THE COUPLING OF SYNTHETIC AND BIOLOGICAL POLYMERS: SILICONE - STARCH COMPOSITES

THE COUPLING OF SYNTHETIC AND BIOLOGICAL POLYMERS: SILICONE - STARCH COMPOSITES

By

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ABSTRACT

This thesis presents a study of the compatiblization of a hydrophobic, synthetic polymer, polydimethylsiloxane (PDMS) and a hydrophilic biopolymer, starch. The Diels-Alder adduct of cyclopentadiene and maleic anhydride, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic-anhydride, **(1)**, was hydrosilylated with hydride- terminated PDMS to yield α,ω-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic-anhydride-polydimethylsiloxane, **(4)** having an average molecular weight of 750 g mol^{-1}. This was then reacted with starch using dimethylaminopyridine as a catalyst in a dimethylsulfoxide medium at 80 °C to yield a silicone-starch graft copolymer having a γ-carboxylic-ester linkage.

In order to study the influences of the quantity of hydrophobic and hydrophilic components, a series of composites were synthesized varying the starch and silicone stoichiometry (series-1).

In order to study the influence of the molecular weight of the silicone, **4** was redistributed with octamethylcyclotetrasiloxane (D_4) via cationic polymerization to yield higher molecular weight derivatives. The products were **7** (1500 g mol^{-1}) and **8** (9000 g mol^{-1}). These were reacted with starch to give a series of composites for each molecular weight of the functionalized silicone.

Spectroscopic and physical properties were analyzed for developing trends

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Introduction

Silane Coupling Agents

Silicones

Silane coupling agents are commonly applied to glass fibers used to reinforce polymeric composite materials. They serve to improve adhesion between an organic polymer and an inorganic surface. Ideally, they are able to react to or interact with both the inorganic surface, in most cases glass, and the polymer.[1] Such alkylsilane coupling agents bind to oxide surfaces through thermally stable siloxane bonds. These bonds are hydrolyzable and the rate of hydrolysis increases with rising temperatures and non-neutral pH values.

Like silanes, functional siloxanes are capable of chemically binding to a variety of surfaces or compounds to serve as a macro-coupling agent.[2] Siloxane polymers can in many cases offer a distinct advantage over their corresponding silane coupling agents since they offer higher degrees of hydrophobicity and higher molecular flexibility.

Polysiloxanes were first synthesized as early as 1872, but their practical potential was not evident until the late 1930's.[3] For thirty years following, much of the research involved optimizing the conditions to make the simple polydimethylsiloxane (PDMS) oligomers. They were treated like monomers and the chemistry involved functional group manipulations. However, the need for bulky or polar functional groups on these silicones altered the focus to the polymerization of strained-ring monomers.[3]

Organosiloxanes are unique among polymeric materials because of their wide range of properties and structural forms. Polydimethylsiloxanes (PDMS) are the most common linear chain polymers and are generically known as silicones (Figure 1).

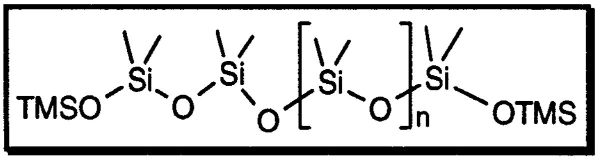


Figure 1

The polar siloxane backbone is well shielded by inert methyl groups, and thus it is said that silicones are chemically unreactive except in the presence of strong acids or bases. Reactions of silicones, therefore, often involve functional organic groups incorporated into the polymer chain. The choice of organic group is unlimited, and the favoured linkage of this substituent with the polymer chain is the propyl group. This spacer is helpful in ensuring thermal and hydrolytic stability, and as well, the 3-carbon spacer allows this organic substituent to act independently from the silicone backbone.

PDMS is the most simple of silicon polymers and it has some very interesting properties. Among these are thermal stability, transparency to UV irradiation, and high permeability to small molecules. These properties originate from the strength and flexibility of the siloxane bond. It has partial ionic character, but there is little interaction between the nonpolar methyl groups. The Si-O bond is a longer bond than Si-O and therefore there is a reduced effect in steric interactions between methyl groups of neighboring silicons. This increased Si-O bond length also allows for free rotation around the Si-O bonds. The partial ionic character of the Si-O bond allows distortion of the bond angle at oxygen, and this distortion works to relieve the steric interactions that are occurring.

There are a number of ways to synthesize organofunctional silanes, one of which comes from the use of a Si-H moiety within the silicone polymer. The addition of Si-H across a site of unsaturation by either photochemical means or by transition metal complex catalysis is called hydrosilylation. Although, hydrosilylations are prone to several by-products, these are primarily soluble, small (not polymeric) molecules which are easily separated from the desired, derivatized silicone. Also, a commonly used application of hydrosilylation is the addition of chloroalkyl groups to form chloroalkyl silanes.[3] Once attached, nucleophilic substitution of chloride allow for a variety of organic functional groups to be added to the silicone polymer and provides another approach to silicone functionalization.

Adding organic functional groups to siloxane polymers alters the physical and chemical properties of the polymer. There is an arbitrary value assigned to organofunctional siloxanes to classify them into two groups, those containing < 5 mol% functional group incorporation, and those containing > 5 mol% functionality. The unique physical properties of PDMS, for example, have already been alluded to. However, the presence of even small amounts of organic functionalities in the molecule will allow new types of physical interactions making them, in many cases, more accessible to substrates (or solvents) with which they normally would not interact.

Hence, polymers containing amine groups would more strongly adsorb onto a titania surface than the corresponding PDMS.[4] Likewise the introduction of carbohydrate substituents into the nonpolar polysiloxane polymer matrix leads to a significant change in its solubility properties (Figure 2).[6,7] The hydrophilicity of the polymers can be increased, depending on the degree of substitution, to a point where they can even become water soluble, in the extreme case.[7]

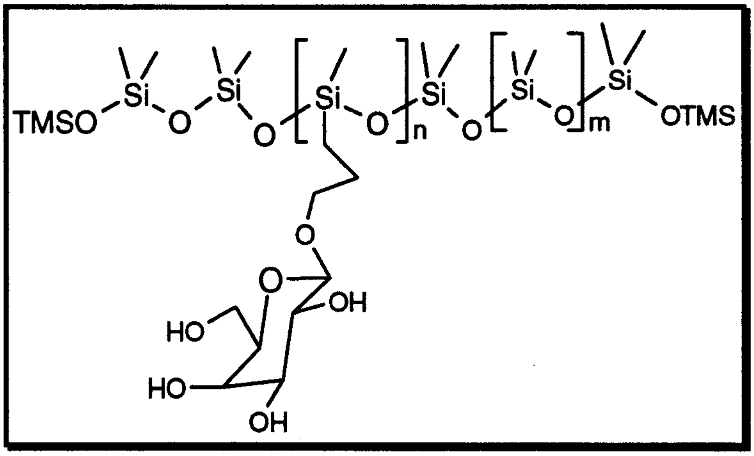


Figure 2

There has been some interest concerning this latter point. An enzymatic approach has recently been undertaken. The synthesis of poly(dimethylsiloxane-graft-(α→4)-glucopyranose by enzymatic polymerization with potato phosphorylase (E.C. 2.4.1.1) was performed using a polyinitiator based on polysiloxane with statistically distributed maltoheptaonamide and maltoheptaoside.[5] While higher molecular weight modified siloxanes remained water insoluble, in an aqueous suspension the carbohydrate side chains were solvated and became accessible for phosphorylase to polymerize the amylose grafts.

The Biopolymer Component

Carbohydrate units are the structural building blocks of many naturally occurring macromolecules.[6,7] Biopolymers with a polysaccharide main chain, e.g. starch, cellulose, etc., as well as polymers with carbohydrate side chains pendant to the polysaccharide main chain (e.g. xanthan) are known; polypeptides with grafted polysaccharides are also known.[6] The dominant interaction which influences the resulting properties of these polymers is hydrogen bonding, both inter- and intramolecular, which in turn is specified by the stereochemistry of the carbohydrate.[7] These factors may be utilized if a nonpolar, synthetic polymer is introduced into a carbohydrate matrix yielding hybrid materials of synthetic and biological origin. This may lead to dramatic changes in physical properties of the polymer or yield a new composite altogether.

