Controlling Silicone-Saccharide Interfaces

CONTROLLING SILICONE-SACCHARIDE INTERFACES THROUGH BORONIC ACID MODIFICATION OF SILICONE POLYMERS

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Title: Controlling Silicone-Saccharide Interfaces Through Boronic Acid Modification of Silicone Polymers

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Abstract

Silicone elastomers, which are normally crosslinked using metal catalysts, are traditionally reinforced with mineral fillers to achieve desired mechanical properties. When alternate, hydrophilic materials are used as fillers the silicone must be modified using amphiphilic moieties to mitigate phase separation. Herein it is reported that renewable saccharides can be used to both crosslink and reinforce silicones. The grafting of boronic acids, which bind to saccharides, to silicone polymers gives materials that, when added to aqueous solutions of mono- or polysaccharides, without catalysts, generated elastomers via the boronic acid interaction with saccharides. The efficiency of crosslinking, as shown by Young's moduli, depended strongly on the specific saccharide and the density of boronic acid groups on the silicone. Simple silicones normally phase separate in water saccharide mixtures. However, pretreatment of silicone boronates with the saccharide phytoglycogen, followed by exposure to water, led to stable aqueous phytoglycogen/silicone dispersions (pastes). The different outcomes arising from the order of addition are attributed to better dispersion of the silicone and saccharide in the latter case. Rheological studies of the pastes showed that, unlike the elastomers, viscosities depended more on the fraction of silicone in saccharide; number of boronic acid contact points between the silicone and saccharide was only a minor contributor. The equilibrium concentration of sugar/boronate contacts, which stabilize the water/oil interfaces, remains high even at high concentrations of water and even when the specific binding constant for an individual saccharide is low.

Additionally, the ability of the surfaces of these modified silicones to adsorb saccharides was investigated. Silicone boronic acids (**SiBA**) with and without permanent (non-hydrolyzable links), were prepared by hydrosilyation of a tartrate-protected styrylboronate. Hydrolysis led to free boronic acids at the interface to which the saccharides sorbitol, pullulan, casein and phytoglycogen, and the glycosylated protein, mucin, chemisorbed. Surface active proteins like

albumin and casein adsorbed on such surfaces too, but only on the **SiBA** surfaces would (poly)saccharides and the glycosylated proteins adsorb; HSA was an exception. It was not possible to exchange polysaccharides like phytoglycogen from the surface, even when using sorbitol, a monosaccharide with a better binding constant to boronic acid. The behaviors of these surfaces are reported.

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Contents

List of Figures and Tables

Chapter 1: Introduction

1.Surface Properties of Silicones

1.1. Silicone Polymers at Surfaces and Interfaces

Incompatible phases do not amalgamate on contact but are separated at a common boundary known as the interface or surface[1]. Specifically, the term surface is used to describe separation between a condensed and gaseous or vacuum phase whereas an interface is used to describe the boundary between two incompatible condensed phases[1]. The thickness of the interface or surface is merely a few atoms; the majority of the bulk phases do not contribute to interfacial interactions or lack thereof[2]. Surfaces and interfaces play a key role in many applications today including, but not limited to semiconducting electronics such as organic photovoltaic devices[3-4], biomedical devices[5-6], cosmetics[7-8], and textiles[9] to name a few. The properties of polymeric materials that determine such applications' utility are based on performance since wettability, lubricity, adhesion, tack, and biocompatibility are interfacial in nature whereas a materials bulk properties affect performance to a weaker extent[10]. These applications often require surface modification to ensure the material is suited to serve its intended purpose while maintaining the properties and performance of the bulk material. Examples of this can be found in applications such as anti-smudge coatings[11], anti-reflective coatings for LED device packaging silicones[12], and biomedical devices such as contact lenses[13]. A prominent material broadly used in interfacial applications is a class of polymer known as silicone.

Silicones are entirely synthetic polymers composed of siloxane $RSi(CH_2)_2OR$ repeat units[14] found ubiquitously in the developed world across many facets of life. They are regarded as high value materials for several reasons, the most significant being the inability of organic replacements to match their superior properties, as well as the efficiency of the material as both

an additive or a bulk material; a small amount of material is often sufficient to achieve desired results. Silicone properties such as thermal stability, electrical resistance, optical transparency, and hydrophobicity are commonly manipulated for a variety of different applications. In the absence of acids or bases silicones are remarkably stable; degradation of dimethylsilicone fluids begins around 350°C, whereas phenylsilicones are known to degrade at even higher temperatures[15]. The relative permittivity of silicones is quite low, between 2.1-2.4 for both low molecular weight cyclics[16] and oligomers as well as high molecular weight linear polymers[17]. Perhaps the most interesting property of silicones though, and the premise for a focus of the present work, is their hydrophobic nature accompanied by high surface activity[18]. The silicone chain is very flexible, a property instated by the large 145° Si-O-Si bond angle and low bending forces required for shaping the material. Hydrophobicity is elicited by the presence of methyl groups that freely rotate around the siloxane backbone; additionally, a rather low glass transition temperature(T_g) (-123°C) allows for further backbone and substituent rearrangement.

Some applications, for example in bio-implantable devices, require bulk properties of silicone for their flexibility yet need to be hydrophilic at the surface to ensure biocompatibility. Surface modification of silicones can be impeded by hydrophobic recovery facilitated by the flexibility of the silicone backbone Figure 1.

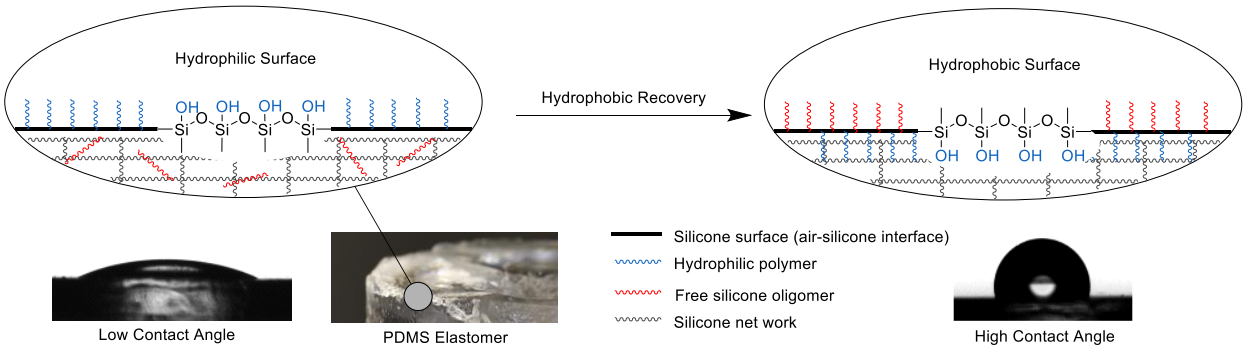

Figure 1. Illustration of hydrophobic recovery of a modified PDMS surface

Methyl groups preferentially orient towards the silicone-air interface, a thermodynamically advantageous state. Above the T_g when the silicone surface is disrupted rearrangement of polar and non-polar functional groups in addition to migration of free oligomers trapped within the bulk of the elastomer network to the surface over time occurs. This mechanism allows for recovery of hydrophobicity after hydrophilic modification. Simple surface modification of silicones is not always sufficient in maintaining coatings or grafted polymers at the interface due to the challenge presented by hydrophobic recovery. Methods for altering the wettability of silicone surfaces from hydrophobic to hydrophilic are outlined as follows.

1.2. Methods for Physically Altering Properties of Silicones

Conventional silicones (simple dimethyl silicones) lack reactive functional groups that can act as tethering groups for functionalization or modification making them difficult to manipulate. In general, the hydrophobic surface predominantly attracts other hydrophobic segments. Three main methods (Figure 2) based upon this interaction are commonly employed to modify silicone surfaces accomplishing two things: 1) the backbone will not be chemically altered, and 2) a silicone with a well-defined and controlled bulk structure can be produced.

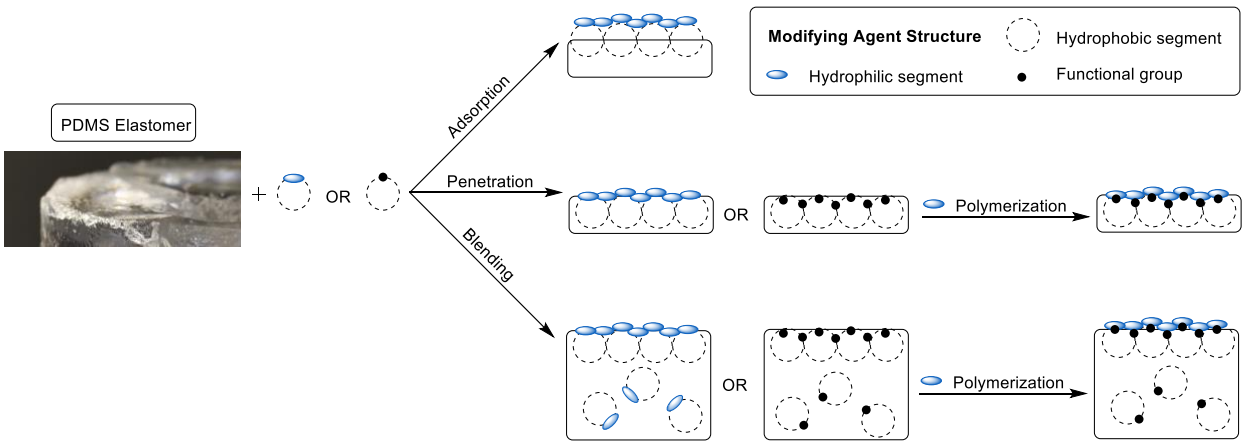

Figure 2. Methods for silicone modification via physical adsorption, blending and polymerization from surface adsorbing or blending reactive reagents.

Surface modification can be achieved through adsorption, penetration or blending of amphiphilic tethering molecules or polymers such as polyethylene oxide with silicones. The simplest of these routes is by adsorption of an amphiphilic moiety to the surface. Coatings deposited on the silicone surface such as self assembling proteins[19] in the case of hydrophobin, which could be further functionalized using biologically relevant materials demonstrates how physisorption can effectively affect a change in surface properties. In addition silicone surfactants such as Silwet-L77[20] and block copolymers such as PDMS-PEO block copolymers[21] have also effectively been used in the same manner to coat hydrophobic surfaces. Another method for physisorption of an amphiphile resulting in a change in wettability can be accomplished by penetrating the bulk of the elastomer via swelling and deswelling processes. Using an effective solvent for silicone such a toluene or chloroform the hydrophobic segments of block copolymers such as (PEO-b-PDMS) can be embedded within the bulk phase of an elastomer while the hydrophilic segments remain phase separated at the surface effectively installing a hydrophilic layer at the materials surface[22-23]. Finally, the third method for installing hydrophilic moieties to a PDMS surface is by blending incompatible phases together through copolymerization resulting in an interpenetrating network[24]. This method combines normally incompatible materials while resisting hydrophobic recovery by locking interdigitating phases together. An example from Abbasi et al.[25] demonstrated this method by first polymerising a silicone network then swelling the silicone elastomer with 2-hydroxyethyl methacrylate (HEMA) in toluene. A polymerization initiator was injected into the HEMA swollen silicone elastomer polymerizing monomer into an interpenetrating network (Figure 3).

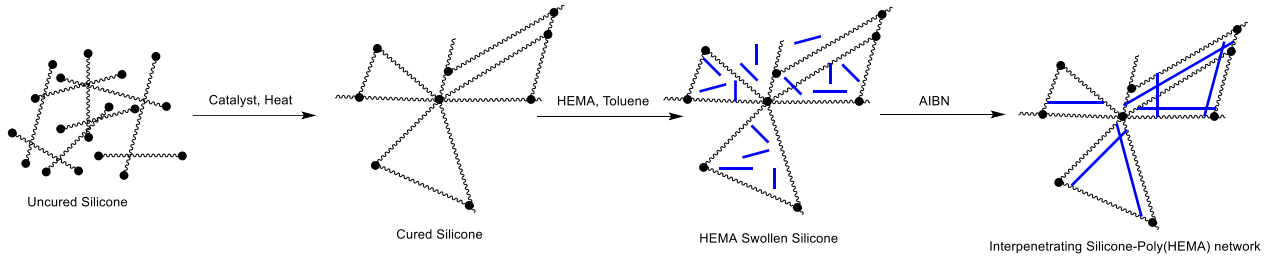

Figure 3. Synthesis of silicone-poly(HEMA) interpenetrating network elastomers.

1.3. Methods for Chemically Altering Properties of Silicones

As previously mentioned silicones lack reactive functional groups making chemical manipulation difficult. This strength of the Si-O bond relative to C-C bond is significantly greater (477-549KJ·mol^{-1} compared to 334KJ·mol^{-1}), manifested in silicones by superior thermal and environmental resistance[14]. The bond length also differs between Si-O and C-C bonds (1.63Å compared to 1.53Å) resulting in easier access to incoming nucleophiles. The siloxane backbone however, is more reactive to acid or base reactivity than carbon-based analogues. This is manifested in conjunction with the partial ionic characteristic of the Si-O bond through dynamic cleavage or reassociation of Si and O bonding otherwise referred to as metathesis (Figure 4).

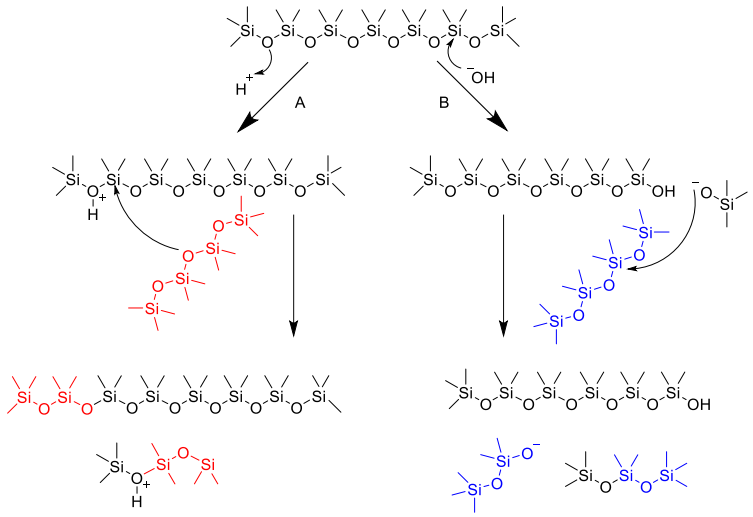

Figure 4. Dynamic cleavage and reassociation of siloxanes under acidic (A) and basic (B) conditions.

Both acid and base catalyzed cleavage of bulk silicone can be achieved when a suitable solvent for silicone is used. When a poor solvent for silicone is used however, efficient degradation of the silicone is not seen, rather controlled surface etching can be achieved. This dynamic cleavage/reassociation is adopted in the synthesis of linear silicones (Figure 5).

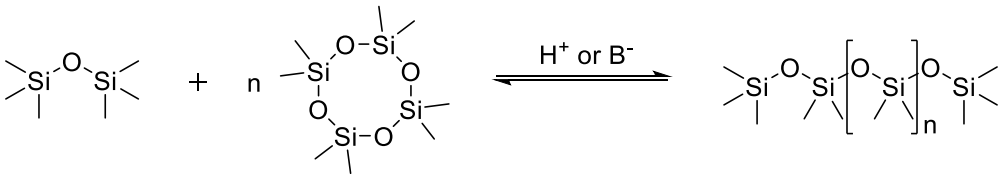

Figure 5. Acid/Base catalyzed synthesis of linear silicones

In this process hexamethyldisiloxane (MM, a commonly used low molecular oligomer) and octamethyltetrasiloxane (D4, a cyclic silicone) are combined under acid or base catalyzed conditions to yield higher molecular weight linear silicones plus small amounts of cyclic species, the concentrations of which depend on the starting ratios of MM to D4. When slightly altered this process can be used to functionalize silicones as either telechelics or pendants (Figure 6) by using a different starting oligomer or cyclic wherein one of the methyl groups is replaced with a functional group.

