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Tuning the viscoelasticity of sugar–silicone polymers using caramelization

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Covalent grafting of sugars onto silicones imparts viscoelasticity *via* hydrogen-bonding among sugar moieties. Catalyst-free caramelization enables programmed, permanent adjustment of these properties by first reducing the OH content on the sugar moieties, which initially lowers viscosity, followed by oligomerization to form viscoelastic materials.

The extremely low surface energy of silicones – manifested in their water repellency – makes them particularly useful in sealants, coatings and adhesives.[1] The target viscoelastic properties of the vast majority of silicones destined for these applications are controlled by the introduction of covalent chemical crosslinks. Although some silicone thermoplastic materials are known[2–6] that may utilize non-traditional bonding motifs, including ionic and hydrogen bonds,[7,8] the vast majority of commercial materials use crosslinks generated by expensive platinum-catalyzed hydrosilylation cure, tin- or titanium-catalyzed moisture cure (room temperature vulcanization, RTV) or high temperature radical cure.[9] Catalyst residues can leach from all three types of materials,[10,11] and concerns about potential toxicity are particularly elevated in the latter two cases.[12]

Silicones can also be generated by using organic chemistry to form crosslinks, taking advantage of high atom economy reactions. For example, click reactions based on Huisgen 3+2 cycloadditions,[13,14] Diels Alder reactions,[15,16] 2+2 photoinitiated cycloadditions,[17] dynamic Schiff base imine formation,[18,19] and aza-Michael reactions[20] can be efficient, do not require catalysts, and can be induced at reasonable temperatures. However, it is still necessary to know the target modulus and other viscoelastic properties to encode the requisite crosslink density. Often achieving these targets is, at best, hit and miss and requires many experiments in order to optimize physical properties. It

would be desirable to have a process that could, on-the-fly, allow one to tune the viscoelasticity of silicone polymers until the desired properties are achieved.

A very old, delightful process to manipulate viscoelastic properties involves the caramelization of sugar. On heating, sugars, including sucrose and many monosaccharides, undergo conversion in a series of not-perfectly-understood processes: from crystalline granules, to pale yellow, then brown soft malleable materials, to viscoelastic intermediates that become dark brown hard, brittle caramel; and, ultimately black carbon. It is known that dehydration, rearrangement, and polymerization processes occur during this sequence;[21] starting from sucrose, the intermediacy of classes of low molecular weight oligomer products including caramelans ($C_{24}H_{36}O_{18}$), caramelens ($C_{36}H_{50}O_{25}$), and caramelins ($C_{125}H_{188}O_{80}$) has been reported.[22]

We previously demonstrated that glucose-capped linear silicone polymers exhibit the ability to form transient polymer networks under compression due to the interactions of the sugars that dynamically are forced together to create dynamic crosslinks.[23] Thus, fluids are readily converted, temporarily, to energy absorbing solids by virtue of these H-bonding interactions. The magnitude of the viscoelastic response is readily tuned by using residues with fewer OH groups,[24] diluting the sugars either by increasing the molecular weight of the silicones, or by diluting the sugar–silicone with nonfunctional silicone oil; different sugars will have slightly different caramelization points. We report that caramelization – a catalyst-free process that is readily turned on/off – provides a convenient method to modify viscoelasticity of a given sugar silicone to desired values.

Aminopropylsilicones are traditionally made by the platinum-catalyzed hydrosilylation of allylamine with hydrosiloxane, although a more sustainable approach from less-expensive vinylsilicones and the natural compound cysteamine has been reported.[25] Either type of aminosilicone works efficiently. Sugar silicones were made using the simple catalyst-free ring opening reaction of gluconolactone by aminopropylsilicones to form

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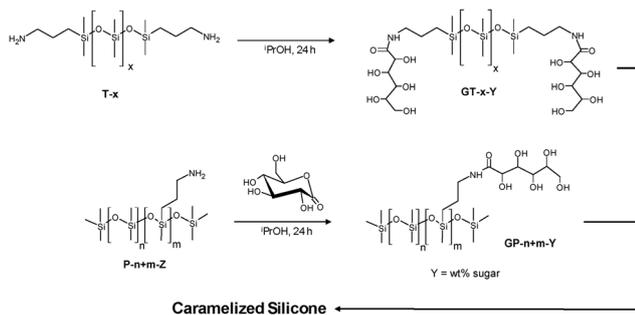
Fig. 1 Preparation of sugar–silicones. Z is the weight% of amine monomers; Y is the weight% of amidosugar monomers ($Z < Y$).

sugar–silicones (Tables S1 and S2 SI).[23] Three telechelic and three pendant polymers with different ratios of sugar/silicone served as starting materials (Fig. 1).