Starch

There are several motivations for the development of starch-synthetic polymer composites (or plastics). Starch is inexpensive ($0.10/lb.) and is available annually in multimillion ton quantities from corn produced in excess of current market needs in the United States and Canada.[8] Since cornstarch is a native agricultural product, replacement of petroleum-based plastics with starch-based plastics might one day reduce the need to import petroleum.[8] As previously mentioned, starch is totally biodegradable in a wide variety of environments and could assist in the development of totally degradable commodities to meet market demands for such materials. Degradation or incineration of starch in plastics would recycle atmospheric CO_2 trapped by the corn plant and would not increase potential global warming.[8]

Starch is a complex mixture of glucans, which may be envisioned as condensation polymers of glucose molecules connected by acetal or glycosidic linkages.[9]

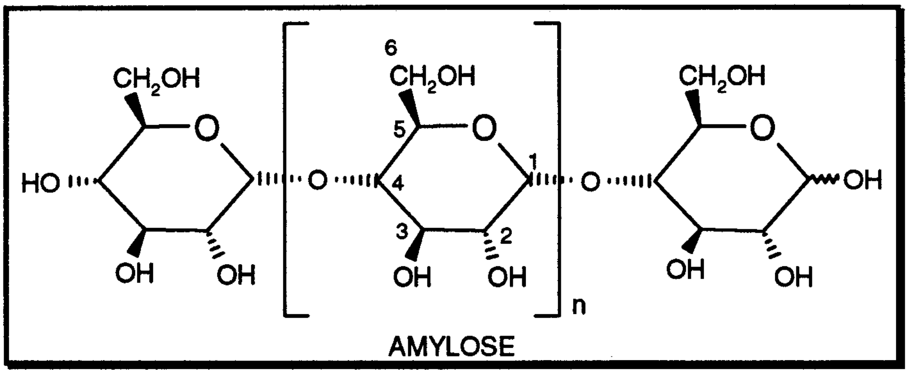


Figure 3

There are two major components, the first, called amylose is a mostly linear polymer (Figure 3). The glucose moieties are linked in an α-D-(1 → 4)-glucan. This linear portion comprises about 30% of common cornstarch and has molecular weights of 200,000 - 700,000. There is also a highly branched component called amylopectin (Figure 4).[9]

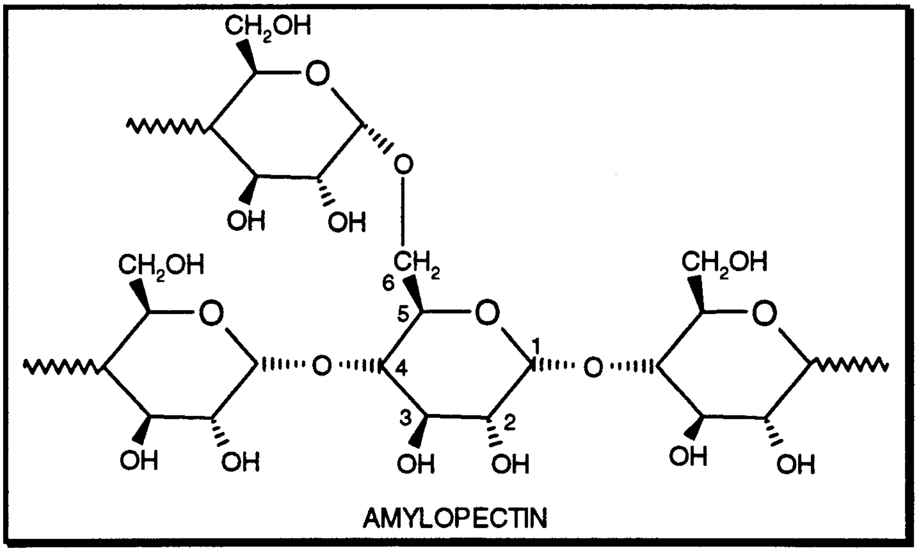


Figure 4

Amylopectin is also an α-D-(1 → 4)-glucan, but it contains many α-D-(1 → 6) linkages at the branch points. These molecules have molecular weights which range from 1 million to as high as 100-200 million.

Starch granules are hydrophilic since each monomer unit contains three free hydroxyl groups. Consequently, starch changes moisture content with relative humidity changes. If 0% relative humidity, starch granules retain about 6% moisture but at a relative humidity of 80% (humidity at equilibrium), starch retains as much as 20% moisture.[8] Granules are thermally stable when heated in an open atmosphere to about 250°C. Above that temperature the starch molecules begin to decompose.

With increased absorption of moisture in starch, there is a decrease in T_g, the temperature above which segmental motion of polymer molecules takes place. At 15-25% moisture, the T_g of destructurized starch is at or above room temperature[10] so that extruded starch will remain in the amorphous state when stored at room temperature and humidities up to approximately 80%.

In the past there have been attempts to develop starch-based plastics. Carbon-based derivatives generating starch esters and ethers were tested as thermoplastic competitors to cellulose esters and ethers in the desire for clear, tough plastic materials. However, the starch-based materials were not as strong or impact resistant as the cellulose analogues.[11] Recently, in the last twenty years, new approaches have been taken. One example involved the preparation of gelatinized starch-synthetic polymer composite films[12] and a process for extrusion compounding and blowing of the starch as a thermoplastic component in these films at 5-10% moisture.[13]

Starch may also be modified by grafting synthetic polymer branches onto the starch backbone via a radical approach. Initiators, such as ceric ammonium nitrate, create radical sites on the starch backbone. Addition of water-dispersible unsaturated monomers to the radical gives rise to graft copolymers of synthetic polymers and starch.[8]

Conventional polyolefin films constitute about 2% of normal household waste, creating a disposal problem if they are not recycled or incinerated.[14] In principle, chemical modifications of starch usually causes loss of its original biodegradability.[14] One approach to biodegradable composites lies in trying to minimize the change in native molecular structure of the starch molecules. As a test of the true biodegradable nature of these materials, the starch-plastic composites were subjected to a suitable environment where microorganisms could consume the accessible starch.[13] The experiment proved successful not only in the starch consumption, but also in the degradation of the components which are normally nonbiodegradable. The increased surface area of the composite relative to solid plastic may speed its degradation by environmental factors.[8]

Studies were actually conducted into factors which affect the adhesion of carbohydrate binding bacteria. Approximately 70% of the cells in a suspension of the amylolytic bacterium *Lactobacillus Amylovorus* were found to bind to cornstarch granules within 30 minutes at 25°C.[15] The bound bacteria could be removed by chemicals such as formaldehyde (2%) or $MgCl_2$ (2M; pH=7.0). Binding of *L. Amylovorus* to cornstarch could be inhibited by such methods as pretreatment with glutaraldehyde, sodium azide or trypsin to name just a few.[15] The most interesting and widely diversified findings involved the effect which the chemical derivatization of starch had on the bacteria binding. It was found that a degree of substitution of 0.09 2-O-butyl starch enhanced adhesion while two palmitate starches (degree of substitution, 0.48 and 0.09) exhibited reduced adhesion activities.[15] Other derivatives such as 2-O-(2-hydroxybutyl)starch and starch-poly(ethylene-co-acrylic acid) ester showed adhesion activities similar to those of the nonderivatized starch controls.

It should be noted that hydrophobic, synthetic polymers are considered to be almost universally incompatible with starch. Differential Scanning Calorimetry of starch-polyethylene blends and even grafts of poly(methylacrylate) onto starch, which have the potential of forming in crevices between starch chains within starch granules, gave no evidence of phases other than starch and the synthetic polymer.[8]

Cellulose

Along with starch, the most common carbohydrate is cellulose. Cellulose forms the main constituent of plant cell walls. Other rich sources of cellulose are wood (approx. 50%), bast fibers, such as flax (80%), and leaf fibers such as hemp (80%) just to name a few.[9] Cellulose is a β-(1 → 4)-glucan (Figure 5). This pattern leads to high quantities of internal hydrogen bonding resulting in the fact that there are few solvents for cellulose.