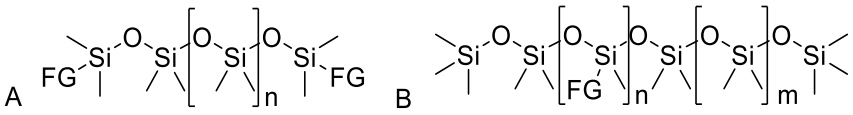

Figure 6. Telechelic (A) and Pendant (B) functionalized silicones.

Often, the surface of PDMS is functionalized as a silanol, as seen in Figure 7, using either an acid or base catalyzed route or by high energy irradiation in the form of UV, plasma, or

corona activation as a first step.

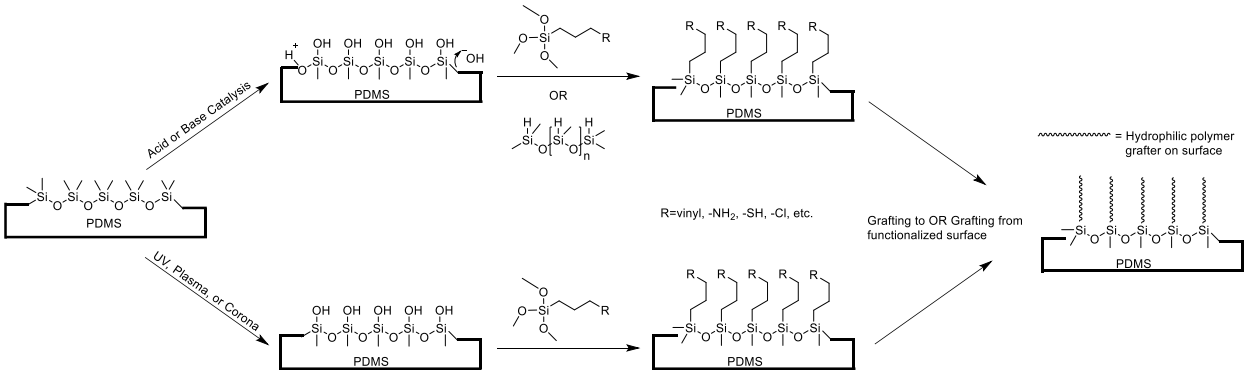

Figure 7. PDMS surface functionalization via acid or base catalyzed backbone cleavage and rearrangement or UV, plasma, or corona activation.

This serves to replace a methyl group with a silanol group, the route to which can be chosen based on the needs of the desired final material. With newly installed silanols after acid/base catalysis or high energy irradiation, further functionalization can be easily achieved using a silane-coupling agent with a reactive functional group. From here, the desired surface modification is carried out using either a grafting to or a grafting from method effectively modifying the silicone surface with the polymer of choice.

The choice between acidic or basic conditions for promotion of silane-coupling to silicone surfaces will depend on what is important to the application. Oxidative-acidic conditions such as H_2SO_4/H_2O_2[26-27] will effectively activate the surface within 30 minutes whereas corresponding basic conditions using NaOH works over a 24 hour period[28]. Base catalysis is ideal because it effectively promotes monomer equilibration of silicone chains however the harsh conditions used can damage the silicone at both the surface and through the bulk of the elastomer[14]. Acid catalysis has the distinct advantage of introducing hydrosilane functionalities[29] to the surface in addition to being less time consuming.

As an alternative to activation by acid/base catalysis, high energy irradiation[30] by means of plasma oxidation[31], ultraviolet radiation (UV)[32], and coronas[33] has been shown to effectively activate silicone surfaces for modification. High energy species produced by plasma oxidation or UV/ozone such as electrons, radicals, and ions, oxidize the surface of the silicone. These reactive species attack the siloxane backbone forming silanol presenting surfaces which additionally condense with one another; the hydrophobic silicone surface is converted to a hydrophilic surface. As with acid/base catalysis the silanol can then be functionalized using a silane-coupling agent via condensation between the silanol and silane.

Until functionalization has occurred hydrophobic recovery is often an issue, therefore further modification is required for permanent surface modification. One such functional group that can be used for hydrophilic surface modification of silicones is boronic acids, the focal point of the present work. Boronic acids have been used in functionalization of various materials applications such as hydrogels[34], saccharide sensors[35], and cell capture[36]. Boronic acid functionalization of silicones however has only recently been studied[37]. The current work builds off this preliminary study that first functionalized silicones with boronic acids in attempt to investigate the effect of boronic acid species on physical silicone properties such as Young's modulus and wettability while further probing what applications may be possible with the incorporation of silicone to a boronic acid presenting polymer.

2. Boronic Acids and Their Derivatives

2.1. Structure and synthesis

Boronic acids are trivalent boron containing organic molecules that contain one alkyl/aryl substituent (a single C-B bond)[38]. Their polar nature, elicited by hydroxyl groups inhabiting the remaining valence along with their Lewis acidic nature caused by a vacant p-orbital on the sp2-hybridized central boron atom, make them dually reactive yet water insoluble (while in non-ionic

form). The molecule adopts a trigonal planar geometry akin to their carbon-based analogues, carboxylic acids, however like silicones, they are completely synthetic and have not been found in nature. Traditionally, boronic acids were prepared by Grignard reaction using a boric acid feedstock. Boronic acids are the product of the second oxidation of boranes, first reported by Frankland in 1860[39]. Diethyl zinc was treated with triethylborate yielding triethylborane, a highly air sensitive compound which further oxidized to give ethyl boronic acid. A third oxidation yields boric acid, a compound that is very stable and relatively benign to humans[38]. The modern approach to synthesis of boronic acids was first reported by Molander et al. in 2010[40] (Figure 8).

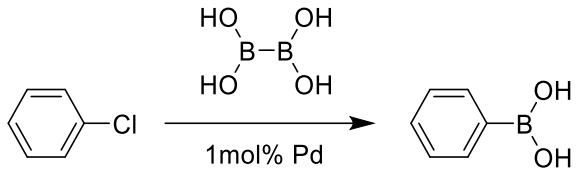

Figure 8. Palladium catalyzed synthesis of aryl-boronic acids from aryl halides using bis-boronic acid.

Aryl chlorides were converted to boronic acids using bis-boronic acid catalyzed by a palladium complex at elevated temperature (80°C) in ethanol. This process quickly became adopted as the standard for production of boronic acids industrially. The product could be further modified to afford trifluoroborates, aryl coupling, or boronic esters, the latter of which is of interest to the current work as a part of general boronic acid reactivity. Additionally, the synthesis of boronic acids has been reported using a number of other methods including treatment of aryl-metal intermediates with borates[41], transmetallation of aryl silanes and stannanes[42], and boronylation by transition metal-catalysed C-H functionalization[43].

2.2. Boronic acid-diol binding mechanism

Boronic acids have two modes of reactivity, the first of which is through geminal hydroxyl groups which fill two of the three valences on the central boron atoms[38]. Like any other polar protic functional group, boronic acids display hydrogen bonding capabilities (Figure 9).

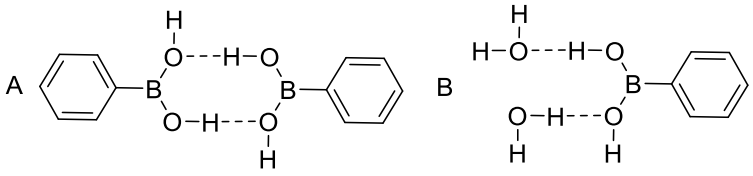

Figure 9.Hydrogen bonding facilitated boronic acid dimerization (A) and complexation with H_2O (B).

Hydrogen bonding occurs between boronic acids and other polar molecules capable of hydrogen bonding; it can also occur between pairs of boronic acids resulting in dimers (Figure 9A). Of particular significance with respect to wettability is the interaction between H_2O and the hydrophilic boronic acid moiety (Figure 9B). Two equivalents of H_2O hydrogen bond with a single equivalent of boronic acid[44]. Boronic acids can also react through their geminal hydroxyl functional groups with vicinal cis-1,2 and cis-1,3 diols producing new compounds (Figure 10)[45-48]. Through a reversible process boronic acids react with other diols to form 5 or 6-membered cyclic boronic esters. Boronic acids are also known to condense forming oligomeric anhydrides known as boroxines. Saccharide binding to boronic acids in particular has been heavily researched for applications including as glucose sensors[49], affinity separation of saccharides[50], enzyme inhibitors[51] and cell capture and culture[36]. These interactions are entirely reversible; existing in dynamic equilibrium they can be manipulated between functional groups simply by controlling the amount of H_2O in the system in which they lie.

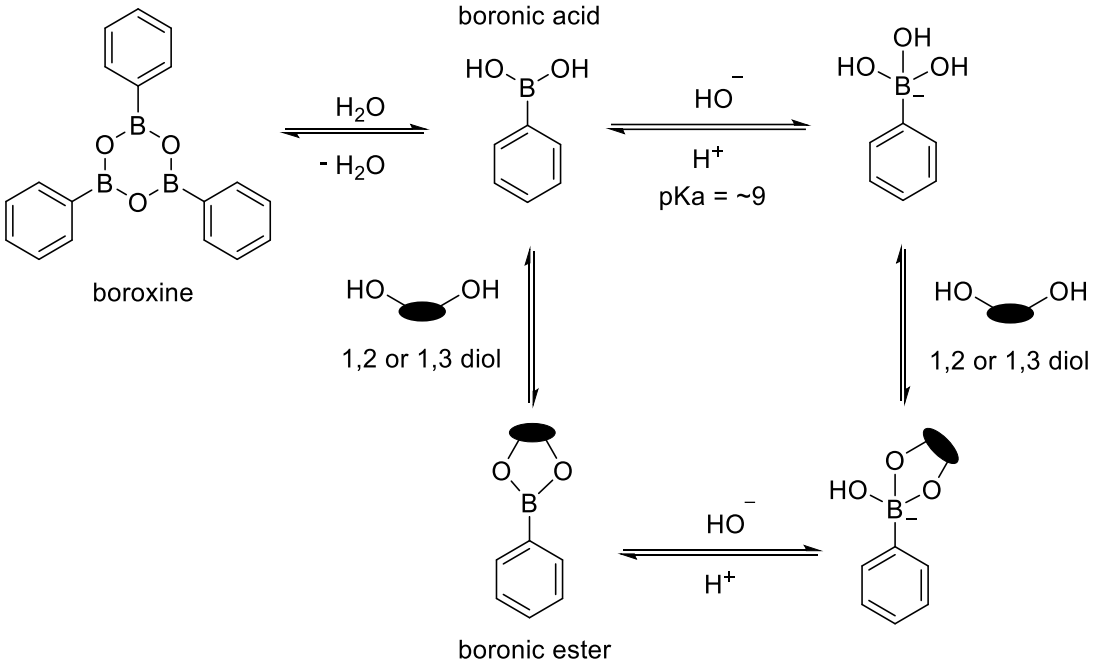

Figure 10. Boronic acid/ester equilibrium mechanism.

The relative rate of these interactions can be influenced considerably by pH[52]. Complexation of the central boron atom via Lewis basic species such as hydroxides and amines convert the geometry about the boron centre from sp2 hybridized trigonal planar to sp3 hybridized tetrahedral arrangements[44]. The Lewis acidity of boronic acids is linked to their Bronsted acidity; they do not lose a proton like from one of their OH groups like traditional Bronsted acids do rather ionize a water molecule through coordination yielding a tetrahedral boronate anion and a proton or hydronium ion. Tetrahedral boronic acids are more acidic than their trigonal planar counterparts, therefore they tend to react with diols much faster[53].

2.3. Boronic ester stability

Ester stability is largely determined by a combination of pH and diol structure. Lewis basic complexation with boronic acids is seen above pH 9, below this three-coordinate boron species are normally seen. pH affects the affinities of boronic acids towards diols however, the structure of the diol itself appears to play a larger role in boronic ester formation as outlined extensively

by Wang and Springsteen[45] which is in agreement with and expands upon the seminal study conducted by Lorand and Edwards[54]. The association constants for phenylboronic acid-diol complexation determined by Wang and Springsteen are presented in Table 1.

Table 1. Association constants (K_{eq}) with phenylboronic acid at pH 7.4, 0.10M phosphate buffer. Values are the average of triplicate runs rounded to two significant figures.

Diol	**$K_{eq}(M^{-1})$**	**Diol**	**$K_{eq}(M^{-1})$**
Alizarin Red S.	1300	Sialic Acid	21
Catechol	830	Cis-1,2-Cyclopentane diol	20
D-Sorbitol	370	Glucoronic Acid	16
D-Fructose	160	D-Galactose	15
D-Tagatose	130	D-Xylose	14
D-Mannitol	120	D-Mannose	13
L-Sorbose	120	D-Glucose	4.6
1,4-Anhydroerythritol	110	Diethyl tartrate	3.7
D-erythronic-γ-lactone	30	Maltose	2.5
L-Arabinose	25	Lactose	1.6
D-Ribose	24	Sucrose	0.67

There is a clear lack of parity in the values presented for compounds containing minor differences in structure; the pKa of the diol plays a major role in ester formation. Electron density about the boron centre largely determines the Bronsted and Lewis acidities of boronic acids with greater electron deficiency leading to higher acidity. Not surprisingly the presence of electron-donating and electron-withdrawing groups significantly increased and decreased the

pKa values of boronic acids respectively, concomitant with boronic acid-diol association constants[46]. Phenylboronic acid (pK_a=8.9) for example can be made more Lewis/Bronsted acidic by nitrating the aromatic ring (4-nitrophenylboronic acid, pK_a=7.1), or less Lewis/Bronsted acidic by adding a methoxy group to the aromatic ring (4-methoxyphenyl boronic acid, pK_a=9.3). In addition to boronic acid pK_a the need for diol isomerization to a more favourable isomer, for example from pyranose to furanose in the case of reducing sugars such as glucose can decrease binding efficiency[38]. Non-reducing sugars such as sorbitol are not inhibited by this step and therefore more efficiently form boronic esters (glucose K_{eq}=5, sorbitol K_{eq}=370). It is possible to use these values to create systems in which selective sugar binding is seen, a concept previously determined where selectivity of several sugars by monoboronic acids was probed (D-fructose K_{eq} > D-galactose K_{eq} > D-glucose K_{eq}) by Lorand and Edwards[54].

2.4. Boronic acid containing polymers

Boronic acids have often been incorporated into polymers for previously mentioned applications[50] providing them with a scaffold to produce stimuli-responsive materials. Anchoring boronic acids provides an easy method for measuring response to various stimuli by swelling[55], fluorescence[45, 56], aggregation induced turbidity[57], and macroscopic associations[58], all of which are measurements not viable for solution based molecular systems. By incorporating boronic acids into polymeric materials it is possible to tailor them towards applications based on stimuli specific to boronic acids. For example, copolymers with both boronic acids containing segments and hydrophilic/hydrophobic segments have been investigated as self-assembling materials based on aggregation in H_2O and dissociation in the presence of saccharides[57, 59]. As previously mentioned, the absence of saccharides promotes boronic acid dimerization. When this concept is applied to polymers self healing abilities are invoked[60]. Although a reversible process when in solution this concept allows for association without dissociation (when dry)

meaning only physical separation by shear force will cause a rupture in the bulk material. Boronic acids find utility in H_2O based polymers in the form of hydrogels as well[61]. Hoare and Pelton showed that boronic acid functionalized microgels can be engineered as glucose responsive sensors for detections of selectable glucose concentrations through swelling measurements. Glucose responsive materials have particularly high potential in minimally invasive medical applications such as monitoring glucose levels for diabetic patients[62]. Similarly, hydrophilic materials can be adhered to hydrophobic materials using boronic acids as a linker. For example, Zhang et al.[63] showed that boronic acid functionalized materials such as latex can reversibly bind to cellulose surfaces, normally incompatible materials.

