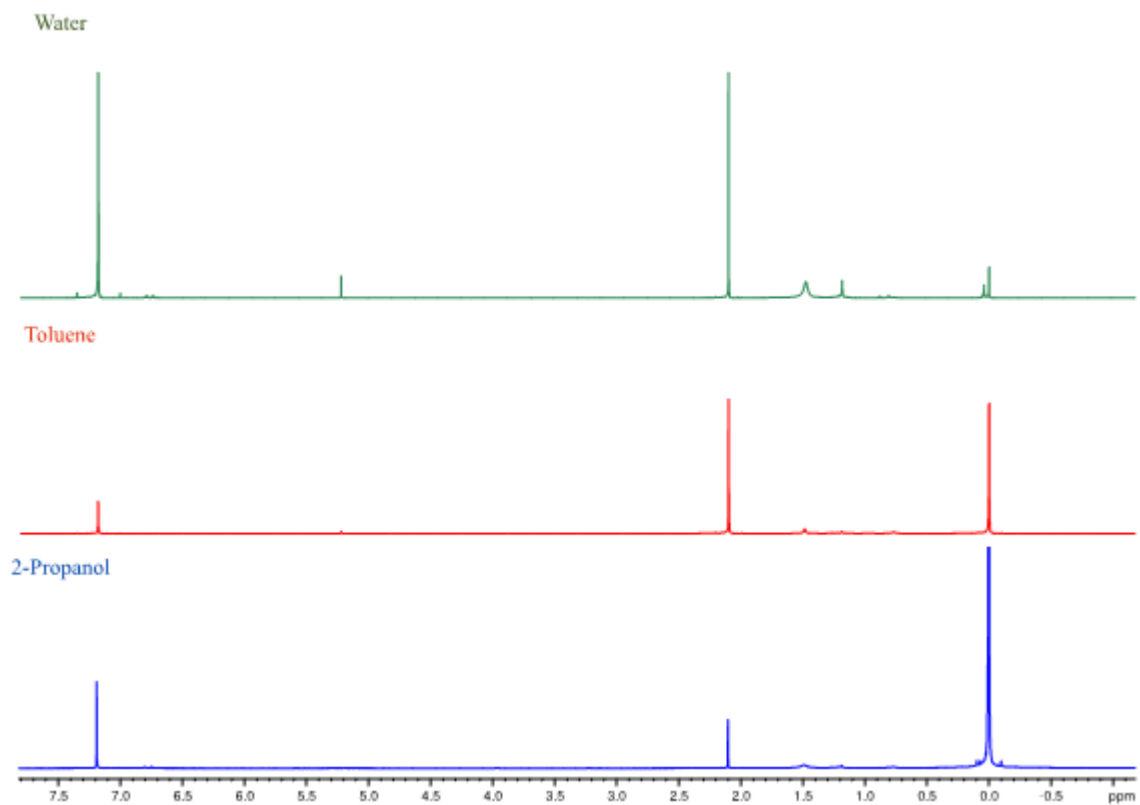


Figure S5.8. ¹H NMR spectra in CDCl₃ of the extractables from the swelling experiments (note: the peak at 2.1 is trace of acetone), which are predominantly recovered silicone.

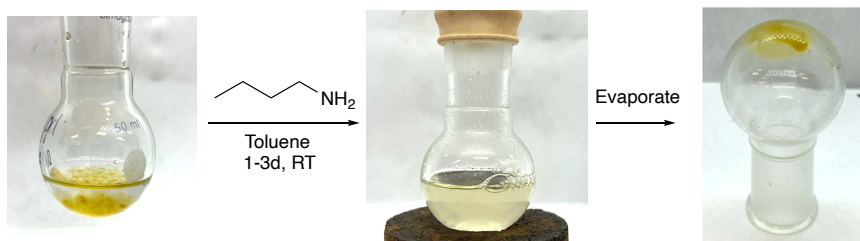


Figure S5.9. 1:1 [ArOH]:[NH₂] Catechol **T334** elastomer degraded using butylamine.