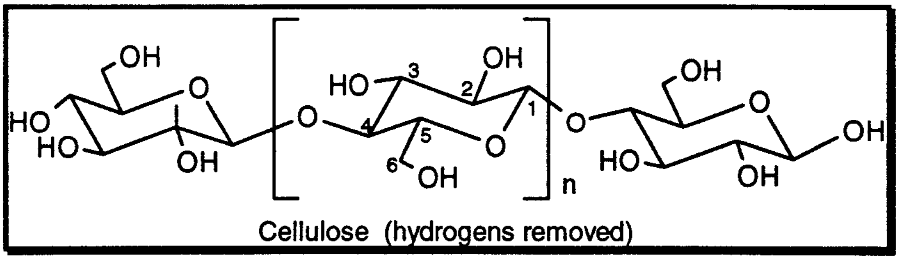


Figure 5

One of the few solvent systems that will dissolve cellulose to some degree is aqueous cuprammonium hydroxide ("Cupra") with which it forms a copper complex.[9] The value for “n” in Figure 5 is in the range of 2000 to 3000 according to physical methods.[9] Chemical methods, in contrast, yielded values for n in the neighborhood of 100 to 150. It was later found that the methods themselves, methylation of hydroxyl groups, caused substantial degradation.

There are numerous examples of cellulose being derivatized.[16] Almost all of them involve esterification[17] or ether[18] formation. Likewise, there is much literature concerning physical properties of derivatized cellulose[16,19] and the biodegradation of these derivatized compounds or graft copolymers.[16,20] Details of these accounts will not be discussed in this paper as the focus of this research is on starch composite formation.

Suffice it to say that the forest industry has been pressured to “do more with less”.[21] This means that there is much work being done to increase the conversion and efficient use of wood fiber resources using environmentally friendly processes and technologies. Consequently, processes have been implemented to satisfy the need for a thermally moldable plastic material comprising of less than 50% petrolium derived materials. Thermoformable polypropylene and wood flour compounds are extruded in sheet form for use in, among others, the automotive industries. Depending on the composition of these materials, one can obtain moldable materials having properties and appearance very close to wood while significantly reducing the amount of forest resources needed.[21]

It is felt that silicones could play a role in these developments if used as a hydrophobic modifier of cellulose. With properly functionalized siloxane polymers, chemical bond formation with the cellulose component in wood might yield a thermoformable wood with improved properties.

Goals Of This Research

Functional siloxanes of varying molecular weights may serve alternative purposes to those of coupling agents. When chemically mixed with appropriate materials, composites with properties that are superior to those of comparable systems are a distinct possibility. Hence, it follows that the combination of synthetic polysiloxane polymers with naturally occurring biopolymers such as starch merits investigation. It may be possible that this association will result in thermoplastic materials that are of equal or better quality than plastics of analogous systems, while simultaneously achieving the desirable advantage of being totally biodegradable.

The siloxane to be used in the "biopolymer-synthetic polymer" combination is an α,ω-functionalized polydimethylsiloxane (PDMS). As mentioned previously, PDMS has high oxygen permeability, high temperature stability, low toxicity, poor water wettability and biocompatibility.[7] Therefore, when combined with hydrophilic starch, it is reasonable to hypothesize that the hydrophobicity presented by the PDMS will be advantageous.

Results and Discussion

Approach Taken

The synthetic aim of this work involved the α,ω-functionalizing of hydride-terminated, linear PDMS via hydrosilylation.[22,23,24] This offers an advantage because one can control the chain length of the silicone synthetically and they are also commercially available in various molecular weights. The funtional termini should have an electrophilic moiety because the intention was to make them susceptible to attack by the nucleophilic hydroxyl groups of the starch to form an ester or ether linkage. Hence the approach was to perform conventional organic functional group manipulations using the functional groups attached to macromolecular entities. These entities were starch, "the nucleophile" and a funtionalized silicone, "the electrophile".

Functional Linking Groups

Various functional "linking groups" have been tested. It has been found that in order for a silicone-bound organic group to be useful, a minimum of a three-carbon spacer must be included if the substituent is to retain functionality of comparable reactivity to the independent precursor.[3] Hence, maleic anhydride, initially considered the ideal choice as the linking group proved to be difficult to graft onto PDMS. This is probably because the Si-C link was less than three atoms from a relatively reactive electrophilic carbonyl carbon. The most successful groups have proven to be allyl glycidyl ether, **1**, and the Diels-Alder adduct of cyclopentadiene and maleic anhydride, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic-anhydride, **2** (Figure 6). They have successfully been reacted with hydroxyl moieties to give an ester or ether linkage.

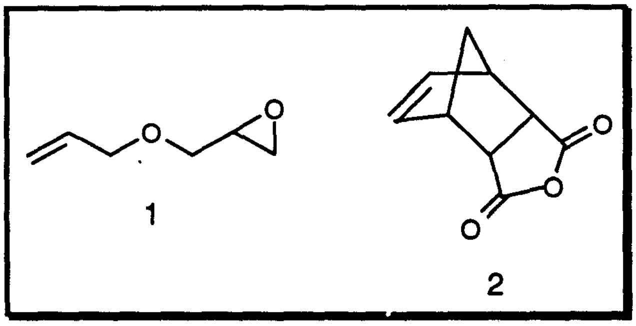


Figure 6

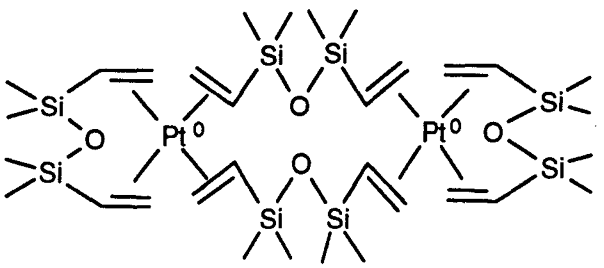
Model Reactions For The Hydrosilylations

Various attempts at reacting monomeric Si-H containing silanes with maleic anhydride, and the bicyclic anhydride, 2, proved to be tedious. Apparently the internal double bond in the cyclic anhydride is too hindered for the approach of the colloidal platinum(0)-silane complex for reduction to occur according to Lewis' mechanism for hydrosilylation.[25]

Hydrosilylation Of The Silicones

In spite of the difficulties encountered with the model hydrosilylation reactions, an investigation involving hydrosilylation of the macromolecular silicone was still deemed to be worthwhile. If a low enough molecular weight siloxane was used (400 g mol^{-1}), conventional spectroscopic techniques for monitoring (NMR or IR) the reaction could be used. Hence, α,ω-diallyl glycidyl ether-polydimethylsiloxane, (**3**) (see Figure 8) was synthesized successfully via the reaction of hydrogen-terminated silicone and allyl glycidyl ether. The yield was greater than 95%. Similarly α,ω-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic-anhydride-polydimethylsiloxane, (**4**) (see Figure 9) was synthesized in 75%

yield. The synthetic goals were achieved by the platinum-catalyzed addition of the olefinic portion of the linking group to the termini of the α,ω-substituted siloxane. The catalyst used was platinum-divinyltetramethyldisiloxane in toluene.[26,27,28] This is better known as Karstedt's catalyst[29] and exists as a dimer as shown in Figure 7.



Platinum-Divinyl-Tetramethyl-Disiloxane
(Karstedt's Catalyst)