Controlled boronic acid functionalization of polymers is key to the success of some applications. A well-defined structure allows materials to be used in quantitative applications. Qin, Cui, and Jaekle[64] presented the controlled synthesis of a boronic acid functionalized polystyrene by atom transfer radical polymerization allowing the ratio of boronic acid to backbone monomer unit to be chosen. This has potential for constructing materials for biomedical applications such as boron neutron capture therapy where a tuneable amount of boron is advantageous[65]. For example, the study by Mi et al. showed that a block copolymer controlling the amount of boron could be tuned to effectiveness for cancer treatment. Polymers that introduced too much boron to tumor containing regions in mice were toxic to surrounding tissues whereas polymers that didn't introduce enough boron to tumors yielded ineffective treatments.

3. Silicone boronates

3.1 Synthesis and unique interfacial behaviour

Current research on silicone boronates, silicone polymers bearing boronic acid moieties, is a field in its infancy. Several reports on the synthesis and characterization of these materials

and their corresponding complexation with sugars[37], their ‘silly-putty’ like behaviour as reversibly crosslinking thermoplastic elastomers[66] as well as their unique interfacial characteristics[67] have been published.

Synthesis of functional silicones as previously discussed, presents functional groups that can be used as handles for further synthesis. In particular, the introduction of hydrosilanes and vinylsilanes have often been used in silicone synthesis by hydrosilylation; the tethering of two silanes together through Si-C bond formation (Figure 11).

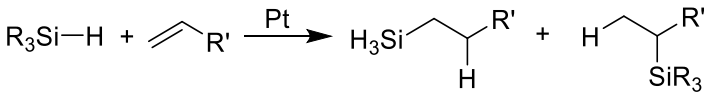

Figure 11. Hydrosilyation of vinylsilanes using Karstedt's Pt catalyst.

This method allows for the precise construction of silicones without sacrificing the structure of the silicone backbone that acid or base catalyzed synthesis suffers from due to backbiting. Hydrosilylation is the method used in the current work to append boronic acids to silicones. Carboxylic acids (the carbon-based analogue of boronic acids) and alcohols are compounds containing active hydrogens. They are known to react with hydrosilanes forming H_2 gas and siloxanes in a process competing with the desired addition to alkenes, retarding the intended reaction from occurring[68]. It is therefore necessary to first protect boronic acids to facilitate their successful appendage to silicone polymers using a reversible boronic ester protecting group. For convenience a diol that forms a boronic ester that is relatively easy to remove, such as dimethyl tartrate, was chosen whereas other protecting groups derived from materials such as pinacol and catechol proved to be too stable for convenient use[69]. Deprotection of compounds with greater stability require conditions that would risk silicone depolymerization/rearrangement

and were therefore not viable solutions for boronic acid protection. Once protected boronic esters could be added to silicone polymers as outlined in Figure 12.

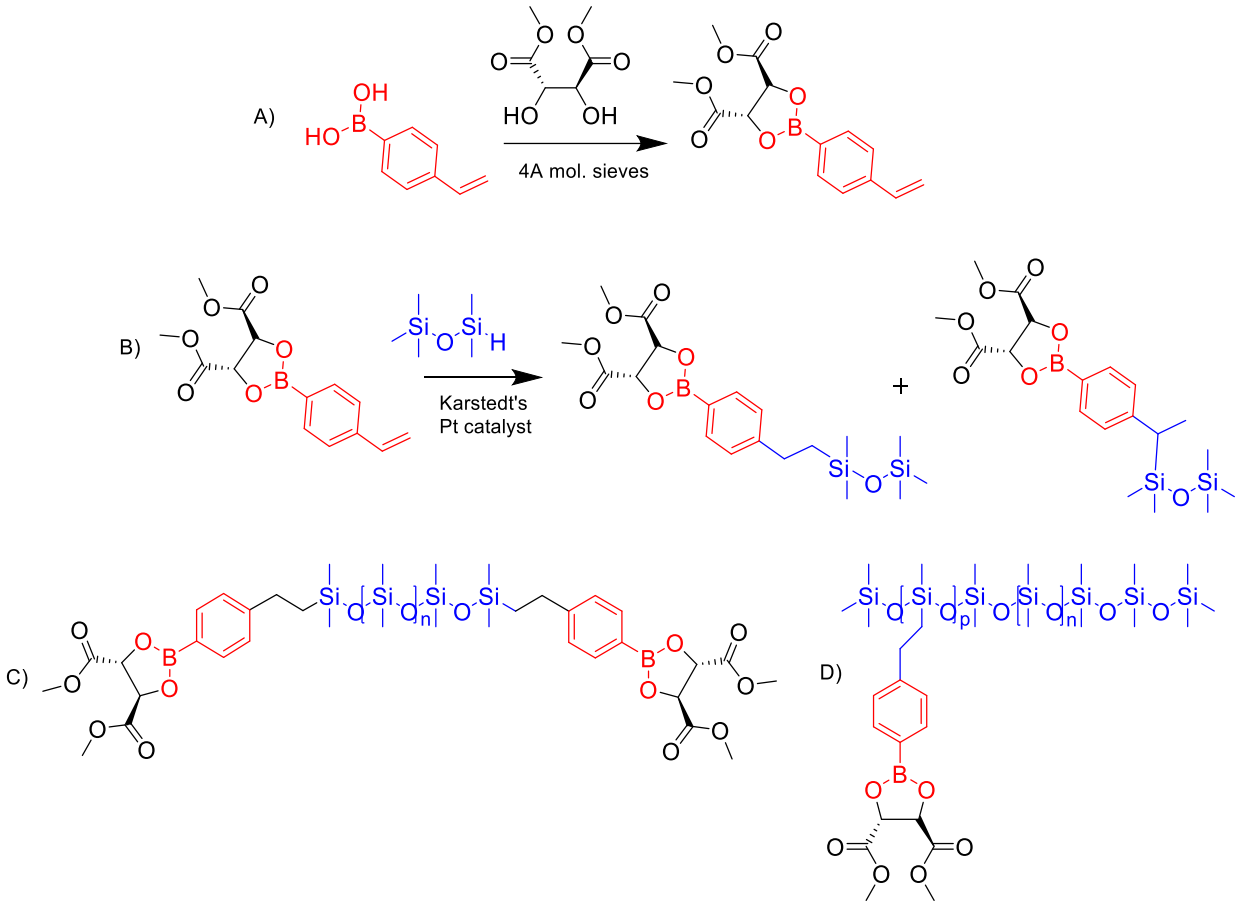

Figure 12. Synthesis of Silicone boronates via boronic acid protection using dimethyl-L-tartrate (A), followed by hydrosilylation to a hydrosilane (B) yielding a mixture of isomers in either telechelic (C) or pendant (D) arrangements.

Hydrosilylation of alkenes then produces a mixture of isomers (Figure 12B), a result of silane addition at either the alpha- or beta-carbon of the alkene. This mixture of products has not been separated for any experiments to date.

Removal of the tartrate protecting group is convenient and efficient; ester hydrolysis occurs instantly resulting in unique and rapid physical changes depending on the diol used for boronic acid protection[67]. After tartrate removal free boronic acids complex with one another via dimerization resulting in chain extension and polymerization. A thin robust silicone film is formed

on aqueous surfaces below pH 9. Above pH 9 tetrahedral boronic acids are forced into the sub phase where they can no longer contribute to chain extension and therefore cannot form a film. Below pH 9 film stability is great enough to support droplets of water. Film formation happens only at the interface meaning only hydrolysed boronate ester will form film; protected silicone boronic acids will still be able to flow, encompassing water droplets in a film of silicone along the way, a process that can be pushed further to produce water on water constructs (Figure 13).

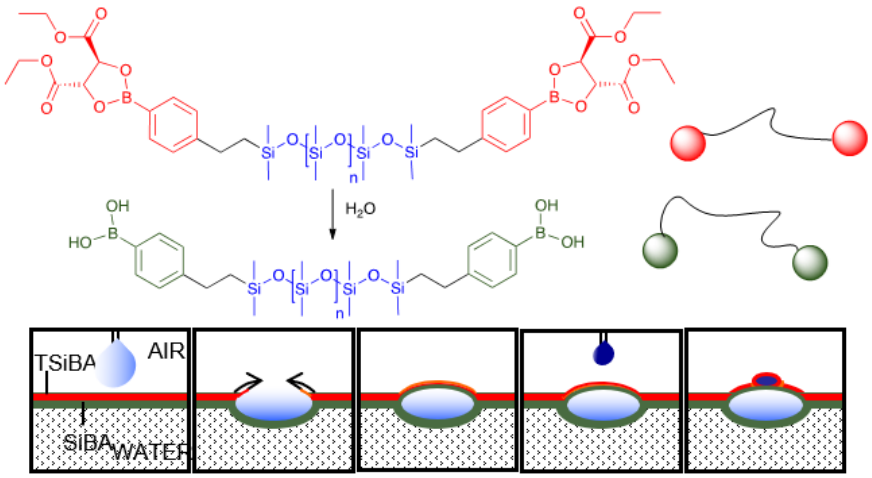

Figure 13. Silicone film formation process facilitated by boronic ester hydrolysis. Protected silicone boronate creeps onto water droplets forming film around the surface of the droplet. Further droplets can be placed onto these surfaces and subsequently encompassed.

The strength of the resulting films can be altered through the addition of various analytes such as NaCl, tris(2-aminoethyl amine) and HCl.

In addition to spread and set film formation these materials also act as non-newtonian fluids: they crack/shatter under high shear stress but flow under low shear stress[66], similar to the material used to make the children's toy, silly putty[70]. This behaviour is facilitated by reversible Lewis acid: Lewis base interactions. Dodge, Chen and Brook[66] showed that addition of a Lewis base in the form of butylamine provides a simple route to reversible crosslinking. Applied compressive stress can be relieved through dynamic B-N dative bond formation. Normally, silicones are thermoset elastomers; once crosslinked they cannot be remoulded. This

dynamic crosslinking system however provides a method for manufacturing reprocessable silicones simply through the addition and subsequent evaporation of Lewis base.

3.2. Objectives

3.2.1. Focus 1: Hydrophobic surfaces bind saccharides and proteins

The need for surface modified silicones in biomedical applications for materials such as catheters, shunts, and contact lenses is evident[71]. Prior to surface modification silicones risk response from the host as a foreign body mitigating device effectiveness. For example, contact lenses will damage the cornea unless the lens is wettable, poor adhesion between percutaneous devices and tissues in the skin creates a dead space between layers where infection is at risk of developing. Surface modification as outlined in chapter 1, sections 1.2 and 1.3 is key to bypassing these phase separations for successful biomaterial implementation. By modifying silicones with boronic acid moieties it is hypothesized that surface wettability and controlled saccharide/protein binding can be elicited. This investigation aims to determine the change in wettability and the efficiency with which different saccharidic materials, particularly biologically interesting ones such as glycogen and mucin, bind to the modified silicone surface. Mucins are a particularly interesting class of biomolecule because of the role they play in food science, gastrophysiology, and the lubricity they impart on the surfaces which they line[72]. Lubricity is key for devices that are inserted into the body via orifices, many of which are lined with mucins, such as catheters and endoscopes.

Since boronic acids are known to form complexes with diols this investigation will determine what impact, if any, being tethered to a silicone has on this interaction, as well as what impact the nature of the saccharide has on the interfacial properties of silicone boronates. In particular, the structure of the saccharidic material whether it be monosaccharide, polysaccharide, or protein is used, will be investigated for its effect on silicone wettability.

3.2.2. Focus 2: Using saccharides as reinforcing fillers for silicones

Industrially, silicones are often reinforced using silica as a filler to prevent erosion of the bulk elastomer[73]. In addition to preservation of the elastomer fillers also contribute to the strength of the material; the young's modulus can be modified using fillers[74]. In this work the use of saccharides as reinforcing fillers (fillers anchored into the elastomer) in place of traditional inorganic silica particles was investigated. We hypothesized that a combination of saccharide structure and boronic acid-saccharide stoichiometry could affect a change in the modulus of silicone boronic acid elastomers and can be tuned accordingly using saccharides as crosslinkers. This represents a method for offsetting the high energy input of making silicone elastomers by diluting them with renewably sourced materials. The added benefit of altering physical properties is not to be overlooked either. In addition to improving the mechanical properties of silicone elastomers the ability to tune them is highly desirable.

4. Conclusions

The incorporation of boronic acids into silicone elastomers equips hydrophobic materials with hydrophilic moieties. Currently, much research has been conducted on surface modification of silicones using various functional groups however, boronic acids are a relatively unexplored functional group for silicone surface modification. The unique properties of boronic acids have been used in a number of applications (section 2.2), none of which have been applied to silicones. The current work suggests a promising new class of material, silicone boronates, hold high potential for use in biomaterials applications. Herein, the use of the interaction between boronic acids and diols for manipulating silicone surface and bulk mechanical properties is reported.

5. References

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Chapter 2: Controlling Silicone-Saccharide Interfaces: Greening Silicones

Benjamin Macphail and Michael A. Brook

Abstract

Silicone elastomers, which are normally crosslinked using metal catalysts, are traditionally reinforced with mineral fillers. We report that renewable saccharides can instead be used to both crosslink and reinforce silicones. The grafting of boronic acids to silicone polymers gives materials that, when added to aqueous solutions of mono- or polysaccharides, without catalysts, generated elastomers via the boronic acid interaction with saccharides. The efficiency of crosslinking, as shown by Young's moduli, depended strongly on the specific saccharide and the density of boronic acid groups on the silicone. Simple silicones normally phase separate in water saccharide mixtures. However, pretreatment of silicone boronates with the saccharide phytoglycogen, followed by exposure to water, led to stable aqueous phytoglycogen/silicone dispersions (pastes). The different outcomes arising from the order of addition are attributed to better dispersion of the silicone and saccharide in the latter case. Rheological studies of the pastes showed that, unlike the elastomers, viscosities depended more on the fraction of silicone in saccharide; number of boronic acid contact points between the silicone and saccharide was only a minor contributor. The equilibrium concentration of sugar/boronate contacts, which stabilize the water/oil interfaces, remains high even at high concentrations of water and even when the specific binding constant for an individual saccharide is low.

Introduction

Silicone polymers are commercially important materials that impact daily life in advanced economies. Silicones do not often appear on the pages of this journal because silicones do not readily fit the 'green' mandate. However, their environmental behavior is excellent.[75] Extensive

studies have shown that silicones in virtually all environmental compartments readily decompose to sand, water and CO_2 following environmentally and biologically-mediated depolymerization and then oxidation.[76] However, silicone synthesis is not environmentally friendly, as the first, key step involves conversion of sand to silicon in a highly energy intensive and CO/CO_2-generating process.[77]

One way to reduce the environmental impact of silicone elastomers is to dilute them with recyclable, biodegradable and renewable materials. A more positive perspective would be to recognize that composites of silicone could be improved by taking advantage of natural materials. Silicone rubbers are weak unless reinforced by fillers;[78] expensive and heavy pyrogenic silica is most commonly used for this process. We reasoned that polysaccharides, which are emblematic green polymers, could simultaneously dilute the impact of silicones and silica on the environment while leading to elastomeric materials with enhanced properties.

Silicone polymers are, of course, known for exceptional hydrophobicity; surface energies are typically about 20 mN m^{-1}.[79] Most saccharides, particularly polysaccharides, are hygroscopic and so working with truly dry materials is problematic. Thus, the main synthetic challenge associated with creating silicone/saccharide composites is overcoming the hydrophobic silicone/hydrophilic saccharide interface.

Silicone interfaces can be controlled by organic modification. For example, grafting polyethers[80-81] or zwitterions[82] to a silicone surface decreases the water contact angle. Such surfaces will have greater physical affinity for (wet) polysaccharides, but at a level not expected to lead to stable composites.

In some cases, the direct bonding of silicones to saccharides is possible. For example, the use of silane coupling agents in wood can improve durability, dimensional stability by hydrophobization,[83] and fire resistance;[84] multistep processes can analogously lead to silicone-

hydrophobed wood.[85] The Piers-Rubinsztajn reaction has been used to directly graft silicone resins to cellulose or to another important natural polyphenolic polymer, lignin, while simultaneously blowing foams (Figure 14).[86-87] The resulting materials exhibited excellent adhesion between silicone and cellulose or lignin, respectively and, surprisingly in the latter case, led to silicone foams that were much better able to withstand exposure to flames than a commercial silicone foam, in spite of the fact that the foam contains an excellent fuel – lignin!