Caramelization is normally undertaken with pure saccharides rather than open-chain sugar–silicones. Therefore, an exploration of the best temperature to use for the caramelization process for these open chain sugars was initially undertaken with the model compound N-butyl gluconamide (BG, control). A balance was struck between the use of higher temperatures to elicit changes rapidly, but not so high such that the reaction would be uncontrollable. The use of 180 °C, ideal for glucose and saccharose caramelization[21] (also to make soft caramel, according to cookbooks) was ultimately chosen for caramelization studies of sugar–silicones. The rate of caramelization was readily followed by color changes at 180 °C over different time periods (Fig. 2). The four rows show results from compounds in which the weight% of sugar moieties in the telechelic silicone polymers decreases from top to bottom, inversely correlating with the molar mass of the telechelic silicones, which ranged from 3000 to 50 000 g mol^{-1}.

To a degree, the caramelization process could be followed by eye, and common practice was to heat until a dark brown (but not black) color was achieved. Heating beyond this stage led to 'burnt' and brittle samples. The time required for caramelization was inversely proportional to the weight% sugar in the
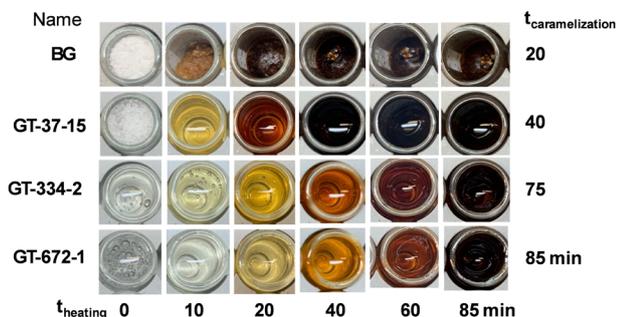
starting sugar–silicone polymer. Determining a precise time for caramelization was challenging; colorimeters proved unhelpful in this regard so rheological measurements were employed to assess material transitions. Rheological measurements enabled tracking of the viscoelastic transition from liquid-like to solid-like behavior by measuring the storage and loss moduli (Tables S6–S11, SI) and by calculating $\tan(\delta)$, representing the ratio of viscous to elastic response. Materials with $\tan(\delta) > 1$ are considered liquid-like, while those with $\tan(\delta) < 1$ are solid-like. Before caramelization, **GT-37-15** was a solid and thus not able to be characterized by $\tan(\delta)$. However, upon heating for 10 minutes at 180 °C, it transitioned into a soft, malleable viscoelastic fluid with $\tan(\delta) = 3.5$. Continued heating resulted in a progressive decrease in $\tan(\delta)$, reaching 0.7 after 60 minutes, indicative of solid-like material formation (Fig. 3).

GT-334-2 and **GT-672-1**, which contain lower sugar-to-siloxane ratios than **GT-37-15**, were already viscoelastic fluids prior to heating. Both exhibited a decrease in $\tan(\delta)$ upon caramelization (Fig. S11, SI). Notably, despite their lower sugar contents, **GT-334-2** and **GT-672-1** maintained a higher $\tan(\delta)$ than **GT-37-15** due to their greater viscosities. A similar behavior was observed for the prepared pendant sugar–silicone samples (Table S12, SI). Additional swelling and mobility experiments supporting the viscoelastic behavior a provided in Fig. S1, S2 and Table S5 in the SI. It should be noted that the influence of the silicone molecular weight on the material properties is inherently coupled to the sugar content of the polymers. Lower-molecular-weight telechelic silicones contain a higher proportion of sugar units, whereas higher-molecular-weight polymers contain correspondingly fewer sugar moieties. As a result, the viscoelastic behavior is governed predominantly by the density of hydrogen-bonding sugar groups rather than by the molecular weight of the silicone backbone. This relationship explains why the effect of molecular weight appears less pronounced than expected based on polymer-physics considerations.
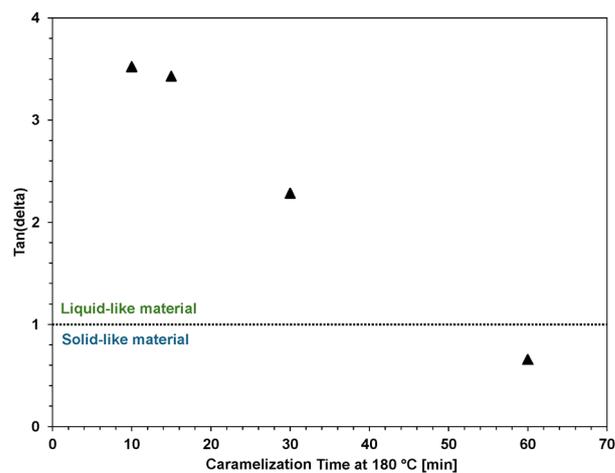

Fig. 2 Color change due to caramelization during heating periods. Panels show representative samples heated in glass vials at 180 °C for: 0, 10, 20, 40, 60, and 85 minutes (t_{heating}), respectively. Over time with heating clear/white samples turning yellow-orange, to dark red, and to dark-brown. Caramelization time for **Gt-64-9** was 45 min.