Figure 7

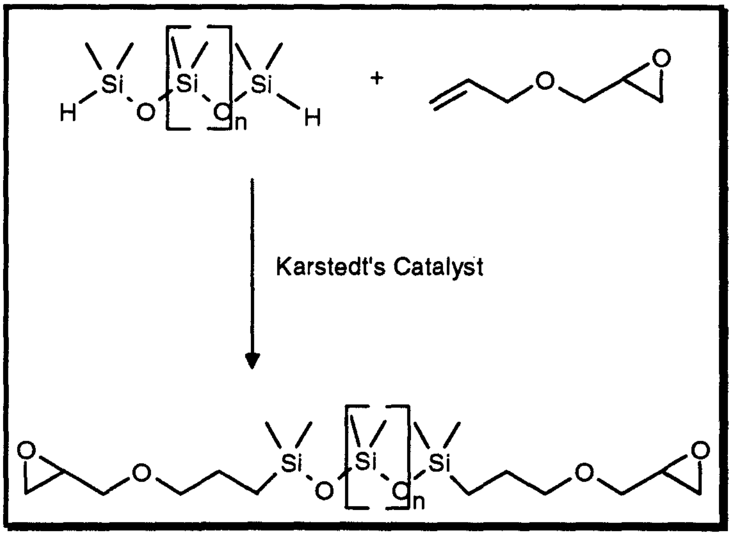


Figure 8

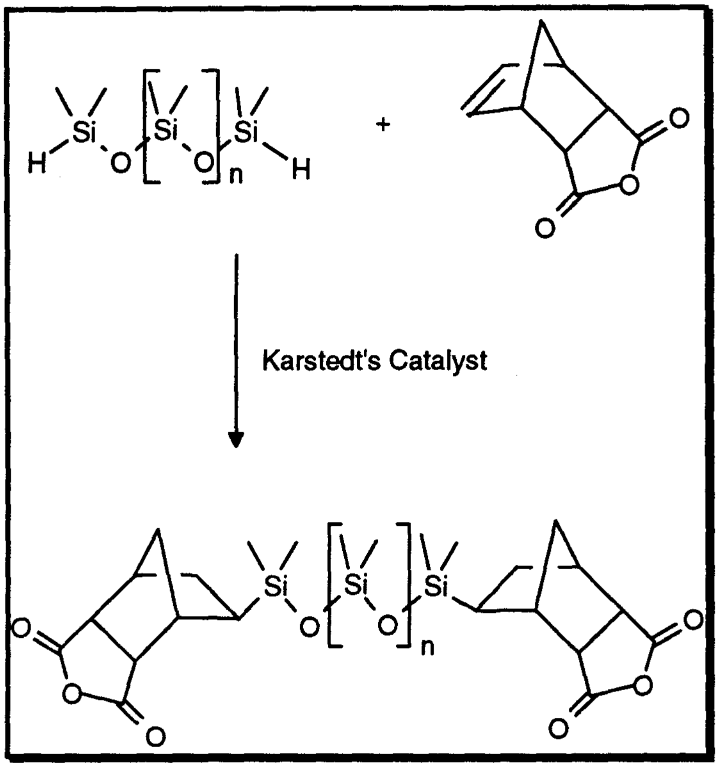


Figure 9

Molecular Weight Increase Of Silicone by Cationic Redistribution

In order to better establish the variables which would influence the starch-silicone composites, (i.e.: [1.] the relative number of ester linkages in a composite and [2.] the relative ratios of -Me_2SiO- units in the silicone polymers versus the number of glucose units in starch) the molecular weight of the silicone component of the α,ω-dianhydride starting material silicone was increased.

The cationic polymerization of cyclosiloxanes has been known for many years, particularly those initiated by sulfuric acid.[30,31] The molecular weight of the polymer can be regulated using controlled amounts of monofunctional endblockers.[31,32] If a cyclic monomer such as octamethylcyclotetrasiloxane (D_4) is mixed with a specific amount of endblocker such as hexamethyldisiloxane in the presence of a catalyst, α,ω-trimethylsilylsilicones result with controllable molecular weights. Excess D_4 is used to accommodate the 10-15% unreacted cyclics which remain in such redistribution polymerizations.[33,34,35,36]

When the low molecular weight α,ω-dianhydride silicone (750 g mol^{-1}) was used as an endblocker, redistribution was successfully used as a route to higher molecular weight α,ω-dianhydride silicones (Figure 10). It was possible to increase the molecular weight from a starting average of 750 g mol^{-1} to 1500 g mol^{-1} and to 9000 g mol^{-1}. Each of these compounds could now be reacted with starch and their products compared. The acid of choice for initiation of the redistribution was trifluoromethanesulfonic acid (triflic acid) which has proven to be the most efficient catalyst for this purpose.[37]

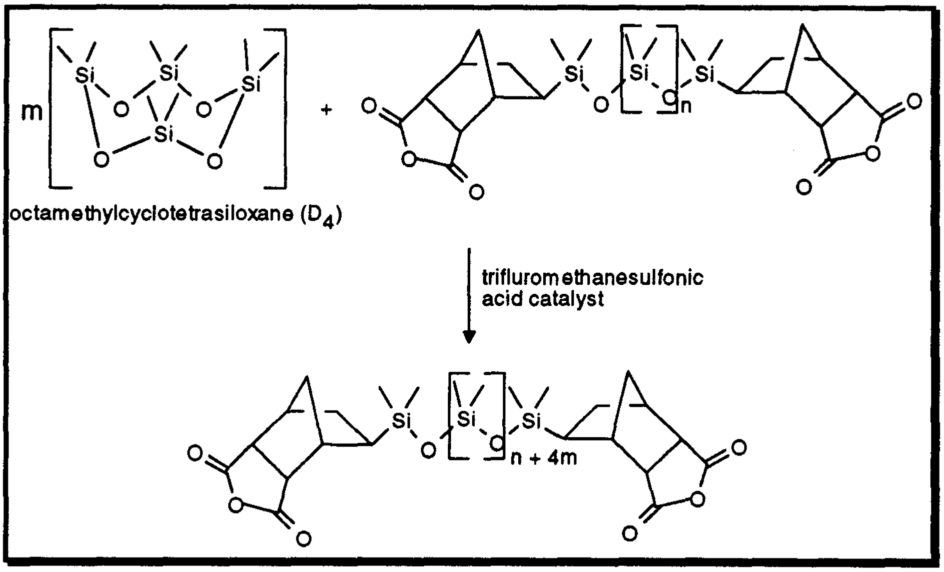


Figure 10

Model Reactions For Silicone-Biopolymer Composite Formation

Model For Protein-Silicone Combination

Model reactions were performed to mimic the reactions between the functionalized silicones and biopolymers. For instance, benzylamine was the model compound used to nucleophilically open the epoxy ring in allyl glycidyl ether (Figure 11) to give the α-hydroxy-secondary amine, (**5**).[38] The success of this reaction (see Experimental section) validates the idea that functionally terminated silicones might be used to be grafted to polypeptides. It is therefore conceivable that "nonpolar" proteinaceous material can be synthesized by this reaction. This might find application in the medicinal industry at membrane interfaces, be they *in vivo* or in the hospital for *in vitro*, intravenous purposes. This is one area to pursue in the future.

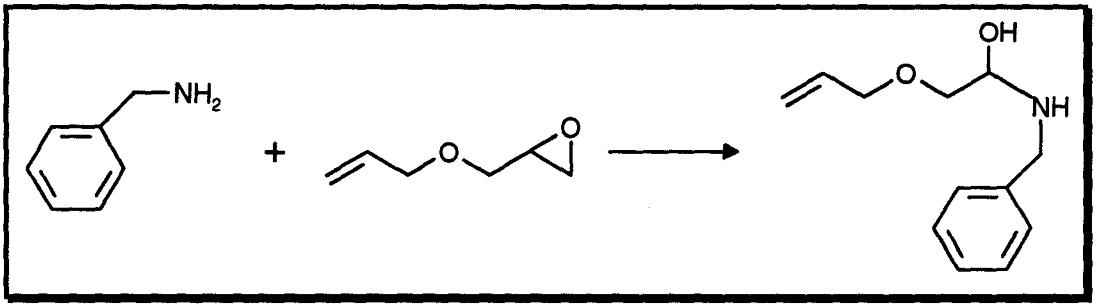


Figure 11

Model For Carbohydrate-Silicone Combination

Once the functionalized siloxanes of different molecular weight were synthesized, each linking moiety had an accessible portion remaining that was available for further chemical modification. The next logical step was to use these remaining functionalities for grafting to starch. Before attempting to react the functionalized silicone with starch, a model reaction was performed to confirm that the proposed esterification, combining the cyclic anhydride units with starch hydroxyl groups, was feasible. As a mimic for starch, a simple secondary alcohol, cyclopentanol, was reacted with the silicone(anhydride)$_2$ yielding α,ω-diesteracidpolydimethylsiloxane adduct, (**6**). The purpose was to optimize conditions prior to the starch-silicone grafting. Several catalysts were tested in an attempt to increase the reaction efficiency once it was observed that little or no reaction occurred without assistance. Pyridine, $BF_3 \cdot EtO$ and dimethylaminopyridine (DMAP) were used. Each reaction exhibited reasonable success. The yields were between 55% and 75 %. The most efficient catalyst was DMAP (Figure 12). Consequently, this was the catalyst used for the formation of the biopolymer-synthetic polymer composites.