Boronic acids efficiently bind to saccharides.[88-89] The binding constant is sufficiently dependent on saccharide structure that physical separation of different sugars based on affinity with boronic acid is the basis of an analytical technique.[90] Previously, we prepared silicone-modified boronic acids (SiBA) (Figure 16). Upon exposure to water the tartrate protecting groups hydrolyze to give crosslinked elastomer films.[88-89] It was shown that the origin of crosslinking in the films was boronic acid dimers; crosslinks disappeared in a 1:1 stoichiometric relationship as monofunctional boronic acids were added to the elastomer.[91] However, these films could be disrupted if the aqueous solution also contained competitive ligands for the boronic acid, which include amines and sugars.[92] We therefore reasoned that either the one-step[88-89] physical or covalent modification of sugars by SiBAs could provide a means to (reversibly) control the silicone/saccharide interface (Figure 15); the strength of the interaction should be a consequence of both their concentrations in water and the specific saccharides and boronic acids chosen. The preparation and characterization of SiBA/sugar composite materials is described below.

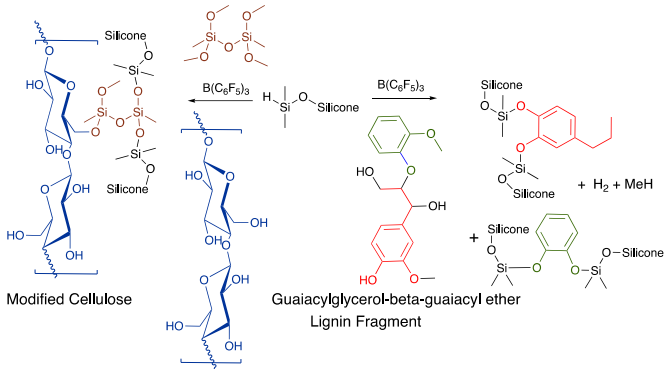

Figure 14. The Piers-Rubinsztajn reaction grafts both saccharides and lignin to silicones.

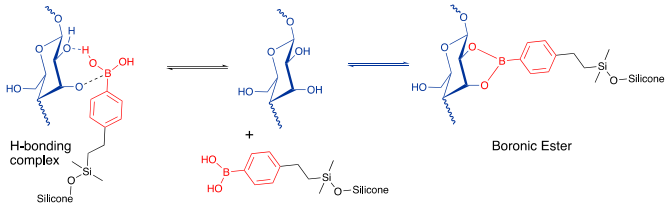

Figure 15: Possible binding motifs for SiBA/saccharides.

Results

SiBAs were prepared by the hydrosilylation of the appropriate SiH-containing silicone oils with tartrate-protected styrylboronic acid (Figure 16). The process occurs in high yield to yield organosoluble polymers with tunable concentrations of boronic acids in a silicone matrix.[37] After the protecting groups were removed by exposure to water – an extremely rapid and efficient process – the strength of the resulting elastomeric films (Young's modulus) was measured as a function of molecular weight of the silicone, and the boronic acid density. The telechelic SiBAs, which possess a lower boronic acid density, exhibited low Young's moduli 15-17 kPa that decreased with increasing silicone molecular weight (Figure 17A, Table 2). The pendant SiBAs exhibited much higher moduli 220-2300 kPa as expected; the crosslink density should ultimately depend on the spacing between boronic acids rather than the overall silicone molecular weight. The modulus of a given SiBA could be tailored simply by mixing starting constituents as shown

in Figure 17B where telechelic silicone SiBA-17 was diluted with the pendant SiBA-P50, which has a higher boronic acid concentration.

An examination of the ability of saccharides to displace boronic acid dimers as a crosslinking mode was undertaken in a of variety ways. Initially, this was expediently done by directly mixing – under high shear – a saturated aqueous solution of the (poly)saccharide into the protected SiBA. Young's moduli were then measured of the resulting silicone elastomers that were doped and crosslinked with saccharides. Survey experiments with different concentrations of sorbitol, a good binder for boronic acids (BA) (K_{eq}=440 M^{-1}),[93] were used to gauge the binding ratios that led to the best crosslinking. The Young's modulus went through a maximum at a 1:2 ratio of [monosaccharide]/[boronic acid unit] (Table 2), suggesting that 2 boronic acids bind to 1 sorbitol to give a crosslink. At low levels of sorbitol, boronic acid dimerization remains the main type of crosslink. With too much sorbitol, on the other hand, each BA is modified by a single saccharide and the (weaker) crosslinking that results is a consequence of the physical separation of the sorbitol in the hydrophobic silicone matrix rather than covalent crosslinking. This mimics the more classic reinforcement of silicones with relatively large mineral structures, except that the saccharide domains are in this case highly hydrated. It is counterintuitive to observe reinforcement of hydrophobic polymer by a water swollen saccharide.

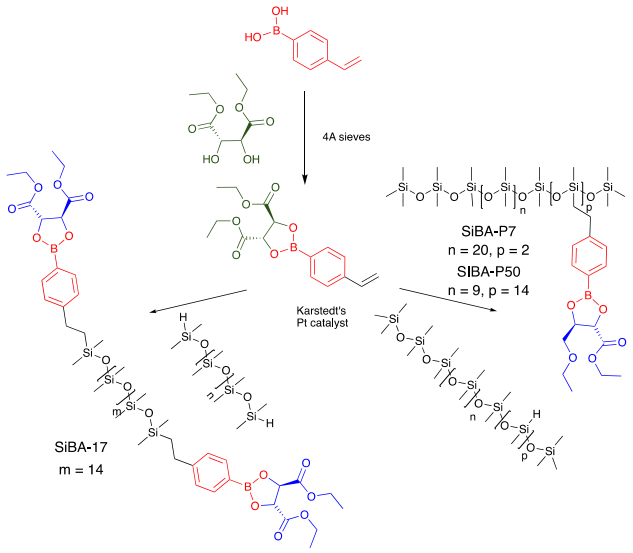

Figure 16: Preparation of SiBAs (two regioisomers form during hydrosilylation, only one of which is shown).

The Young's modulus of silicone/glucose composites at the same concentrations was significantly lower (30-60 kPa, Table 2), consistent both with a weaker binding constant (K_{eq} = 5)[93] and with glucose forming only a single ester with boronic acids and, therefore, not being able to act as a chemical crosslinker.

The ability of a long chain, branched saccharide pullulan (MW 200,000) to act as a crosslinker was also examined. This polysaccharide is surprisingly soluble in water, with saturation concentrations above 30wt%. As it is comprised entirely of glucose monomers (note: the fraction of saccharide units available for binding to BAs is unknown) it is not possible to deconvolute crosslinking due to specific binding interactions from simple phase segregation.

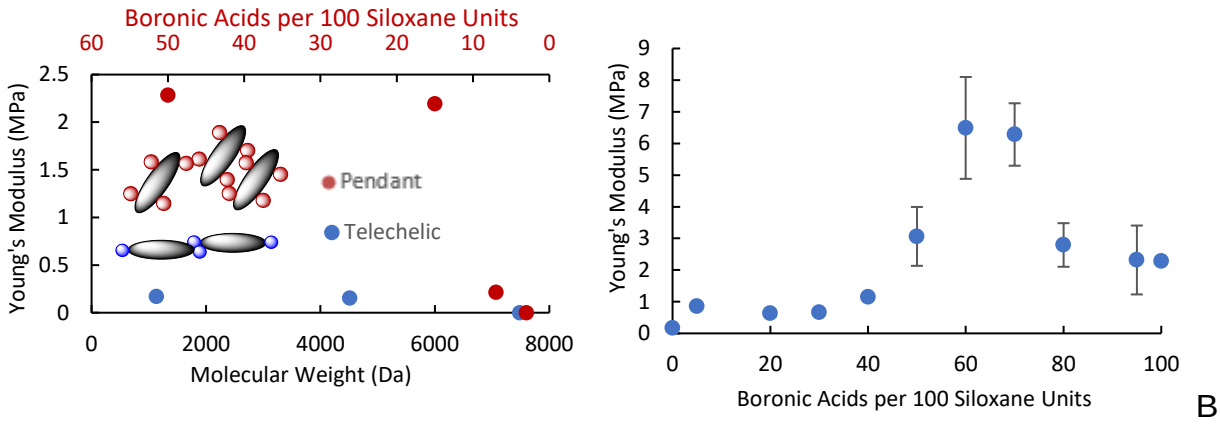

Figure 17 Moduli of Silicone Boronic Acid Elastomers A: homopolymers telechelic SiBA-17 and pendant SiBA-P50, B: mixtures of telechelic SiBA-17 when diluted with pendant SiBA-P7.

A selection of concentrations of pullulan in water was utilized in the attempt to find a concentration where the polysaccharide would best reinforce the silicone. It can be seen that the efficiency of reinforcement was enhanced compared to the boronic acid dimers themselves *at the same water concentration*, indicative of a reinforcement of the silicone by the pullulan (Table 2). However, the reinforcement was not appreciably different from glucose itself.

To further probe the nature of these interactions, SiBA was first mixed with different concentrations of phytoglycogen, a 35nm spherical, monodisperse nanoparticle that swells to 70 nm diameter in water (GlyNP, MW 15 million according to the manufacturer); the silicone saccharide was then dispersed in water at the same concentrations as the elastomers (phytoglycogen+SiBA 500 mg / 1 g H_2O; the ratio of SiBA to GlyNP was varied, using SiBA-17 or SiBA-P7). In the absence of the saccharide, silicone films formed at the air water interface, or formed an elastomeric ball that floated in water. Surprisingly, unlike the elastomers formed co-mixing of silicone/saccharide/water, premixing the saccharide with silicones and then adding water led to stable white pastes of differing viscosity. These were shown, by drying the material and then imaging with SEM, to be coarse emulsions in which the saccharide/silicone interface is stabilized by the boronate/saccharide interaction (ESI‡). By contrast, if any of the phytoglycogen

solutions was mixed with normal silicone oil of any viscosity, immediate gross phase separation occurred (Figure 18).

The rheological properties of these pastes were measured to better understand the nature of the boronic acid/saccharide interactions (Figure 18D). Viscosities of the white pastes increased with boronic acid concentration, but this was a less significant factor than the total quantity of available silicone. At 0.1% strain (shear rate of 0.1 s^{-1}) viscosities for pastes containing telechelic silicone boronic acids ranged between ~9KPa·s-33 kPa·s, whereas those containing pendant silicone boronic acids were slightly higher, ranging from between ~11 KPa·s and 44 KPa·s. A 5% (w/w) addition of either pendant or telechelic SiBA was enough to increase the viscosity above that of a phytoglycogen paste containing no added SiBA.

Table 2: Young's moduli of SiBA-17 saccharide mixtures

Saccharide[a] (mol): Boronic Acid (mol)	Young's Modulus (kPa)
Using Telechelic SiBA-17	
No saccharide, 1 BA/8 Me_2SiO groups	170 ± 18
Sorbitol	
1:4	110 ± 23
1:2	600 ± 51
3:4	350 ± 43
1:1	340 ± 95
Glucose	
1:4	120 ± 51
1:2[c]	70 ± 27
Pullulan	
1:4[d]	140 ± 30
1:2	110 ± 17
3:4	140 ± 60
1:1	110 ± 35

[a] Saccharide concentrations in polysaccharides are based on monosaccharide constituents. In pullulan, only a fraction of the saccharide units in pullulan will be available. [b] The same amount of water as that added with the saccharide solutions. [c] Best ratio based on sorbitol. [d] Pullulan 35 mg: SiBA-17 500 mg. Diluting this solution with water led to weaker composites.

SiBA Binding Affects Phytoglycogen Nanoparticle Diameter: DLS

In dimethylsulfoxide (DMSO) solution, the phytoglycogen nanoparticles used in these experiments have a diameter of about 66 nm; the particles are rather monodisperse; note that commercially available phytoglycogen samples are typically polydisperse.[94] SiBA appear to dissolve in DMSO, but dynamic light scattering (DLS) data shows instead that they form aggregates, with telechelic SiBA-17 forming ~82 nm aggregates, and pendant SiBA-P7 creating larger aggregates ~ 143 nm diameter. These silicone aggregates were not monodisperse and

some very large (micron sized) particles existed prior to the addition of phytoglycogen. It is inferred that adventitious water leads to tartrate deprotection and boronic acid crosslinking.[91]

The ability of the silicone and SiBA to interact was tested by titrating phytoglycogen/DMSO into silicone/DMSO dispersions (Figure 19). Immediately upon addition of phytoglycogen the large SiBA aggregates broke up; the resulting smaller particles shown reflect SiBA-modified phytoglycogen and the presence of much smaller SiBA aggregates. As the phytoglycogen concentration increased, the average particle size increased to slightly larger than that of the native phytoglycogen. We interpret these data to indicate that rapid loss of the SiBA aggregates occurs once a compatible glycogen surface is present (Figure 19A); the silicone becomes grafted to the surface of the GlyNP.

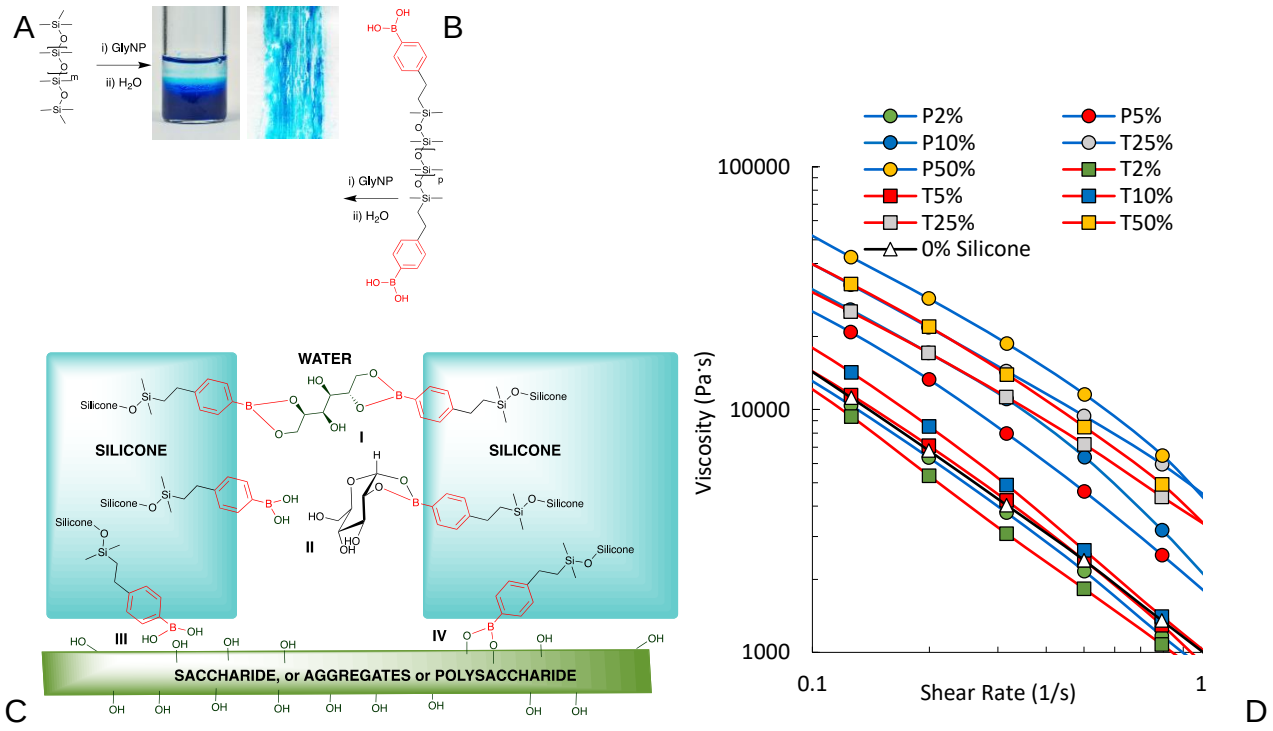

Figure 18. A) Phase separated mixture of PDMS and phytoglycogen-in-water (with blue food color). B) 200 µm thick film cast from paste mixture of SiBA-17 (**1**) and phytoglycogen-in-water. The different color intensities reflect layers of different thickness. C) Cartoon of the interface of an oil-in-water SiBA/saccharide dispersion. D) Viscosity of silicone-phytoglycogen pastes changes with relative silicone and phytoglycogen concentrations.