Full dissolution can be seen after 2 days. Rotary evaporation leads to reformation of an elastomer.

5.2 Supporting Information for Chapter 3: Antioxidant Silicone without Covalent Crosslinks

'Oaked' Silicones: Natural Tannins as Crosslinkers for Sustainable Silicones

Khaled Tamim and Michael A. Brook*

Electronic Supporting Information

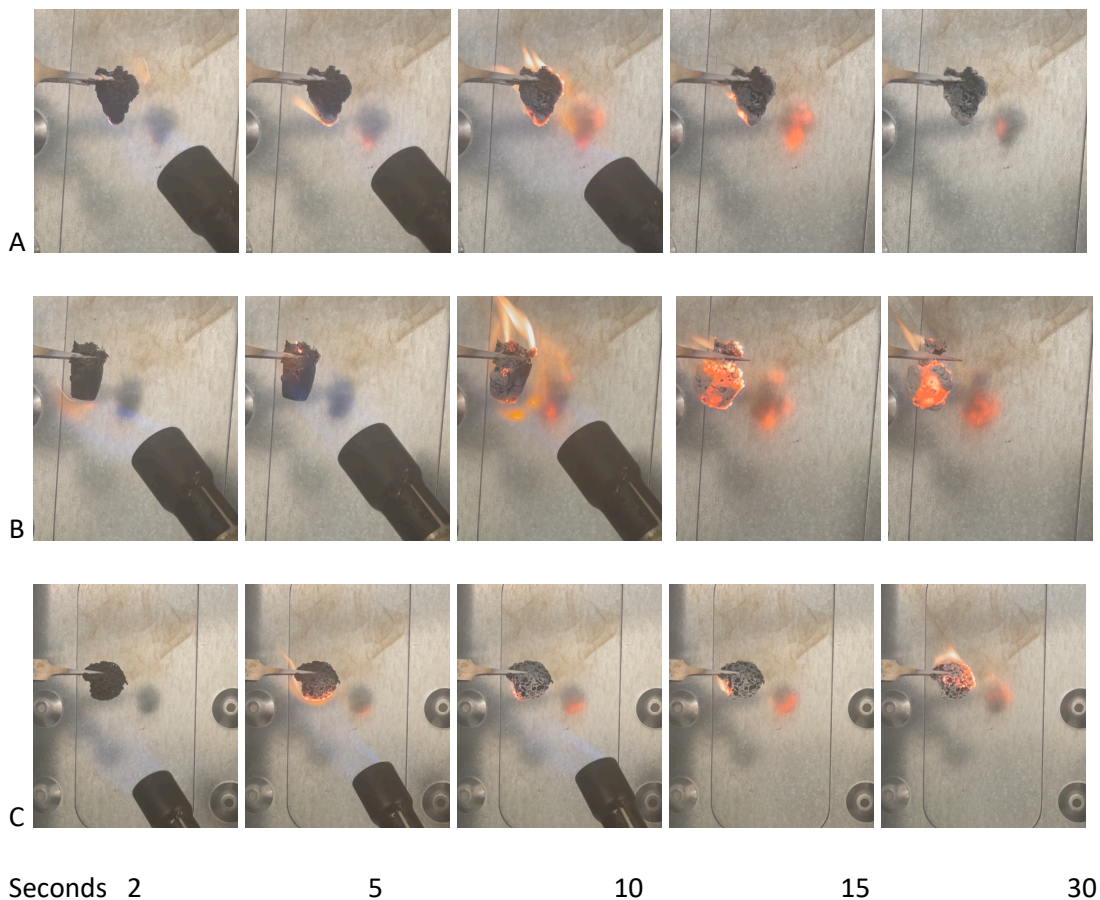


Figure S5.10. Combustion over first 10 s in a flame (first three images) and then self-perpetuated burning for up to 30 s. Quantity of tannin foam: A) 20% Quertanin B) 20% Tan'cor Grand Cru C) 50% Tan'cor Grand Cru