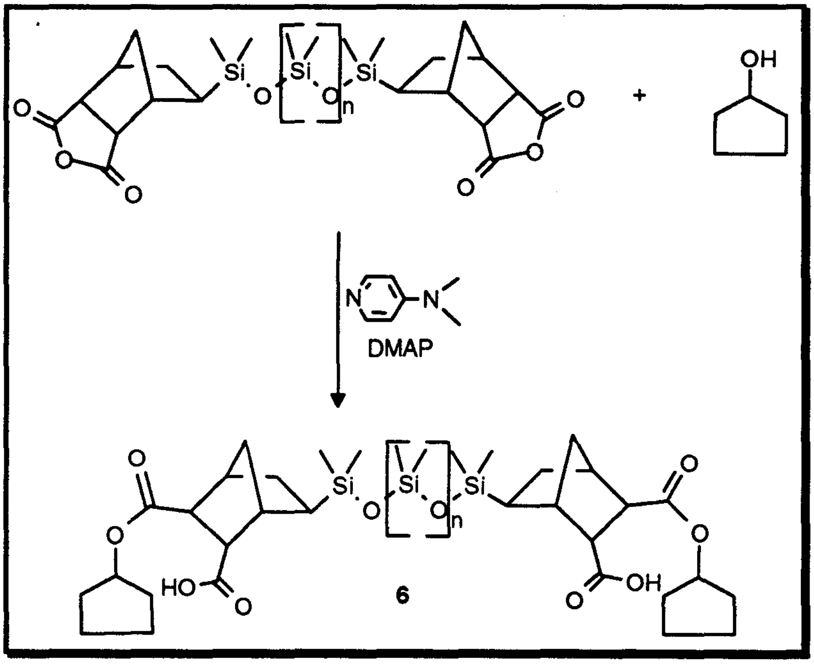


Figure 12

Starch - Silicone Composites

With conditions for the reaction optimized, using DMAP as the catalyst and having control of the length of the siloxane chain (either by commercial availability of hydride terminated PDMS or redistribution of the low molecular weight silicone, **4**), the silicone-starch composites could be synthesized. The PDMS(bicyclic anhydride)$_2$, **4**, had the dianhydride functionality available for ring opening (Figure 13). This yielded an ester linkage and a carboxylic acid functionality γ to that newly formed ester.

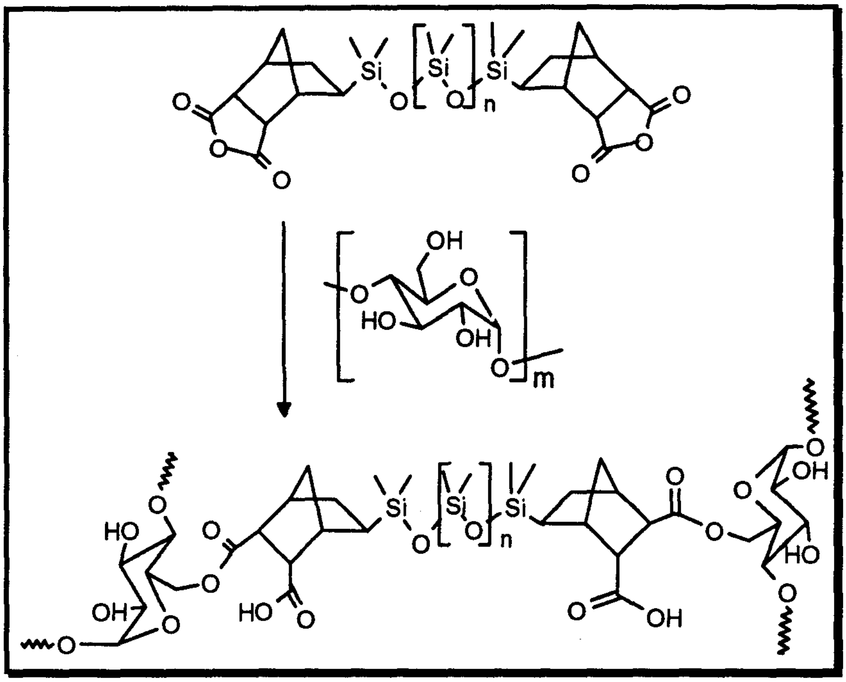


Figure 13

The reaction probably proceeds by the formation of a DMAP activated carbonyl center which is then attacked by a starch hydroxyl group represented in Figure 14 by R-OH. The hydroxyl group is simultaneously deprotonated by the carboxylate anion that is held in close proximity due to the cyclic nature of the anhydride.

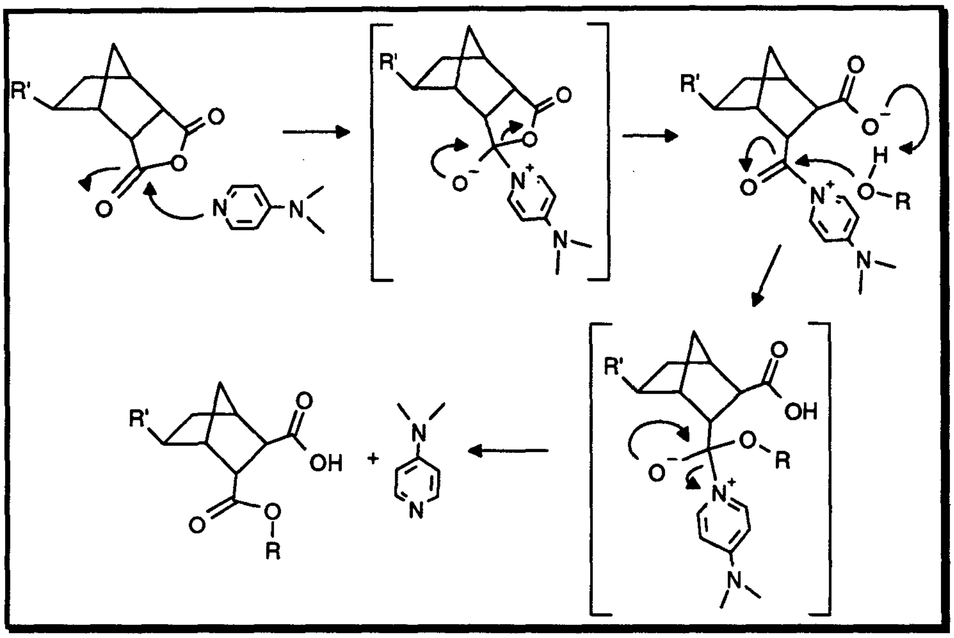


Figure 14

The ability of DMAP to catalyze the reaction with substantial success lies in the low energy, resonance-stabilized intermediate (Figure 15).

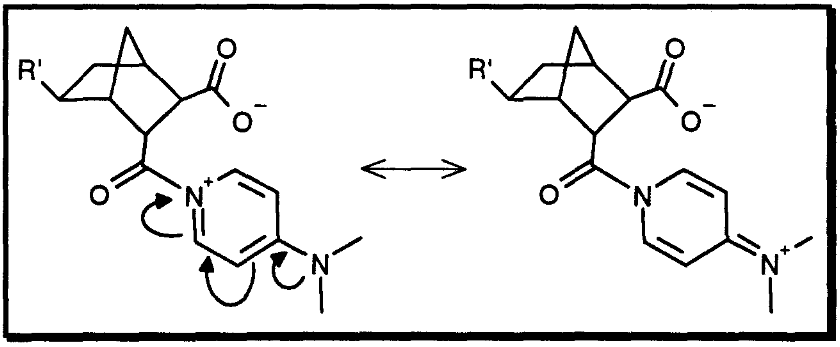


Figure 15

The analogous PDMS-(glycidyl ether)$_2$ synthetic silicone (**3**), would also be susceptible to nucleophilic attack on the epoxy group by the carbohydrate hydroxyl anions yielding an ether linkage with a newly formed hydroxyl group α to the graft point (Figure 16). This may be the next set of experiments to pursue.