Discussion

Boronic acids reversibly form boronic esters with diols, of which saccharides are emblematic as a class (Figure 15).[95] The equilibrium constant for ester formation is very sensitive to structure, particular of the diol. As noted above, the binding equilibrium constant for the monosaccharide sorbitol is two orders of magnitude larger than that for glucose. Other factors also influence the location of the equilibrium, including higher pH and the presence of Lewis base ligands for boron, both of which favor the ester side of the equation. Dilution with water will also move the equilibrium towards starting materials.

In the absence of ligands for the boronic acids, including saccharides, SiBA formed dimeric structures that crosslink the silicones (note that secondary crosslinking arises from Lewis acid/base interactions between boron and oxygen atoms on the silicone backbone).[92] The higher the boronic acid and therefore crosslink density – the shorter the distance between crosslink sites – the higher the modulus (Figure 17A). More robust elastomers arose from pendant functional silicones that can generate more crosslinks per unit volume. It is possible to tune the modulus simply by mixing structurally different boronic acids (e.g., pendant + telechelic) to tune the crosslink density and adding sufficient water to deprotect the tartrates (Figure 17B).

If the SiBA was wet with aqueous saccharide solutions a product elastomer rapidly formed that was phase separated from water. Here, the nature of the saccharide played an important role in the physical properties of the elastomer. In the case of sorbitol, the outcome is consistent with insertion of the sorbitol into the boronic acid dimer to give a new type of covalent, bifunctional crosslinker sorbitol. The strongest elastomers formed at the optimal 2:1 ratio of sorbitol:boronic acid (Figure 18C I). At higher concentrations of sorbitol, or in the case of saccharides that have poorer binding constants, or possibly have difficulty in achieving a proper geometry to bind more

than once,[96] the less effective crosslinking likely arises through physical interactions with individual polysaccharides or aggregates of (poly)saccharides (Figure 18C II). The strength of the latter interaction was weaker than the former, at least at an optimal stoichiometric balance (Table 2). At lower saccharide concentrations, the net crosslinking can be ascribed to a composite of boronic acid dimers and boronic acid/saccharide complexes.

These observations support the conclusion that the stabilization of the silicone/water interface requires saccharides to be present in the aqueous phase (Figure 18C). The strength of that interaction depends on the concentration of sugars in water, the number of available boronic acid sites/number of available saccharides and, in some cases, the binding equilibrium constant. It is not possible to tease out the relative impact of each of these. Although the Young's moduli were lower in the presence of saccharides with low binding constants, it nevertheless demonstrates that the saccharides remain bound to the SiBA. There is a statistical advantage here. Even though the boronic acid/sugar interactions are equilibria, multiple contact points on the saccharides favor net binding; there will always be a sufficient population of bound sugars such that the SiBA are not released from the sugars. That is, the fact that water rich silicone elastomers are stable demonstrates it is the boronic acid that stabilizes the silicone at the water interface. This is even more evident with the pastes (see below).

When 'dry' SiBA was exposed to a dry saccharide in the absence of water, and then water was added in a subsequent step, stable oil-in-water dispersions were formed as pastes. The viscosities of the pastes were directly related to the relative quantities of silicone/saccharide; the density of boronic acid groups was less important (Figure 18B,D). The binding constant of boronic acids for glucose or glucose-based polymers is relatively low. Thus, it is expected that the interaction between silicone and (poly)saccharide in this case is physical, although it is not possible to discount boronate esters in equilibrium with such structures (Figure 18C III vs IV).

Irrespective, the binding reflects an equilibrium; the pastes were stable over weeks (so far). We infer that the build in viscosity is associated with silicone domains on adjacent saccharide surfaces that associate through a hydrophobic effect to reduce the exposure of silicone to water (Figure 19).[97] The more silicone on saccharides, the 'stickier' will be the particles to each other in water. This hypothesis is supported by the solution studies in DMSO, which show competitive binding of SiBA to a saccharide surface, when compared to the formation of a separate silicone phase.

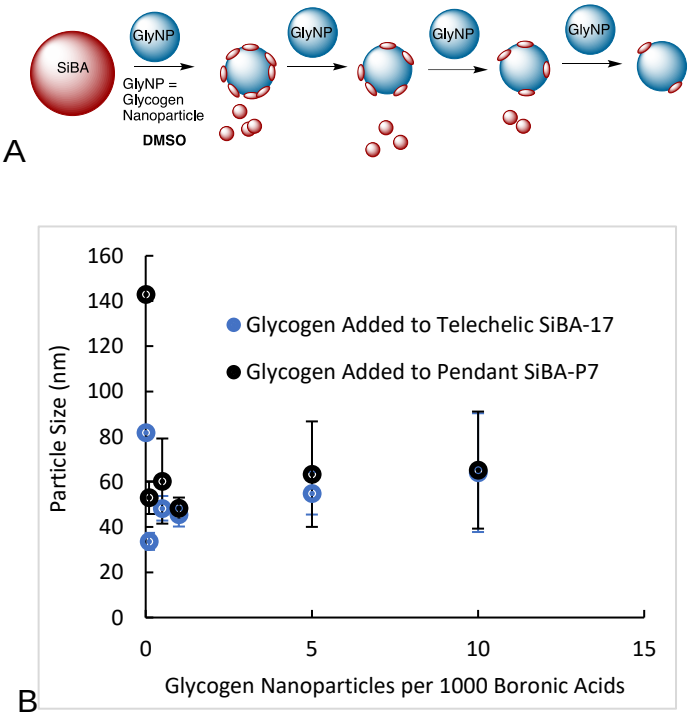

Figure 19. A: Cartoon showing breakup of SiBA aggregates and subsequent adsorption onto GlyNP. B: Particle diameter upon titration of SiBA with GlyNP in DMSO.

Dimethylsilicones have little affinity for water. The solubility of the most soluble silicone materials D_4 $(Me_2SiO)_4$ is about 50 ppb (literature reports range from ~20 - 900 µg /L H_2O); higher molecular weight materials are less soluble. The presence of a sugar in the aqueous phase does nothing to change this (Figure 18A). However, boronic acid anchor groups can be

used to link silicones to saccharides. If this is done in the absence of water pastes are produced, while if done in the presence of water, sugar-crosslinked, phase separated elastomers are formed. That is, while specific sugar/SiBA interaction will be similar in both cases, the efficiency with which they are established depends on the availability of silicone-phobic water during synthesis. Irrespective of the mode of synthesis, it is possible to choose how those interactions lead to the formation of a given material.

In recent years, there has been some pushback against silicones, particularly in the cosmetics industry, because they are 'not green.' As noted above, that is not correct from a degradation point of view, but the degree to which silicones are 'green' is challenged by their energy input cost. They possess very interesting properties that are not matched by organic materials and they fulfill many needs in developed economies. The study here shows that useful silicone-based materials, with enhanced interfacial properties, may be prepared by taking advantage of readily available (poly)saccharides that can be loaded at levels up to 50 wt%. The properties of the resulting products are readily tuned by the nature of the SiBA and, more importantly, the saccharide. In the latter case, factors including molecular weight and particularly nature of the saccharide and its binding constant with the boronic acid can affect the nature of the product. The use of boronic acids provides a mechanism to control the properties of silicones by doping them with saccharides, thereby improving the environmental profile of silicones.

Experimental

Materials

Sorbitol (VWR), glucose (BDH), pullulan (Hayashibara Company), phytoglycogen nanoparticles (PhytoSpherix, Mirexus Biotechnologies) and DMSO (Caledon Laboratories Ltd., anhydrous) were used as received. Synthesis of silicone boronate dimethyl tartrate esters followed literature procedures.[37] Distilled water was used throughout.

Methods

Young's Modulus Measurement: Modulus data was collected within 96-well plates using a MACH-1 micromechanical testing instrument equipped with a 0.5mm hemispherical indenter using a Poisson ratio of 0.3, 24 h after elastomer formation.

Rheometry: The viscosity of the pastes were measured using a TA instruments Discovery HR-3 Hybrid Rheometer equipped with a 40mm parallel Peltier steel plate geometry. Trios software (TA instruments) was used for data acquisition. The first experiment was to find the linear viscoelastic zone by strain-sweep testing between 0.1%-100% strain. Angular frequency was set at 10 rad s^{-1}. The strain for the linear region was used in subsequent frequency-sweep experiments. Frequency-sweep measurements were performed at a frequency range between 0.05 s^{-1} to 10.0 s^{-1}. All experiments were performed at 25 °C.

DLS: Phytoglycogen nanoparticle size was characterized using a Malvern Zetasizer Nano dynamic light scattering unit at 25 °C.

Elastomer Formation

General procedure for preparing silicone boronic acid elastomers by immersion in H_2O followed by agitation, No Saccharide: SiBA (500 mg) was weighed into a 2 dram glass vial to which distilled H_2O (1 mL) was added. The solution was agitated for one minute using a vortex mixer. The resulting elastomers, which formed a 'puck' on the base of the vial were transferred to a 96-well plate using a spatula.

General procedure for preparing silicone boronic acid elastomers by immersion in H_2O followed by agitation, Mixtures of Pendant and Telechelic SiBAs (shown for 1:1 telechelic SiBA-17: SiBA-P7): SiBA-17 (500 mg) and SiBA-P7 (500 mg) weighed into a 2 dram vial; the mixture was agitated for one minute using a vortex mixer. Distilled H_2O (1 mL) was added to the solution

which then agitated again for one minute using a vortex mixer. The resulting elastomer was transferred to a 96-well plate using a spatula and allowed to cure overnight.

General procedure for preparing silicone boronic acid elastomers by immersion in H_2O followed by agitation, Saccharide Reinforced Elastomers: 1M solutions of sorbitol and glucose were prepared by adding sorbitol (182 mg, 1 mmol) or glucose (180 mg, 1 mmol), respectively ,to a 2dram glass vial; distilled H_2O (1 mL) was then added to each using an Eppendorf pipette and the solution was sonicated for 1 min to ensure complete dissolution. Solutions of pullulan (1,016 mg, MW ~ 1,811,800, 56 nmol in distilled H_2O mL, converts to ~ 5.7 mmol glucose equiv.). Elastomers were formed by adding the appropriate SiBA (500 mg, 0.139 mmol) and saccharide solution/H_2O (70 µL-350 µL, 0.07 mmol-0.35 mmol) to a polypropylene mixing cup (Flaktek, size 10). The mixture was then mixed under high shear at 3000 rpm for 2 min using a Flaktek Speedmixer (model: DAC 150.1 FVZ-K). The resulting elastomer was transferred to a 96-well plate using a spatula.

Stoichiometric Saccharide Addition

500mg (0.139mmol) SiBA-17 was added to a speed mixing polypropylene cup for all experiments. 0.5mol, 1mol, 1.5mol, 2mol, and 2.5mol equivalents of saccharide were added per boronic acid by pipetting 69.9 µL (0.0699 mmol), 139.9 µL (0.139mmol), 209.8 µL (0.2098 mmol), 279.8 µL (0.2798 mmol), 349.7 µL (0.3497 mmol) of saccharide solution, respectively, into Flaktek mixing cups. The SiBA-17-saccharide solutions were then mixed at 3000rpm for 2 min using a Flaktek Speedmixer (model: DAC 150.1 FVZ-K). The resulting elastomers were transferred to a polypropylene 96-well plate using a spatula and allowed to cure (a few minutes).

Paste formation and rheology

Pastes were prepared by combining silicone and phytoglycogen in a 2-dram vial. The relative amounts of silicone and phytoglycogen were varied to create a suite of formulations by adding 5 mg, 10 mg, 25 mg, 50 mg, 125 mg, and 250 mg of SiBA-17, respectively, to separate vials then adding enough phytoglycogen to each vial to give a total of 500mg (**Error! Reference source not found.**); a control formulation consisting solely of phytoglycogen and H_2O was also made. Distilled H_2O (1 g) was then added to each vial and the dispersion was mixed using a vortex mixer for 2 min. Films (200 µm thick) of these pastes were cast onto Teflon sheets using a stainless-steel film applicator (Elcometer 3540).

DLS characterization of GlyNP/SiBA solutions

Phytoglycogen solutions (1wt%) were prepared by weighing 1g phytoglycogen in a 10 mL volumetric flask, dissolving in dimethylsulfoxide (DMSO), and the performing a serial dilution in DMSO. SiBA-17 (0.58 mM) and SiBA-P7 (0.55 mM) solutions were prepared by weighing 100 mg of the silicone and diluting into DMSO (10 mL, followed by 2 serial dilutions). All solutions were prepared immediately prior to measurement. Particle sizes were collected for each of these solutions; 7 sequential scans were run in triplicate. Varying amounts of phytoglycogen solution (0.1:1000, 0.5:1000, 1:1000, 5:1000, 10:1000 phytoglycogen:boronic acid) were added to 10mL of pendant silicone boronic acid solutions and telechelic silicone boronic acid solutions respectively. The particle sizes of these solutions were collected for each of these solutions; 7 sequential scans were run in triplicate. The opposite addition sequence was performed by starting with 10 mL solutions of phytoglycogen and adding varying amounts of pendant silicone boronic acid solution and telechelic silicone boronic acid solution respectively (0.1:1000, 0.5:1000, 1:1000, 5:1000, 10:1000 phytoglycogen:boronic acid). All solutions made were mixed for two minutes using a vortex mixer prior to particle size measurement.

Conclusions

Boronic acids, while bound to silicone polymers, maintain their ability to bind saccharides. Effective boronic acid dimerization provides one mechanism of crosslinking, which is supplemented by boronic acid-saccharide complexation or boronate ester formation. Although the binding constant with glucose units is low, polysaccharides based on glucose lead to reinforced silicones or, depending on relative concentration, reinforced phytoglycogen materials because of statistical efficiency of holding more than zero linkage between the two materials at any given time. Even under the stress of higher water concentration, it is difficult to separate the two materials. As a consequence, depending on volume ratio, the copolymers behave as hydrophobically modified natural materials or natural material-reinforced silicone elastomers.

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Chapter 3: Saccharide-on-Silicone Elastomer Surfaces Using Boronates

Benjamin Macphail, Emil Gustafsson, Robert H. Pelton and Michael A. Brook

Abstract

Boronic acids effectively bind to sugars. This principle was used to prepare saccharide-modified silicone elastomer surfaces. Silicone boronic acids (SiBA) with and without permanent (non-hydrolyzable) links were prepared by hydrosilyation of a tartrate-protected styrylboronate. Hydrolysis led to free boronic acids at the interface to which the saccharides sorbitol, pullulan, casein and phytoglycogen, and the glycosylated protein, mucin, were shown to chemisorb. Surface active proteins like albumin and casein adsorbed on such surfaces too, but only on the SiBA surfaces would (poly)saccharides and the glycosylated proteins adsorb; casein was an exception. Once adhered, it was not possible to exchange polysaccharides like phytoglycogen from the surface, even when using a monosaccharide with a better binding constant to boronic acid, such as sorbitol.