Fig. 3 Tan(δ) values of **GT-37-15** after different caramelization times at 180 °C. Tan(δ) values were determined via rheological analysis and calculated from the storage and loss modulus at an angular frequency of 1 rad s^{-1}.
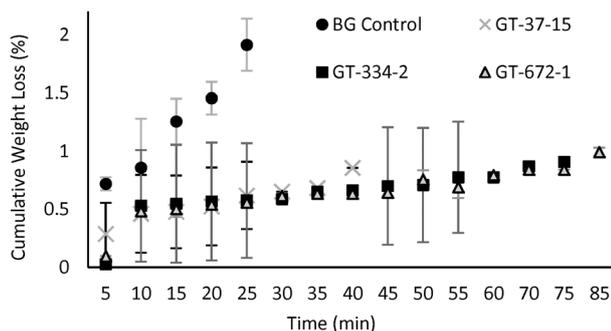
Fig. 4 Cumulative weight loss during heating (caramelization) at 180 °C. Error bars represent standard deviation of 3 samples.

The control *N*-butyl gluconamide showed a weight loss of 1.9% during caramelization, but the sugar–silicones lost less than 1 wt% (Fig. 4). Thus, changes in viscoelastic properties are not a consequence of material loss. Shore OO hardness values were taken for all samples that showed a tan(δ) below 1 after a certain caramelization time (Table S3 and S4, SI).

DSC (differential scanning calorimetry) measurements were performed on samples before heating and after full caramelization. The **GT-37-15**, which is a solid at room temperature, exhibited a T_c of 43.2 °C and a transition (likely water evaporation) at ~100 °C; neither transition was seen after caramelization (heating to 180 °C for 40 min, Fig. S3 SI)†. By contrast, TGA exhibited thermal transitions for **GT-37-15** near 200 °C, which reflects the caramelization step and, for all the sugar–silicones, decomposition of the silicone chain near 400 °C. Note that further heating of caramelized samples still results in weight loss at 200 °C as further dehydration/crosslinking occurs to give rigid samples (Table S14, SI).

Anyone who has made caramel will understand the challenges with this system. As the process occurs, any solids initially present first melt; the resulting fluids increase in viscosity, become viscoelastic, then rigid and finally brittle, black solids. These changes challenged physical characterization. For example, adhesion of a sticky caramel to probe surfaces can impact the apparent results; multiple measurements were required. The outcomes when sugar was bound to silicone polymers correlated with sugar concentration and also structure. For example, the high sugar content **GT-37-15** is a solid at room temperature, melts with heating to form a lower viscosity fluid and then, with further caramelization, a solid. The other two telechelic polymers, with lower sugar content, started as viscous fluids and ended as soft solids at the caramelization point.

The pendant polymers were all fluids before heating, even with much higher sugar content than the telechelic analogues. This suggests that individual pendant polymers can have sugars that undergo intramolecular, rather than intermolecular crosslinking interactions.

The chemistry of the caramelization process is complex and leads to small molecules that give caramel its typical (pleasant) odors and flavors, including a butterscotch flavor (diacetyl) and a 'toasty flavor' (*e.g.*, in bread, maltol). Dehydration, molecular fragmentation and polymerization lead to increases in molecular weight and then crosslinking.[26] In the case of glucose $C_6H_{12}O_6$ as precursor, oligomers from C_{24}–C_{125} have been reported.[22] In the limit, the full dehydration of sugar, for example using sulfuric acid, leads to carbon, as in the 'carbon snake demonstration' often shown to undergraduates.[27]

The gluconamide residue on the GT and GP silicone polymers behaves as a typical sugar upon heating. Viscosity builds and then viscoelastic materials form. These programmed changes allow one to select the desired precursor viscosity of a sealant or coating, for example, by controlling both molar mass and sugar density. The GP-based polymers we prepared had much higher sugar content than the telechelic polymers, except **GT-37-15**, which was a solid before heating. Simply heating the powders or fluids, for example using a heat gun, leads in a straightforward manner to elastic materials that should perform in similar fashion to traditional silicones, particularly water repellency. The pendant samples would appear to be the most practical here, as liquid samples are converted in a few minutes to viscoelastic materials with starting viscosity and final Shore hardness (modulus) that correlate with sugar content – it is straightforward to identify the optimal properties. A limitation of the current study is that no long-term aging or storage-stability data are available. Sugar-based materials can undergo time-dependent changes in stiffness due to continued dehydration or crosslinking. Systematic long-term studies will be required to assess whether the caramelized sugar–silicones maintain their mechanical properties over extended periods.

We note that chewing gum based on silicones has been considered as an alternative to hydrocarbon based chewing gums; several patents exist. So a natural question would be, "What do the caramelized silicones taste like?" We don't know – we are following our own admonition not to eat anything in the lab.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: full experimental protocols; tables or recipes; details on caramelization, swelling behavior, and mobility experiments; changes in tan(δ) and Shore OO hardness as a function of heating; charts of rheology, TGA, and DSC of telechelic and

pendant sugar–silicones before and after caramelization. See DOI: https://doi.org/10.1039/d5cc05934h.

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† Similar thermal transitions as for GT-37-15 were not observed with GT-64-9, GT-334-2, and GT-672-1 prior to heating; the samples do not contain sufficient sugar content.

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