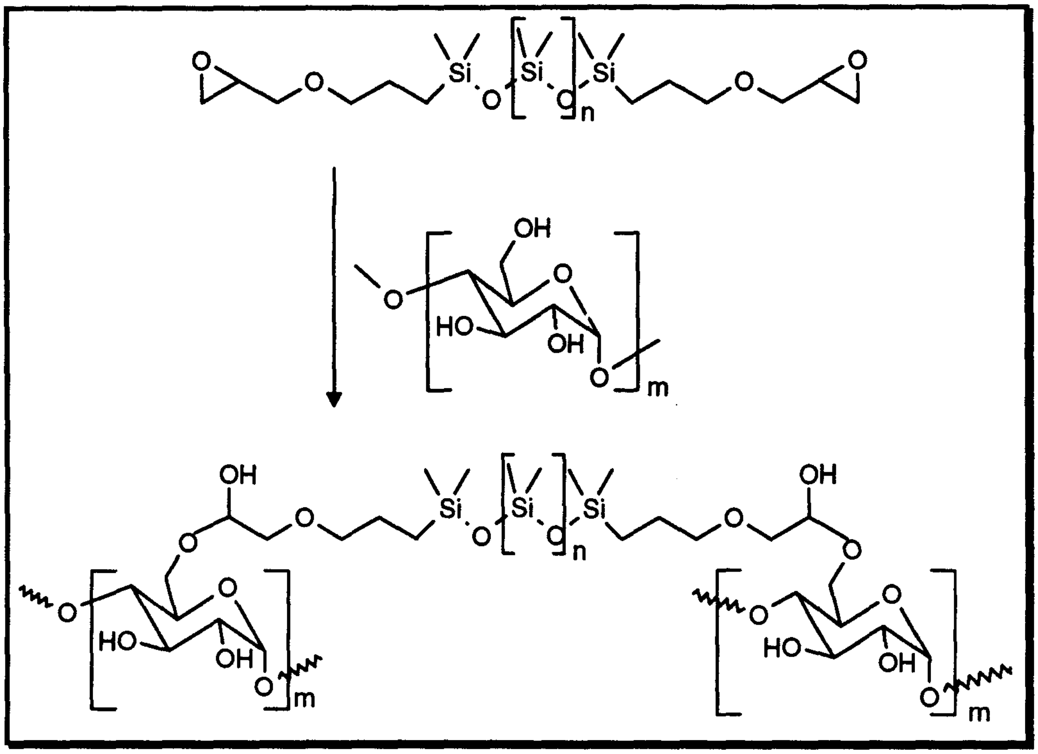


Figure 16

Series 1: Low Molecular Weight (750) α,ω-Dianhydride-Silicone-Starch Composites

Some information has been accumulated concerning the silicone-starch composite formation. The protocol (see Experimental section) involves starch at ambient moisture levels, the silicone and DMAP in dry DMSO heated at approximately 70 °C. The reaction seems to occur rapidly, requiring only twenty minutes of stirring before a product can be obtained. Upon completion of the reaction, the product was purified by kugelrohr distillation to remove the DMSO. The reaction has also been attempted without catalyst and without solvent in separate reactions. In both cases the result was a heterogeneous mixture of unreacted starch and silicone. Removal of DMSO by kugelrohr distillation was performed both times for consistency.

Once the starch-silicone grafting conditions were optimized, a series of reactions with different relative amounts of the starting materials was performed. The resulting physical properties for each of the respective starch-silicone composites varied according to the relative ratio between anhydride (A) unit attached to the silicone and glucose (G) units in starch (see Table 1).

Table 1: Physical Properties of Series-1 Silicone-Starch Composites

STARCH (GLUCOSE UNITS)	SILICONE (ANHYDRIDE UNITS)	PROPERTIES	GLASS TRANSITION (T_g in °C)	T_m (decomp.) (°C)
1	3	tacky	-38	280
1	1	plastic-like	-17 ?	240
5 (DMSO removed)	1	brittle-flaky	-	230
5 (DMSO not removed)	1	gelatin-like	-	230
20	1	rubbery	-	230
50	1	rubbery	-	230

Differential Scanning Calorimetry For Series-1

Differential scanning calorimetry analysis was performed on the starting materials and the respective composites. As expected, starch does not show a glass transition temperature (Table 1). It decomposes at approximately 280 °C. The silicone(cyclic anhydride)$_2$ has a glass transition temperature at -33.38 °C. This is a substantial increase over the hydride-terminated PDMS which typically has glass transition temperatures around -150 to -100 °C depending on chain length of the polymer.[3] This is one of the lowest glass transitions temperatures known, presumably because the silicon-oxygen bonds have considerable torsional mobility.[47] The higher T_g value for the silicone(dianhydride)$_2$ is easily rationalized when the rigid, bulky anhydride termini are considered. Their size would reduce the overall segmental mobility.

The T_g values for series-1 composites were difficult to obtain (Table 1). It was difficult to ascertain whether these were true values or artifacts caused by unreacted silicone at low starch content levels. At higher starch content levels, the starch dominated the thermal properties of the composites. It will be interesting to see if lower T_g values will be observed in the series-2 composites that have an increased -Me$_2$SiO- content.

Swelling Tests for Series-1

Water-soluble (uncrosslinked) polymers such as amylose absorb water, swell and concomitantly dissolve (or erode).[16] In certain cases, depending on the desired application of the starch composite formed, this is an advantageous property. In other instances, it may be desired to have analogous polymers which absorb water and do not begin to erode. To ascertain the swelling capacity of each of the synthesized composites, a series of “solubility” or “swelling” tests were conducted. In one set of tests, a sample of each composite was placed in a capped vial filled with 1 milliliter of either water at 25°C, water at 100°C sealed in resistant plastic screw-cap vials, deuterated chloroform, or water at pH = 9. After 24 hours, the solvent was removed and the samples were weighed at maximum swell (Table 2).

Table 2: Swelling Test Results "Maximum Swell" for Series-1 Composites

Composite	1A:0.3G	1A:1G	1A:5G DMSO removed	1A:5G DMSO not removed	1A:20G	1A:50G
Sample Mass (g)	0.0837	0.0236	0.1198	0.3093	0.1273	0.0613
Swelled in H_2O (g)	0.1641	0.0573	0.1877	0.1879	0.3966	0.1984
% weight gain	96	143	57	-39	211	224
Sample Mass (g)	0.0691	0.0276	0.1836	0.4416	0.2359	0.0649
Swelled in $CDCl_3$ (g)	0.0977	0.0523	0.2450	0.3563	0.2845	0.0643
% weight gain	41	89	33	-19	21	-1
Sample Mass (g)	0.0373	0.0333	0.0329	0.2922	0.1451	0.0722
Swelled in (pH=9) H_2O (g)	0.1054	0.0955	0.1053	0.4768	0.7311	0.0369
% weight gain	183	187	220	63	404	-49
Sample Mass (g)	0.0374	0.0394	0.0448	0.1004	0.0725	0.0481
Swelled in boiling water	0.0899	0.0306	0.1926	0.0313	0.0516	soluble yellow
% weight gain	140	-22	330	-69	-29	-

Table 2 clearly shows a trend in which the water-swelled composite is nearly twice the weight of the dry sample. This weight increase is especially noticeable in the 1A:20G composite and even more so in the 1A:50G composite where there is an increase in weight of 211 and 224% respectively in mass. This may be rationalized by considering that as the hydrophilic starch content increases, the composite's capacity for water uptake should do likewise.

For the $CDCl_3$ tests, it was observed that the swelled sample is approximately 50% heavier for each composite. It will be interesting to see if these trends will reverse when composites are made using silicones of higher (1500 g mol^{-1}) molecular weight. It should be noted that the 1A:5G (not kugelrohred) sample lost weight in both solvent tests. This is presumably the result of DMSO leaching out into the solvent. This point has been confirmed by proton NMR of the $CDCl_3$ solvent extracts. Dimethylsulfoxide was present in all of the extracts.

The only other signals seen in the NMR were those of unreacted silicone(bicyclic anhydride)$_2$. It was present in substantial amount in the 1A:0.3G sample as was expected and in tiny (barely present compared to DMSO) amounts in the 1A:1G extract. This suggests that the upper limit for the ratio of this reaction using the low molecular weight silicone is approximately 1A:1.1G. To study this further, a known amount of liquid N_2 crushed 1A:0.3G will be "washed" by Sohxlet extraction. Masses of the composite and unreacted silicone in the flask will then be determined more accurately. Calculating by difference should give a fair indication of the exact maximum moles of A that can be reacted with a known amount of starch.

The swelling tests conducted in slightly basic (pH = 9) water allowed a determination of the relationship between abstraction of the γ carboxylic proton by base and the swelling properties of the composites. The anion formed should allow for more water uptake (Figure 17).