Introduction

Saccharidic materials constitute the largest volume material products produced by nature. Subtle differences in structures lead to enormous differences in bioreactivity, as can be seen by the simple comparison of cellulose, which cannot be digested by humans, with starch, which can. Nature utilizes saccharides in a variety of other important roles including at interfaces, to control physical properties and physiological function. For example, antigens that differentiate blood types are oligosaccharides[98], the shear thinning properties of hyaluronic acids are used to lubricate movement at joints.[99]

One important subset of saccharidic materials involves glycosylated proteins, which have special interfacial properties. Such materials can be 'protective' by acting as a barrier, for example, in the mucosal immune system. Their interfacial role is particularly exemplified by mucin, a lubricious protein that sits on the cornea and facilitates movement of the eyelid over the cornea.[100]

Silicone elastomers have found utility as both topical and implanted devices. In topical applications, the high hydrophobicity of silicones[79] can be both beneficial and detrimental. In wound dressings,[101] the hydrophobic interface decreases the adhesion of a healing wound to the dressing, facilitating its removal. However, such hydrophobic characteristics are less welcome in other applications. Silicone catheters are widely used, but are subject to fouling by a variety of species, including proteins, as a consequence of the characteristics, including hydrophobicity, of the silicone elastomer interface.[102] In the eye,

lipid uptake into silicone hydrogel lenses[103] has been associated with discomfort and, in some cases, with disease.[104-105]

We reasoned that benefit could accrue from combining silicones with saccharides, particularly in biomaterials applications, due either to inexplicit benefits of increased hydrophilicity or explicit benefits provided by the biological activity of the saccharide. The limited number of examples of silicone/saccharide composites (e.g., silicone-on-cellulose release papers) is associated with the challenge associated with the enormous difference of surface energies between the two classes of materials; saccharides are highly hydrophilic, while silicones have surface energies near 20 mN m^{-1}.[106]

How does one overcome the 'oil/water' problem to permit saccharides to bind to the silicone, a material that is water repellent? It is very challenging to find a common solvent for the two species.[107] One approach has utilized the protection of hydroxyl groups in monosaccharides so that silicone surfactants could be prepared in organic solvents, with the hydroxyl groups being liberated later.[108-111] Silicon-based protecting groups, commonly used in organic synthesis,[112] can aid in this type of synthetic approach.[113] Increased efficiency, however, should result from avoiding protection/deprotection sequences. Linking of siloxane compounds to various saccharides can be accomplished without the need for protecting groups (Figure 20) by ring opening of sugar lactones, formed at the reducing end of mono- or polysaccharides.[114] Another reaction that lends itself to this approach is the click reaction, in which the azide-modified silicone phase is dispersed in an aqueous solution of alkyne-modified sugar.[115] The high mobility of even

high molecular weight silicones allows efficient reaction at the siloxane/water interface leading to surface active silicone saccharides.

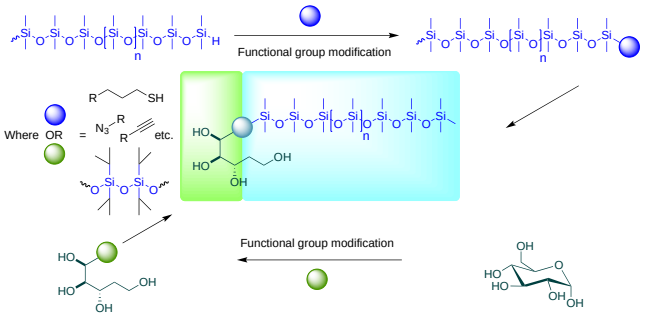

Figure 20. Generic scheme for modification of silicone and saccharidic materials for mitigation of phase separation.

We have previously shown that silicone boronic acids (SiBA) exhibited unusual self-adhesive properties at the air/water interface via boronic acid dimers; these could be interrupted by the presence of binding agents found in an aqueous subphase. Since boronic acids are well known to bind to saccharides,[95, 116] we wondered if such interactions could be similarly used to manipulate surface characteristics, including hydrophobicity, of a silicone elastomer interface. The efficient chemisorption of saccharides, including glycosylated proteins, from aqueous solutions onto two types of silicone boronate elastomers is reported.

Experimental

Materials

Sorbitol (VWR), glucose (BDH), pullulan (200kDa, Hayashibara Company), phytoglycogen nanoparticles (PhytoSpherix, Mirexus Biotechnologies), human serum albumin (Sigma Aldrich), mucin from bovine submaxillary gland, type 1-S (Sigma Aldrich), lysozyme from chicken egg white (Sigma Aldrich), casein from bovine milk (Sigma Aldrich), fluorescein isothiocyanate (Sigma Aldrich), DTAF (5-(4,6-dichlorotriazinyl)

aminofluorescein), single isomer (Sigma Aldrich) (25-35% hydromethylsiloxane)-dimethylsiloxane copolymer, trimethylsilyl-terminated (25-35 cSt, MW =5905 g mol^{-1} HMS-301) (Gelest), vinyl-terminated polydimethylsiloxanes (100 cSt, 8325 g mol^{-1} DMS-V21) (Gelest) dimethyl-L-tartrate (Sigma Aldrich), 4-vinylphenylboronic acid (Sigma Aldrich), Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, ~2% Pt, Sigma Aldrich), NaOH (EMD), $NaHCO_3$ (EMD), DMF (Caledon Laboratories Ltd., anhydrous), DMSO (Caledon Laboratories Ltd., anhydrous) and Membra cel dialysis membranes (membra-cel dialysis tubing md25-14, MWCO 3500) were used as received. QCM sensors (Q-sense QSX 303 SiO_2) were used as received. THF (Caledon Laboratories Ltd., anhydrous) and toluene (Caledon Laboratories Ltd., anhydrous) were dried over a column of alumina. Synthesis of silicone boronate dimethyl tartrate esters **SiBA-17** (**1**) and **SiBA-P50** (**2**) followed literature procedures.[37] Deionized water was used throughout unless specified otherwise.

Methods

Spin coating of silicone boronate elastomers on substrates, including QCM sensors, was accomplished using a SCS G3-8 Spincoat system (Specialty Coating Systems, Inc. Indianapolis, IN).

Young's moduli were measured using a MACH-1 micromechanical system instrument equipped with a 0.500 mm hemispherical indenter radius, using a Poisson ratio of 0.3.

A Biolin Scientific Q-Sense E4 Auto quartz crystal microbalance with dissipation was used to measure biomolecule adsorption from aqueous solutions onto silicone boronate, spin-coated surfaces. A steady resonant frequency was recorded while Millipore 18.2 MΩ·cm H2O was injected at 0.2 □L/minute over the sensors. Solutions of biomolecules

(sorbitol, glucose, phytoglycogen, HSA, lysozyme, and mucin) prepared in Millipore 18.2 MΩ·cm H_2O (0.2 g/L) were then injected at 0.2 µL/minute and allowed to pass across silicone boronic acid hydrosilylation cure coated QCM sensors for until frequency stabilized (between 20 and 40 minutes). The change in resonant frequency and dissipation was then recorded at the third overtone.

Optical images were obtained with a Nikon Eclipse LV100N POL epifluorescence microscope (Nikon Instruments, Mississauga, ON, Canada), equipped with a CFI TU Plan Fluor EPI 60X physiological objective. An excitation and emission filter for FITC 495 was used. The elastomer films were visualized using a Retiga 2000R cooled CCD camera (Q Imaging, Surrey, BC, Canada) and images were captured using NIS-Elements AR software (Nikon Instruments, Mississauga, ON, Canada.

Sessile drop contact angles of silicone films were measured using a Future Digital Scientific OCA 20 goniometer. A 5 µL drop volume of Milli-Q H_2O (18M Ω/cm) was used. Measurements were taken 3 min after drops were dispensed.

Permanently Crosslinked Silicone Boronates

General Procedure for preparing platinum cure silicone boronic acid elastomers shown for the elastomer composed of 50% boronic acid crosslinks and 50% silicone crosslinks. Formulations for all elastomers are provided in Table S1 (Supporting Information):

Bulk platinum cure silicone boronic acid elastomers were prepared in 48-well plates. HMS-301 (0.10 g, 0.17 mmol), DMS-V21 (0.74 g, 0.088 mmol) and tartrate-protected vinylphenylboronic acid (52 mg, 0.17 mmol) were combined in anhydrous toluene (20 mL). Karstedt's catalyst (0.78 mol%, 2.1 µmol), was added to the mixture and then the

materials were immediately mixed using a vortex mixer for 10 s. Young's moduli were measured after curing for 24 h. Wet strength moduli were measured after soaking cured elastomers in deionized H_2O (10 mL) for an additional 24 h. Separate cured elastomers were mixed under high shear for two min at 2500 rpm in triethylamine solution (0.1M, 10mL, see Supporting Information). These elastomers soaked for 24 h before their moduli were measured. (Figure 21, Table S2).

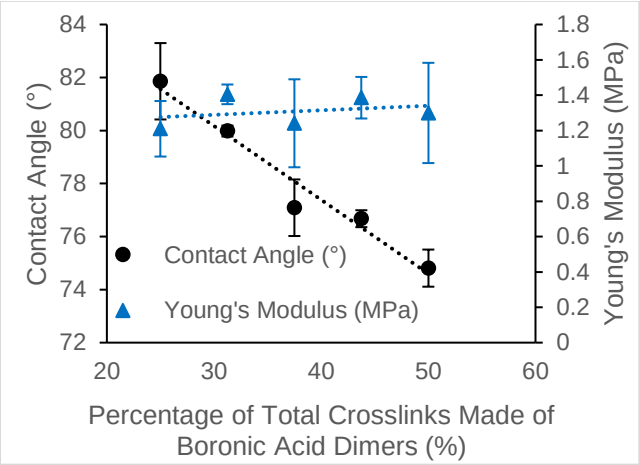

Figure 21. Physical properties of silicone boronic acid elastomers as a function of varying crosslink type.

Spin coating

The process was repeated to make thin coatings. HMS-301 (0.10 g, 0.17 mmol), DMS-V21 (0.74 g, 0.088 mmol) and tartrate-protected vinylphenylboronic acid (52 mg, 0.17 mmol) were combined in anhydrous toluene (20 mL). Karstedt's catalyst (0.78 mol%, 2.1 µmol), was added to the mixture and then immediately mixed using a vortex mixer for 10 s. This mixture (1 mL) was then spincast onto QCM sensors at 3500 rpm over 5 min to give a coating of ~ 900 nm thickness.

Fluorescent labeling

Saccharides were tagged with fluorophores using either fluorescein isothiocyanate or 5-(4,6-dichlorotriazinyl) aminofluorescein (DTAF).

Sorbitol and phytoglycogen

Sorbitol (5.2 mg, 28.5 µmol) was added to a cleaned and dried 10 mL round-bottomed flask equipped with a magnetic stir bar and containing deionized H_2O (5 mL). DTAF (3.8 mg, 7.7 µmol) was then added to the reaction flask along with NaOH (1 mL of 0.1 M); upon addition of NaOH the solution changed from colorless to bright yellow. After 24 h, the reaction mixed was concentrated in vacuo then purified using column chromatography with 1:1 THF:toluene as eluent. The final product when purified was an orange powder (yellow when solvated by H_2O). Yield: 90% (4.7 mg).

This experiment was repeated with phytoglycogen (4.2 mg, 0.28 nmol (23 □mol based on glucose monomer equiv.)) and DTAF (11.5 mg, 23 □mol); the reaction mixture was purified by dialysis. The reaction mixture was pipetted into a dialysis membrane (MWCO = 3500) and dialyzed against deionized H_2O for 3 h. The dialysate was refreshed and the mixture was further purified for an additional 3 h. This was repeated thrice. Yield: 85% (9.1 mg).

Casein, human serum albumin (HSA) and mucin from bovine submaxillary gland

Solutions of protein were prepared by dissolving casein (22.4 mg, 0.9 µmol), HSA (21.2 mg, 0.3 µmol), or mucin (24.8 mg, 15.5 nmol), respectively, in 0.1M $NaHCO_3$ (1 mL) in a 10 mL round-bottomed flask equipped with a magnetic stir bar. FITC (0.1 g, 0.2 mmol) was added to a separate 25mL round-bottomed flask and dissolved in anhydrous DMF (10 mL). An FITC solution (100 µL, 0.8mmol) was added to each protein-containing flask. The reactions were then stirred for 1 h at room temperature at which point

hydroxylamine (the 0.1mL, 1.5 M, 0.15 mmol) was added. The reaction mixtures were then individually purified by dialysis using the method for phytoglycogen.

Elastomer films

Casting spread and set cure silicone boronate films onto glass cover slips

A glass microscope cover slip (22mm x 22mm) was placed near the apex into a conical glass funnel ($9.5cm_{diameter}$, $7.5cm_{depth}$) that was plugged at the base with a rubber septum (see Supporting Information). The funnel was then filled with 100 mL deionized water ensuring the cover slip was completely submerged. **SiBA-17** (**1**, **2**) (10 µL, 4.0 µmol) was added to the funnel using a micropipette. A **SiBA** film immediately formed (5 µm calculated thickness). The septum was then removed 1 min after film casting to allow the water to drain and deposit the SiBA film onto the surface of the cover slip. Coating thicknesses were measured using VSI mode on a WYKO NT1100 optical profiling system.

Saccharide/Protein coating SiBA (**1**, **2**) surfaces

Purified fluorophore tagged saccharides/proteins (0.27mM, pH 7.8) were dropcast onto silicone boronic acid (hydrolysis-cured) elastomer films mounted on glass cover slips (22 mm x 22 mm). The mounted films were then placed in an oven for 12 h at 55 °C to evaporate solvents; unbound materials were washed from the surface by submerging the cover slip in H_2O and stirring with a magnetic stir bar for 5 min. The film was allowed to dry for 24 h at 55 °C, at which point the material was observed under fluorescence microscopy; contact angles were measured (Figure 23).

Results

Silicone preparation

Silicone boronate fluids have previously been prepared by the hydrosilylation of tartrate-protected styrylboronic acid (Figure 22).[37, 91-92, 117] Once hydrolyzed, they rapidly crosslink to give silicone elastomers from **1**, and **2**, the properties of which depended on crosslink density that, in turn, depended on the weight fraction of boronic acids in the matrix. As will be discussed below, these crosslinks, which arise from boronic acid dimerization, can be disrupted by addition of ligands that bind to the boron or to B-OH groups.

Silicone elastomers with permanent crosslinks, and boronic acid moieties, could be prepared in an analogous manner. In this case, hydrosilylation of an H-Si pendant polymer was simultaneously performed with two different types of vinyl groups: telechelic vinylsilicones Vi-PDMS-Vi and the protected boronate (Figure 22). Provided the SiH/SiVi stoichiometry was kept near 1:1, it was simple make a series of elastomers **3** that varied in permanent crosslink density *and* boronic acid content. The percentage of those crosslinks composed of boronic acid dimers is designated in brackets (e.g., **3-(50)**).

The physical properties of the permanently crosslinked elastomers, before hydrolysis, depended on the chain length between crosslinks, which was determined by the value of n in $ViMe_2Si(OSiMe_2)_nOSiMe_2Vi$ and the spacing and number of SiH groups that were modified on the starting material backbone. Hydrolysis of either type of silicone boronate (Figure 22), which deprotected the tartrate protecting groups, liberated boronic acids that were then able to self-crosslink. This was confirmed by the measurement of Young's moduli before and after hydrolysis and after exposure to trimethylamine; as is discussed below, the presence of a Lewis base converts the boron to a 4-coordinate species which is more stable than its 3-coordinate analogue.[44] It was therefore possible to prepare a

library of silicone elastomers that varied broadly in their physical properties. Some of these materials were prepared only as a thin film (see below), but the process was also amenable to bulk synthesis, as shown for several examples (see also Supporting Information).

Preparation of Surfaces - Spin coating

Elastomer surfaces in which the crosslinks were only provided by boronic acids were prepared by casting a film of **SiBA** (telechelic **SiBA-17** (**1**) or pendant **SiBA-P50** (**2**)) onto a water/air interface (Supporting Information). Permanently crosslinked films were prepared by spincoating a mixture of the pre-cured constituents of **3** onto a silica QCM (quartz crystal microbalance) sensor and allowing cure to take place over room temperature for 24 hours. The cure fully manifests once protected boronic acids were liberated, simply by soaking the film in water for 24 hours.

Surface behavior - Binding of biomolecules

Wetting

The surface energies of the silicone boronates **1**, **2** were compared with a pure silicone elastomer using sessile drop contact angle measurements (Figure 23). It can be clearly seen that the presence of free B-OH groups on the surface were shown by a decrease in

contact angle from 110° to about 75°. An increase in the boronic acid concentration in the elastomer led to an increase in the water wettability of the surface.