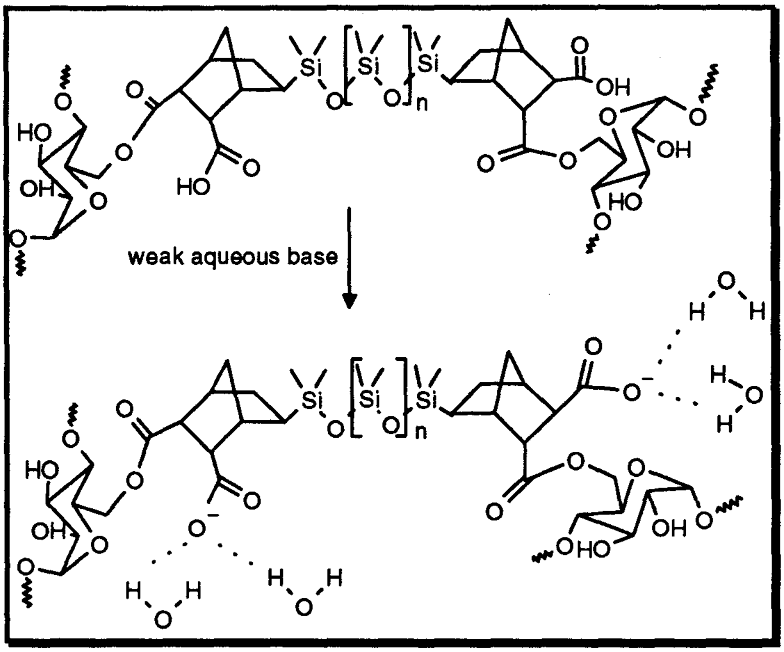


Figure 17

The results (Table 2) seem to indicate that the degree of ionization of the carboxylic acid influences the swelling properties of the samples. The swelled samples weighed 3-5 times more than the corresponding dry ones. The exceptions were the 1A:5G (DMSO not removed) and the 1A:50G composites. The 1A:5G material clearly lost mass due to DMSO loss, however still weighed more swelled than dry. The 1A:50G compound actually weighed less when at "full swell". This suggests that at this starch composition, the material was actually dissolving under these conditions and there was not enough silicone cross-linking to contribute new properties to the mixture. Starch was the dominant component. Thus, when the solvent was removed, some dissolved material was removed with it, actually skewing the results. See the discussion below concerning appearance (or lack of) a signal in the ester, carbonyl (C=O) region.

Swelling in boiling water gave somewhat puzzling results. The 1A:0.3G material actually doubled in mass when swelled while the 1A:1G material essentially remained constant. This at first seemed strange considering the material with less relative starch content seemed to swell more than the other did. However, if one imagines thermal opening of unreacted α,ω-dianhydride silicone or ester hydroysis of the starch-silicone composites in hot water, regardless of the hydrophobicity of the silicone, a diacid results which would increase hydrophilicity. Since the silicone oligomers are short-chained (5-6 -Me_2SiO- units) polymers, it is plausible to envision the polar termini interacting with the boiling, aqueous environment. For the 1A:5G (DMSO removed) material, the swelling properties seem to follow the expected tendency to swell (5 times original weight) due to higher starch content without decomposing because the relative silicone content must be high enough to deter this from occurring. The loss of DMSO in the other 1A:5G composite is the dominating factor causing a loss of weight at full swell, while at relative starch compositions higher than this, dissolution of the starch or thermal decomposition (hydrolysis of the ester linkages or decomposition of starch as indicated by the yellow homogeneous solution with no solid remaining) of the material ensues.

In a separate set of tests, a sample of each composite was placed in a vial filled with 1 milliliter of water or deuterated chloroform, but this time after 24 hours, the solvent was removed and the sample was left to sit open to the atmosphere and was weighed after 24 hours of air drying on the lab bench (Table 3).

Table 3: Swelling Test Results "After Drying" for Series-1 Composites

Composite	1A:0.3G	1A:1G	1A:5G DMSO removed	1A:5G DMSO not removed	1A:20G
Sample Weight (g)	0.0303	0.0190	0.2262	0.1477	0.2023
Swelled in Water then dried (g)	0.0297	0.0169	0.1164	0.0717	0.4405
% weight gain	-198	-11	-49	-51	118
Sample Weight (g)	0.0361	0.0236	0.0240	0.1974	0.1594
Swelled in $CDCl_3$ then dried (g)	0.0142	0.0211	0.0209	0.0587	0.1173
% weight gain	-61	-11	-13	-70	-26

The trend gathered from Table 3 indicates that all of the samples (except for the 1A:20G composite which retained enough water to double in weight) do not retain any type of moisture. When left to stand after swelling, all of the solvent dissipated. In fact, all of the other samples actually lost weight indicating a loss of unreacted silicone or DMSO leaching out of the respective sample.

Spectroscopic Data For Series-1

Solid state NMR (^{13}C CPMAS) was performed on the 1A:1G composite. The results revealed a spectrum which included signals representing the starting material starch and the peaks representing the bicyclic anhydride linking groups in the expected positions as well as signals indicating the presence of silicone methyls. They were present in the silyl-methyl region upfield at δ=1.7 ppm (see Experimental section). This was the expected result and is encouraging considering the starting material is a refined white powder and the product is a clear, colorless, plastic-like material.

It is noteworthy that proof of actual chemical bond formation in the starch-silicone composites has been acquired. Fourier transformed infrared spectroscopy has been carried out on KBr pellet samples of each composite. The pellets were made from finely crushed (under liquid N_2) aliquots of each composite. In all reaction ratios, a new signal was observed between 1733 cm^{-1} and 1745 cm^{-1} (see Experimental section). This range represents the C=O stretch of an ester bond. In the case of the 1A:0.3G sample, a relatively strong signal was present in addition to signals at 1778 cm^{-1} and 1854 cm^{-1} which represent the C=O stretches and vibrations of the unreacted cyclic anhydride moiety. For each successive sample, as starch content increased, the magnitude of the ester carbonyl stretch diminished as was to be expected. In these spectra, there were no signals indicating the presence representing the silicone starting material.

For all of the samples, the ester carbonyl peak was broad. It is almost certain that the width of the signal is caused because it is overlapping with the γ C=O stretches of the carboxyl moiety created in the cyclic anhydride opening. For some of the composites, 1A:0.3G, 1A:1G, and 1A:1G (DMSO removed), there are distinct shoulders around 1710 cm^{-1}. This is where these carboxyl signals are expected to appear as determined by the model study in which water hydrolysis of the anhydride termini was carried out.

For the composite with 1A:50G composition, no carbonyl peak was observed. A limit of detection of the instrument must prohibit the detection of the relatively minute number of ester cross-linkages. However, the physical appearance of the product is different from the starting material starch, suggesting that there is ester formation in the small proportion that was intended.

Series 2: Mid-Range Molecular Weight (1500) α,ω-Dianhydride-Silicone-Starch Composites

The redistribution polymerization of "mid-range" (1000-3000 g mol^{-1}, compound **7**) and "higher" (9000 g mol^{-1}, compound **8**) molecular weight α,ω-dianhydride silicones were successfully carried out as previously discussed. All characterization suggests that the desired products were produced (Figure 18). To be more specific, other than NMR integration and GPC analysis, the products were identical in all respects to the short chained α,ω-difunctionalized starting material.

Compound **7** was reacted with starch in various ratios of anhydride termini (A) and monomeric glucose units in starch (G). With the higher molecular weight silicone, less moles of anhydride termini (A) (and thus, less subsequent ester linkages) would be needed to introduce the same amount of $-Me_2SiO-$ units into a composite with comparison to a series-1 product.

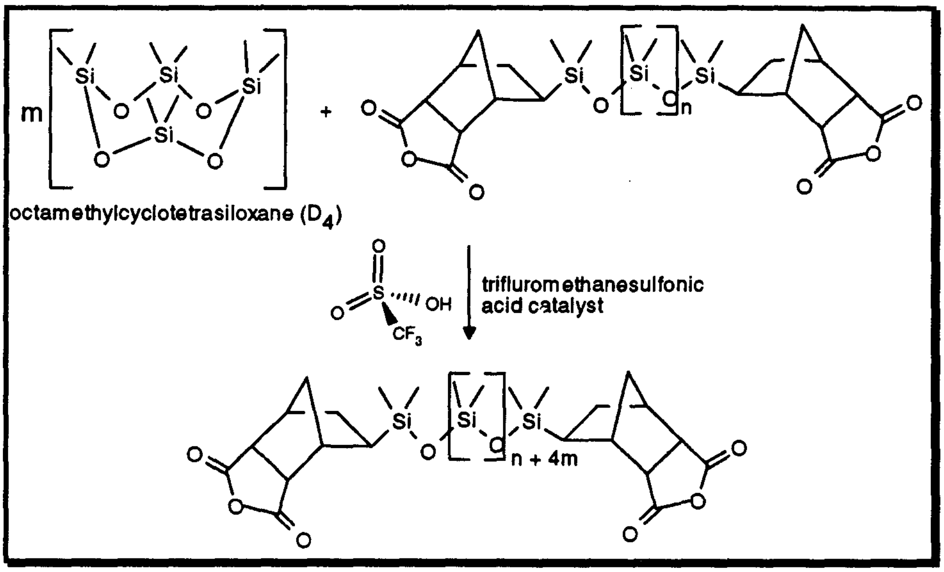


Figure 18

Syntheses of these series-2 starch-silicone compounds were carried out under the identical conditions as for the series-1 materials. The resulting physical properties for each composition, as for series-1, seemed to vary according to the relative proportions of starting materials (Table 4). The series-2 1A:1G composite product was plastic-like, but opaque in nature. Upon removal of DMSO, the material seemed to still have an oily texture distinguishing the increased quantity of $-Me_2SiO-$ units of the longer chained silicone. The number of cross-links was not at its limit, using series-1 as a measuring stick. The series-2 1A:5G composite product was a glassy, transparent, colorless plastic-like material very similar to the series-1 1A:1G composite. The series-2 1A:20G composite was soft but not quite gooey translucent material like warmed Saran Wrap. The series-2 1A:50G composite was an orange-yellow gummy material which until proven otherwise seems quite unappealing at the present time.