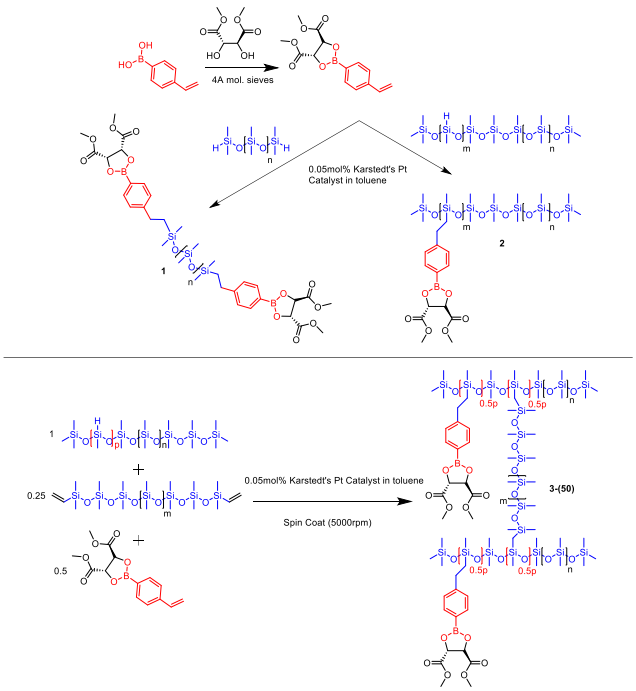

Figure 22: Preparation of silicone boronic acid elastomers consisting of 100% boronic acid dimer crosslinks (**1** (telechelic) and **2** (pendant)) and ratios of both boronic acid dimer and silicone crosslinks (**3**-(%boronic acid dimer crosslinks)).

The exposure of biomolecules to silicone boronate interfaces led to changes in surface wettability. Control experiments were first used determined the interfacial behavior of simple silicone elastomers. Sugars (sorbitol, glycogen) and the hard, highly charged protein lysozyme adsorbed ineffectively, at best, to Sylgard 184 elastomer; there was little change in contact angles from the parent silicone. By contrast, HSA and, to a lesser degree, casein adsorbed on the surface, as shown by the reduction in sessile drop contact angles (Figure 23). These proteins are known to efficiently adsorb to hydrophobic substrates (see below).[118-120]

Silicone boronic acid elastomers showed very different affinities to the same sugar-containing biomolecules, as judged by contact angle; the non-glycosylated protein

lysozyme didn't bind at all. The surface of the crosslinked telechelic silicone boronic acid, **SiBA-17 1**, became more wettable when treated with saccharidic solutions, including sorbitol and casein, but not glycogen; HSA also bound to the surface (Figure 23). Elastomers with higher concentrations of boronic acid groups derived from pendant **SiBA-P50 2** showed analogous behavior but generally with more efficient biomolecule binding. These data suggest that binding affinity is affected by the boronic acid concentration and also by the structural motif and size of the (poly)saccharide units. Both surfaces **1** and **2** were modified by sorbitol but the much larger saccharide phytoglycogen nanoparticles (15 million Da according to the manufacturer) was only able to effectively bind when higher concentration of boronic acids presented at the interface.

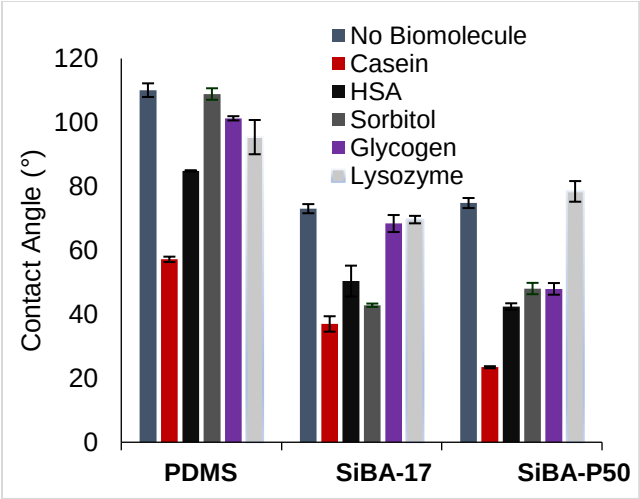

Figure 23. Sessile water drop contact angles of silicone coated glass cover slips after treatment with saccharide solutions for both SiBA-17 and SiBA-P50 as determined by contact angle.

Fluorescence

The magnitude of binding of biomolecules was additionally demonstrated qualitatively using fluorescence measurements. A suite of saccharides comprising monosaccharides, polysaccharides, and proteins with varying degrees of glycosylation, including sorbitol, pullulan, phytoglycogen, human serum albumin, casein, and mucin from bovine

submaxillary gland, were tagged with fluorescein groups (Figure S2). Solutions of these fluorophore-tagged saccharides/proteins were placed onto **SiBA** (**1**)-coated cover slips or a pure PDMS elastomer, respectively (Figure S2b). Saccharide binding (after unbound material had been rinsed away) after exposure for 12 hours was observed using fluorescence microscopy (Figure 24). (Poly)saccharides and glycosylated proteins effectively bound to **1** surfaces (Figure 24B), but not to simple silicone elastomers (Figure 24A). HSA bound to both types of silicone surfaces (Figure 24A-5B).

QCM

The magnitude of binding of various biomolecules to **SiBA** (**3 – 50%** of the crosslinks proviced by Si-C linkages and 50% by BA-BA dimers) surfaces, spin coated onto commercial silica sensors, was determined using a quartz crystal microbalance (QCM). Saccharidic or protein solutions were allowed to flow over the sensor and binding was followed by monitoring sensor frequency at the third overtone of oscillation. The mass of

different saccharidic materials bound to the surface of **3-(50)** coated sensors was calculated using the Sauerbrey equation (Equation S1).

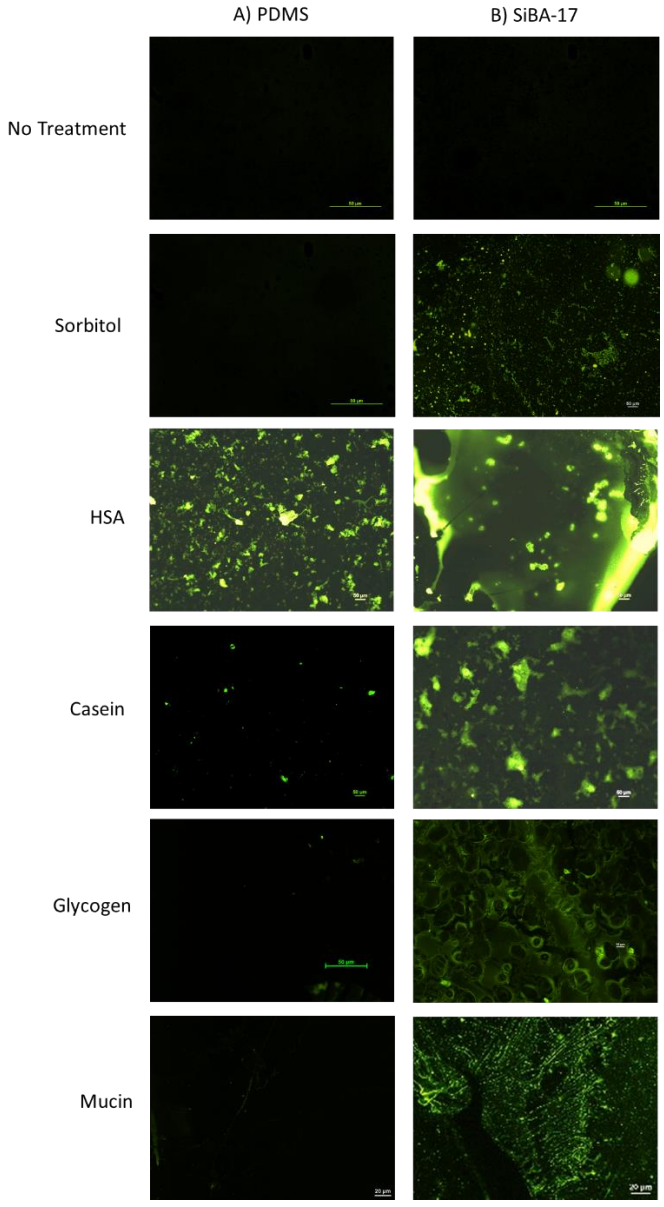

Figure 24. Fluorescence microscopy images of saccharide-treated PDMS elastomers (A) and saccharide treated SiBA (**1**) coated cover slips (B).

A hydrophobic silicone elastomer without boronic acids was sequentially exposed to sorbitol, pullulan, glycogen and finally HSA. As with the wetting and fluorescence experiments, no binding was observed to the non-functional silicone surface, with the

exception of HSA, which is promiscuous with respect to binding (Supporting Information).[121] By contrast, sorbitol, pullulan, phytoglycogen, and mucin all bound very effectively to the SiBA surface, in values ranging between 0.1 and 0.2 mg/cm^2; HSA also bound to these boronic acid-modified surfaces, but at lower levels than saccharidic species (Table 3).

Reversibility of binding

It was anticipated, based on their relative binding constants,[93] that the better binder, sorbitol, would be able to 'bump" more poorly bound, glucose-based polymers, such as phytoglycogen, from the **SiBA** surface. To test this, a sorbitol solution was allowed to flow over a pre-bound phytoglycogen/**3-(50)** surface. No change in the surface mass was observed over 20 minutes.

Table 3. Adsorption of saccharides and proteins onto SiBA-coated and PDMS-coated QCM sensors.

	SiBA 1		PDMS	
Biomolecule Solution	Adsorbed Mass (μg)[a]	mol cm^{-2}	Adsorbed Mass (μg)	mol cm^{-2}
Sorbitol	0.0210	1.15x10^{-10}	None	None
Pullulan	0.1627	8.98x10^{-14}	None	None
Phytoglycogen	0.2120	1.41x10^{-14}	None	None
HSA	0.08904	1.34x10^{-12}	0.72706	1.09x10^{-11}
Mucin	0.1447	3.62x10^{-14}	None	None

[a] Sauerbrey Mass (see SI).

Discussion

Boronic acids reversibly bind to diols – a process that is the basis of a variety of analytical techniques beautifully reviewed by Wu et al.[93, 96] (Figure 25). The degree of binding, as determined by an equilibrium binding constant, is highly dependent on the structure of the diol, and is enhanced by conversion of boron from 3 to 4 coordinate[44]. For

example, the subtly different compounds glucose and sorbitol have very different equilibrium binding constants: K_{eq}=5 *vs* K_{eq}=440.[93]

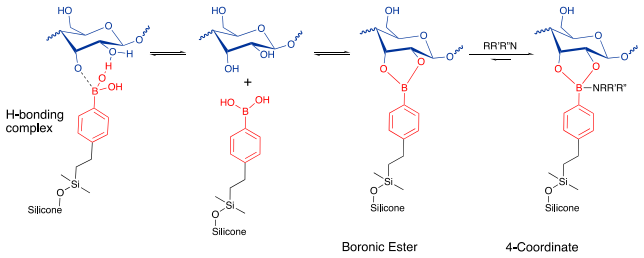

Figure 25: Reversible binding of silicone boronic acids to saccharides

Saccharides, including those that are protein constituents, were found to bind well to **SiBA** surfaces, but not to simple silicones, as shown qualitatively by wetting and fluorescence measurements and quantitatively by QCM. We now rationalize the observed efficiency of binding of saccharidic materials.

Boronic acids tethered to silicone polymers interact with ligands in a similar fashion to the more commonly explored organic boronic acids.[122-123] We previously reported that elastomeric films of silicone boronates formed at the air/water interface with crosslinking provided by boronic acid dimers. The elastomeric films could be destabilized by removing crosslinks in the presence of competitive ligands for boron; BA/BA complexes were replaced with Lewis acid/base complexes.[91] Here an analogous outcome is demonstrated. Once the protective tartrate group was removed, chemisorption of saccharides to the surface of **SiBA** elastomers was facile. The data reported above – wetting, fluorescence and binding by gravimetry (QCM) – is consistent with this claim.

Proteins that are neither surface active nor glycosylated did not bind either to silicone surfaces or SiBA elastomer surfaces. Casein, which is glycosylated, and HSA, which is not, are both surface active species, and have previously been reported to bind to hydrophobic substrates.[118-120] Both bound to simple silicones and **SiBA** elastomer

surfaces (Figure 24, Table 3), and binding was more effective with the pendant **SiBA 2**, which has a higher boronic acid density. Note that HSA binds much more effectively to simple silicones than to the **SiBA** surfaces.

The adhesion of saccharidic materials to the silicone was manifested through an immediate change in surface wettability. Boronic acid-functionalized silicone elastomers were much more wettable after saccharide treatment than PDMS elastomers (Figure 23). In several cases, notably, phytoglycogen, this was further facilitated by the higher boronic acid concentration with **SiBA-P50** (**2**) > **SiBA-17** (**1**). The equilibrium binding constant of the saccharide did not appear to play a role with respect to wettability as much as saccharide size and flexibility. Large polysaccharides such as glycogen and pullulan cover a greater amount of surface area relative to monosaccharides (Figure 26). A single polysaccharide molecule can therefore increase surface wettability much more efficiently than a monosaccharide on a per boronic acid binding basis. The efficiency of establishing the binding in the first place reflects the flexibility of the polysaccharide. In addition to owning a spherical nature which reduces contactable surface area with the silicone substrate, phytoglycogen is a highly crosslinked material that is not readily able to undergo deformation in solution (Figure 26). By contrast, mucin and pullulan are both highly flexible polymers that adapt to the surface (Figure 26) leading to a more effective binding profile. Fluorescence measurements, used qualitatively here, support these claims.

QCM provided quantitation of the degree of binding. Sorbitol readily bound to SiBA surfaces, as did pullulan, phytoglycogen and mucin (Table 3). The mass loading of polymeric saccharides was higher than that of sorbitol. This is unsurprising because a

monolayer of the polymer like phytoglycogen will inevitably be much thicker (with higher mass) than that of sorbitol (Figure 26), even if the polymer is relatively flexible, as in the case of mucin.

The surface of the **SiBA** elastomer can become saturated, for example, with the excellent binder sorbitol. However, good binders like sorbitol were unable to bump off what were expected to be poorer binding entities, based on glucose, for example, phytoglycogen. As is the case with protein adsorption, it is possible for one better binding protein to displace a more rapidly bound protein (the Vroman effect).[124] However, the binding equilibrium constant of a single residue (sorbitol) will be much less than the additive binding arising from multiple sites of a given polymer binding to the surface, as is the case with phytoglycogen, casein, pullulan and mucin.

Two classes of **SiBA** were used in these studies: those with BA/BA crosslinks only, and those which combined BA/BA crosslinks with permanent crosslinks formed by hydrosilylation. The latter compounds showed no dynamic changes upon exposure the solutions of saccharide in water. This is unsurprisingly because water will not easily swell a silicone elastomer and bind only at the water/silicone interface is anticipated. By contrast, the elastomer formed only with BA/BA crosslinked was expected to undergo gradual erosion as saccharides, mobile low molecular weight compounds like sorbitol in particular, penetrate and remove crosslinks. However, this was not observed, we believe, because there is too high a cost to bring water into the hydrophilic silicone environment, which would be a precursor to de-crosslinking.

Silicone elastomers are often used in biomaterials applications because their properties include biocompatibility, gas permeability, transparency and tuneable mechanical

properties.[75, 125] The surfaces of materials for these applications, however, often require manipulation to ensure compatibility at PDMS-biological interfaces. This may include passivation with grafted polymers such as poly(ethylene glycol)[126-127] layers of surfactants or zwitterionic species,[82, 128] or explicitly tethered proteins or other entities to the silicone surface.[129-130] In all cases, these layers separate the biological substrate from the hydrophobic PDMS surface. The resulting surfaces, particularly when utilizing PEG, suffer from oxidation under biological conditions.[131]

A variety of biomaterials link their utility to surface interactions. For example, boronic acid/sugar interactions have been utilized to deliver drugs from mucosae.[132] Drug loaded nanoparticles self-adhere and delivery to specific targets through BA/saccharide interactions. Similar protocols were described for vaginal drug delivery.[133] In one particularly relevant example, binding in the eye was performed using boronic acid interactions.[134]

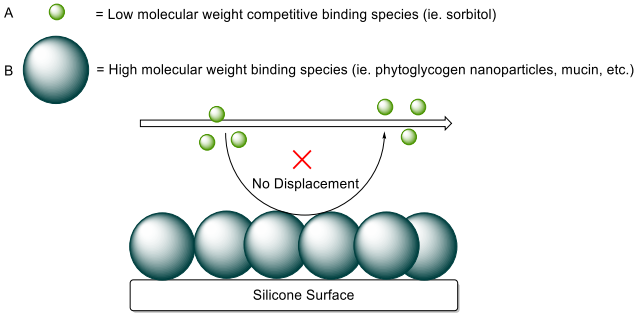

Figure 26: Reversible binding of silicone boronic acids to saccharides

Alternative strategies for hydrophilic surface modification are needed for further development of silicones as biomaterials. The current work presents such an approach. SiBA surfaces maybe used anchor desired saccharides to surfaces by physisorption and then chemisorption. Our thesis is that such layers will permit silicone surfaces to be tuned for specific applications, for example, to provide more lubricious ophthalmic

surfaces. The examples just noted suggest the current materials could have similarly applications at or near mucosal surfaces. Further testing in this regard is underway.

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Chapter 4: General Conclusions

The role of surfaces and interfaces in silicone chemistry is manifested in the phase separation resulting from the mixture of silicones with saccharidic materials/solutions. Ameliorating this phase separation is beneficial to the use of silicone elastomers in applications where controlling elastomer mechanical properties and surface wettability is advantageous. There are few methods for modification of silicones to facilitate silicone-saccharide interaction, thus the need for new methods exists. The introduction of certain functional groups to both the silicone and the saccharide moieties provides a general route for the repelling phases to interact. In the current work, the silicone is modified with a boronic acid moiety while the saccharide is unmodified, limiting the amount of steps required for interaction. The focus of this thesis was to use the interaction between silicones modified with boronic acids and unmodified saccharides to impart improvements to the mechanical properties and the interfacial properties, mainly wettability of silicone elastomers.

In chapter 2 the mechanical properties were used as a measure of the effect saccharides had on stabilizing the phase boundary between silicones and saccharides by acting as crosslinkers. The type of saccharide greatly affected the extent to which the elastomer performed with respect to mechanical properties due to its ability to bind to boronic acid functional groups. A stoichiometric amount of saccharide filler can be used to improve elastomer mechanical properties, however the use of polysaccharides such as phytoglycogen and pullulan were ineffective fillers due to the size density of binding

moieties imparted by the large size of the saccharide relative to the boronic acid-boronic acid distance on the silicone.

In chapter 3 the ability of silicone boronic acid elastomers to attract and adsorb saccharidic materials to their surfaces was investigated using a combination of contact angle, QCM and fluorescence imaging measurements. The wettability change caused by saccharides adsorbed to the surface of boronic acid modified silicones was manifested by large differences in contact angle when compared to unmodified PDMS elastomers. Adsorbed saccharides could be seen when tagged with fluorophores and imaged using fluorescence microscopy. The amount of saccharidic material adsorbed to the surface was quantified using QCM sensors coated with boronic acid modified silicone elastomers. High molecular weight species adsorbed with greater efficiency regardless of binding efficiency due to the absolute number of binding sites available to boronic acid moieties.

This work produced a method for controlling silicone-saccharide interfaces by stabilizing the phase boundary through the use of an amphiphilic linker in the form of phenylboronic acids. It can be seen from the results in chapter 2 that the interaction between saccharides and boronic acids is unaffected by the presence of silicones. The resulting materials have high potential for use in biomedical materials applications such as contact lenses and catheters.

Chapter 5: Appendix

Supporting information for chapter 2

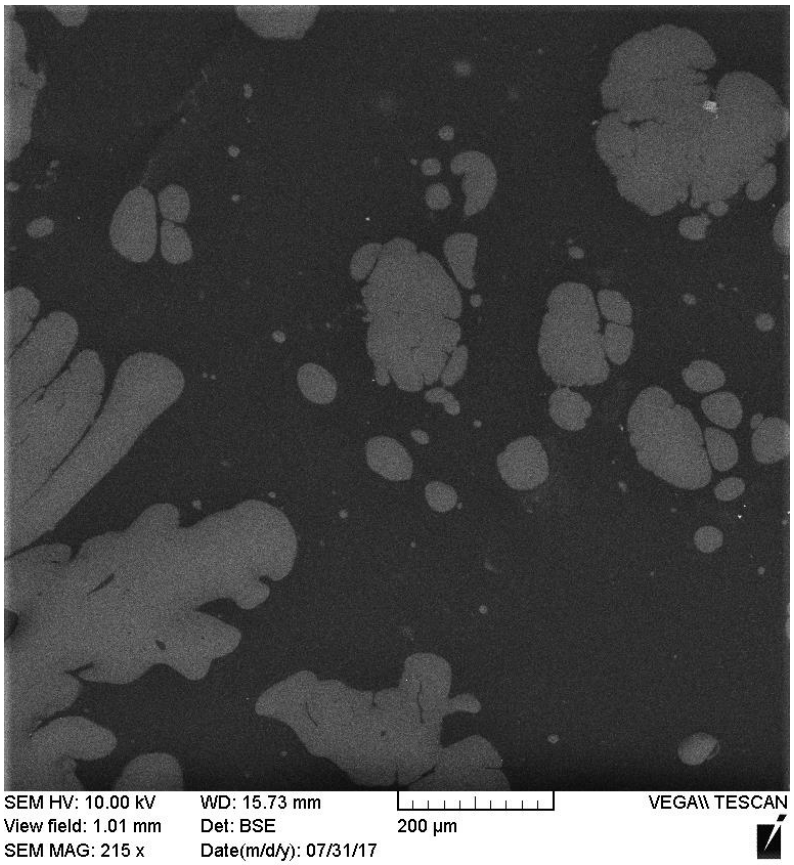

Figure S1: SEM image, after drying, of the 50:50 SiBA-17:phytoglycogen paste showing that it is a coarse emulsion.

Telechelic Silicone Boronic Acid Elastomers	
Silicone Molecular Weight (Da)	Young's Modulus (MPa)
1135	0.170 ± 0.018
4512	0.150 ± 0.027
7485	N/A[a]
Pendant Silicone Boronic Acid Elastomers	
Boronic Acids per Siloxane Unit	Young's Modulus (MPa)
50	2.290 ± 0.023
15	2.190 ± 0.033
7	0.220 ± 0.028
3	N/A[a]
Telechelic (SiBA-17) - Pendant (SiBA-P7) Mixtures	
Telechelic:Pendant Ratio of Mixture	Young's Modulus (MPa)
95:5	0.860 ± 0.070
80:20	0.630 ± 0.12
70:30	0.670 ± 0.075
60:40	1.140 ± 0.029
50:50	2.530 ± 0.16
40:60	4.630 ± 0.14
30:70	5.590 ± 1.20
20:80	2.790 ± 0.69
5:95	2.320 ± 1.10
Saccharide-Doped Silicone Boronic Acid Elastomers (SiBA-17)	
Saccharide (mol): Boronic Acid(mol)	Young's Modulus (MPa)
Sorbitol	SiBA-17 = 0.171 ± 0.018
0.5:1	0.110 ± 0.023
1:1	0.600 ± 0.051
1.5:1	0.350± 0.043
2:1	0.340 ± 0.095
Pullulan	
0.5:1	0.140 ± 0.030
1:1	0.110 ± 0.017
1.5:1	0.140 ± 0.060
2:1	0.110 ± 0.035
Glucose	
1:1	0.070 ± 0.027

Supporting information for chapter 3

Silicone boronic acid elastomers were produced with varying ratios of boronic acid dimer:silicone crosslinks. Elastomers consisting of 100% boronic acid dimer crosslinks were produced according to a previously described procedure[37]. Elastomers consisting of 100% silicone crosslinks, PDMS with no functionalization, were produced using a commercial PDMS elastomer kit, SylGard 184 using a 1 curing agent: 10 elastomer base ratio. Elastomers consisting of crosslink ratios between 0% - 100% boronic acid dimer crosslinks were produced using the formulations in Table S4.

Table S4. Preparation of silicone boronic acid elastomers containing varying amounts of crosslinks. All formulations are presented for elastomers containing permanent silicone crosslinks as well as dynamic boronic acid dimer crosslinks. All materials were combined in a 48-well plate for elastomer formation.

Boronic Acid Crosslinks %	HMS-301 Added	Tartrate-Protected Vinylphenyl Boronic Acid Added	DMS-V21 Added	Karstedt's Catalyst
50	0.1g, 16.9µmol	52.0mg, 177.8µmol	0.74g, 88.8µmol	2.1µmol
43.75	0.1g, 16.9µmol	46.3mg, 155.5µmol	0.83g, 99.9µmol	2.1µmol
37.5	0.1g, 16.9µmol	39.7mg, 133.2µmol	0.92g, 111.1µmol	2.1µmol
31.25	0.1g, 16.9µmol	33.1mg, 111.1µmol	1.01g, 122.1µmol	2.1µmol
25	0.1g, 16.9µmol	26.5mg, 88.8µmol	1.11g, 133.3µmol	2.1µmol

Table S5. Physical Characteristics of Silicone Boronate Elastomers

Boronic acid	Cure Status or Treatment Applied	Young's Moduli (MPa)	Contact Angle (°)

crosslink (%)			
50	Cured	1.30MPa ± 0.28	74.80 ± 0.70
50	H_2O Soaked 24h	1.10MPa ± 0.07	-
50	NEt_3 Soaked 24h	1.30MPa ± 0.05	-
50	H_2O soaked 24h then dried	2.40MPa ± 0.02	-
50	NEt_3 Soaked 24h then dried	1.30MPa ± 0.09	-
43.75	Cured	1.40MPa ± 0.12	76.70 ± 0.32
37.5	Cured	1.20MPa ± 0.16	77.10 ± 1.06
31.25	Cured	1.20MPa ± 0.25	80.00 ± 0.21
25	Cured	1.40MPa ± 0.06	81.90 ± 1.44

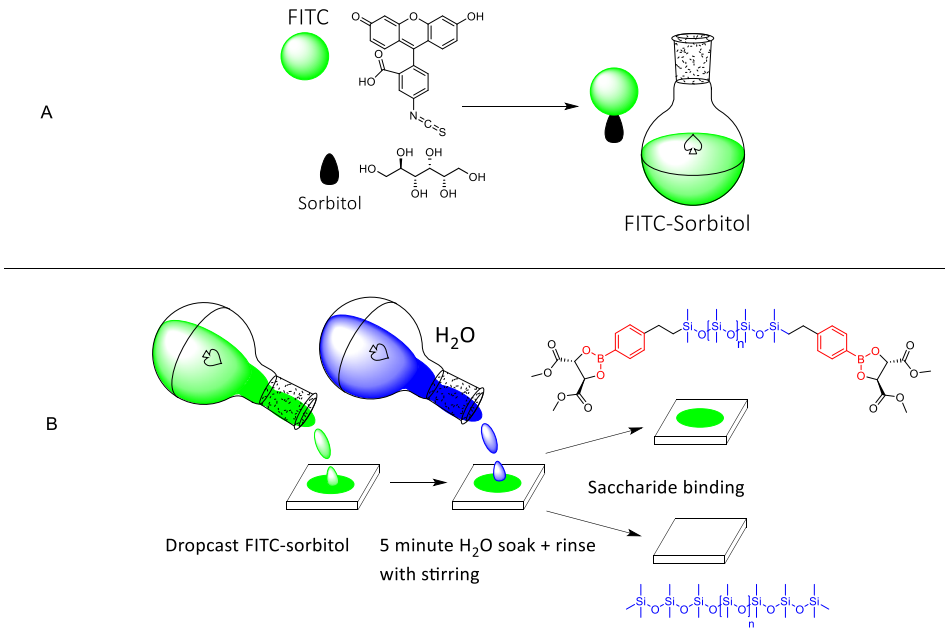

Figure S1. Preparation of FITC-tagged sorbitol (A) in DMF followed by binding to Silicone surfaces (B) by dropcasting FITC-sorbitol solution. Unbound fragments were

then rinsed away by submersion in water with stirring. Silicone surfaces were then dried at 50°C overnight prior to analysis.

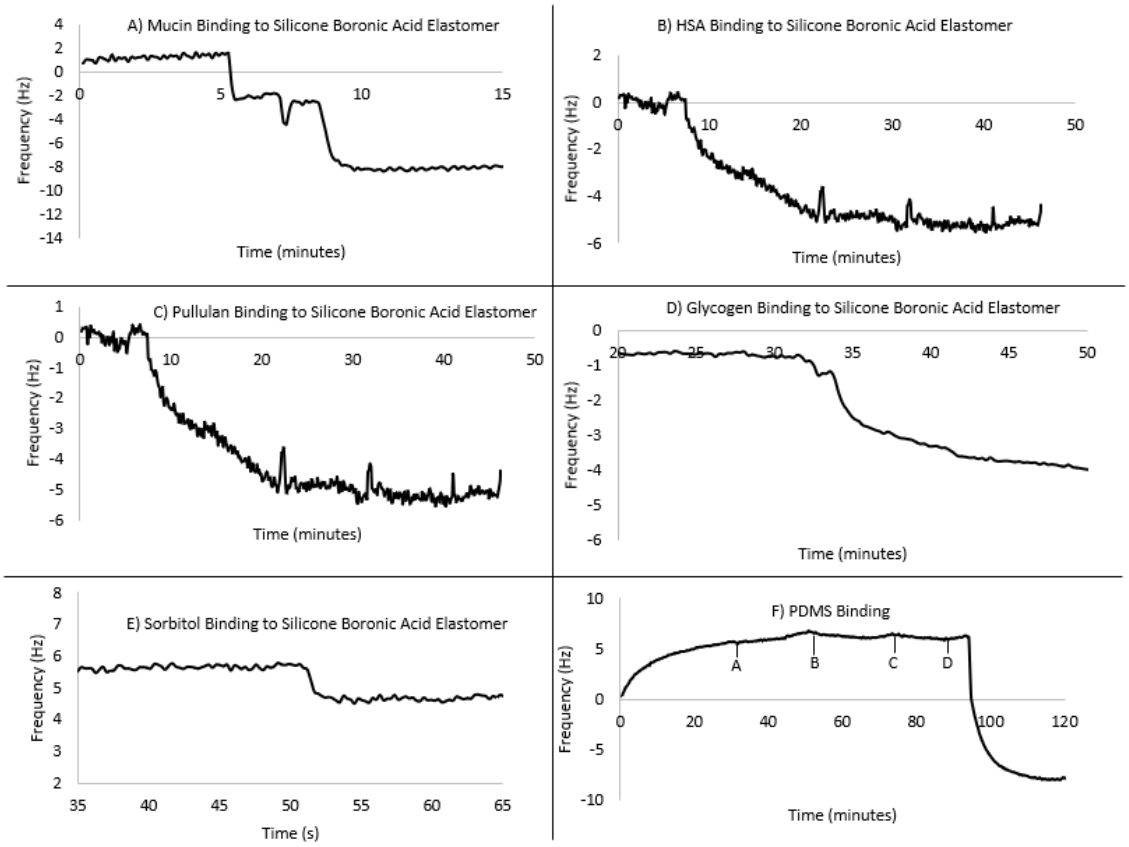

Figure S2. Adsorption of saccharides and proteins by SiBA-coated QCM sensors. Mucin (a), HSA (b), pullulan (c), and phytoglycogen (d) and sorbitol (e) all adsorbed to the sensor surfaces. Adsorption of saccharides and proteins by PDMS-coated QCM sensors was not seen for sorbitol (F-A), pullulan (F-B), or glycogen (F-C) whereas HSA (F-D) adsorbed to the sensor.

Equation S1. Sauerbrey equation used to calculate mass of material adsorbed to the surface. Where Δf is the frequency change (Hz), C_f is the sensitivity factor for the crystal used (56.6 Hz·μg^{-1}·cm^2), Δm is the mass change per unit area (μg/cm^2).

$$\Delta f = -C_f \Delta M$$

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