Table 4: Physical Properties for Series-2 Silicone-Starch Composites

STARCH (GLUCOSE UNITS)	SILICONE (ANHYDRIDE UNITS)	PROPERTIES	GLASS TRANSITION (T_g in °C)	T_m (decomp.) (°C)
1	1	opaque plastic-like		
5	1	plastic-like		
20	1	soft-translucent		
50	1	orange-gummy		

Differential Scanning Calorimetry For Series-2

Swelling Test for Series-2

As above for series-1 (Table 2), swelling tests were conducted to gauge the physical properties of this series of composites so as to serve as a comparison to series-1 compounds which utilized the smaller chained oligomeric silicone in their synthesis (see Table 5).

Table 5: Swell Test Results for Series-2 Composites

Composite	1A:1G	1A:5G	1A:20G	1A:50G
Sample Mass (g)	0.0144	0.0244	0.0546	0.0587
Swelled in H_2O (g)	0.0547	0.0817	0.1879	0.2574
% weight gain	280	235	244	339
Sample Mass (g)	0.0143	0.0164	0.0410	0.1246
Swelled in $CDCl_3$ (g)	0.0630	0.0330	0.0827	0.1439
% weight gain	341	101	102	15
Sample Mass (g)	0.0114	0.0164	0.0617	0.1479
Swelled in (pH=9) H_2O (g)	0.0360	0.0754	0.2617	0.6262
% weight gain	216	360	326	323
Sample Mass (g)	0.0088	0.0094	0.1349	0.0795
Swelled in boiling water	0.0869	0.0896	solubilized	solubilized
% weight gain	888	853	-	-

Just as in the series-1 tests, the trend was for the swelling to increase in water with increasing starch content. The masses of the swelled series-2 1A:1G composite were approximately 300% heavier than when dry, while the 1A:50G material was heavier by about 450%. The reverse trend, with similar quantitative increases, was observed for the swelling tests in chloroform. For the tests in basic water, the tendency was again similar to that of neutral water and the values of swell were also comparable. There was no greater swelling of the series-2 composites in basic (pH=9) water over neutral water. This increased swelling was anticipated because of the reasons stated above (Figure 17) as well as the fact that series-1 exhibited these observations. Thus, in spite of the fact that the pK_a of the γ-carboxylic group is around 4-5 (assumption based on the pK_a of acetic acid) suggesting all of these moieties may be ionized in neutral water also, increased swelling was anticipated. The absence of this trend was likely due to the fact that less cross-linking existed with respect to the amount of material in the sample. Because of the longer chained silicone, a more "hydrophobic presence" persisted.

The boiling water swell tests for series-2 revealed results that were difficult to rationalize. While the higher starch content composites, 1A:20G and 1A:50G both completely dissolved (or decomposed), the lower starch content materials seemingly swelled to as high as ten times their original weights.

This ability to swell with greater capacity for series-2 composites is a general characteristic seen throughout all of the tests. Trends of swelling were similar to those of series-1, but mass differentials were greater. To rationalize this behavior, one may think of the silicone cross-linkers. Since the number of ester linkages is relatively the same, it must be the longer silicone chains that influence this effect. For the lower molecular weight chains, the cross-linking was shorter and thus created tighter packing of the starch-silicone grafts. The longer chains allow for more "loosely packed" particles, thus leading to the slightly more amorphous material for this series of composites (Figure 19). This leaves "more room" for the solvent molecules to fit into.

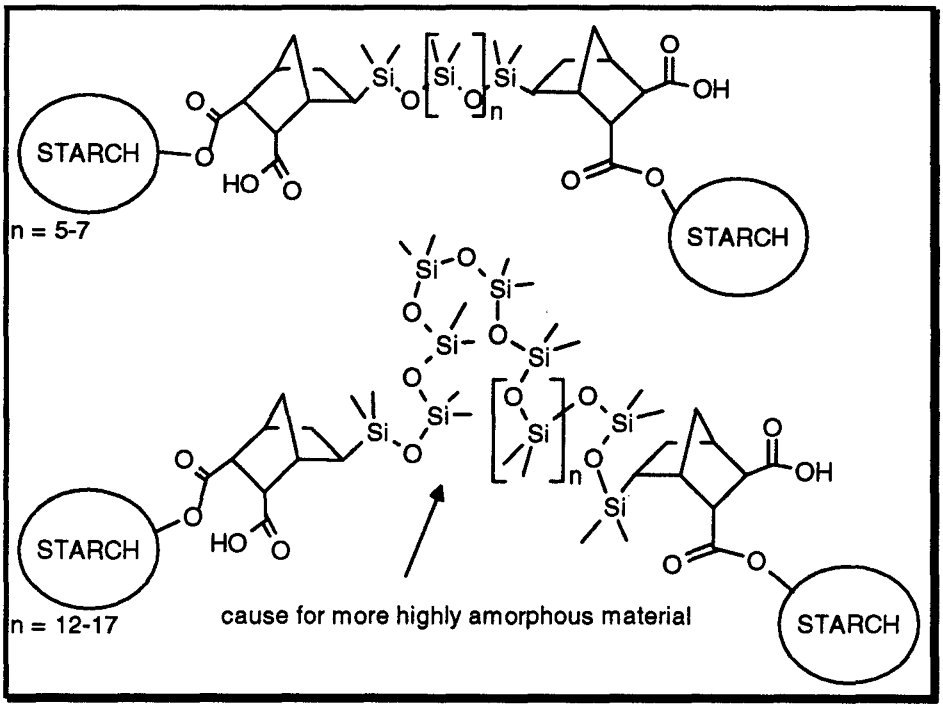


Figure 19

Spectroscopic Data For Series-2

Conclusions and Future Directions

Now that evidence for a true chemical linkage in the form of an ester bond has been found (e.g. FTIR), the next step is to perform solid state Nuclear Magnetic Resonance (^{13}C-CPMAS) on the rest of the starch-silicone composites (other than 1A:1G) to verify the presence of methyl carbons from the silicone. This information in combination with the water (neutral, basic and boiling) and $CDCl_3$ swelling tests that have been completed serve to assist us in determining the cross-linking density of the materials synthesized. It would seem that at higher ratios of the silicone (A) for series-1, the properties of the products take on a more brittle quality. This may be rationalized by the higher number of ester (cross linking) linkages which exist in these samples. However, a higher quantity of cross-linking also means a higher proportion of hydrophobic silicone present. This would explain why these samples swell less in water than the higher starch content composites did. Furthermore, if the number of cross-links is constant, but more -Me_2SiO- groups are present via longer chained polymers (series-2 and series-3), it would seem that the material may actually be able to swell more because the increased pliancy of the material seems to allows more space for the solvent to penetrate. Conversely, it seems that higher starch content with a moderate amount of cross-linking lends itself to the formation of flowing, gel-like substances.

It would be extremely interesting to see what would result if the degree of cross-linking is again kept constant (do not alter the magnitude of A), while the degree of hydrophobicity is increased even further. For this reason, a third series of composites has been synthesized using 9000 g mol^{-1} silicone with the same α,ω-cyclic anhydride functionality. The silicone was formed using the same approach as depicted in Figure 18. It remains to be seen if the data for these materials fit the trends already described. It is anticipated that the next series of composites will have even more favorable characteristics.

Another line of analysis that may be accomplished involves acquiring contact angles of each composite as well as the starting material starch. One strategy attempted was to take 100 mg of each sample crushed by the liquid nitrogen technique and make a pellet using the pellet press WITHOUT using KBr. This was done using the series-1 compounds in the hope that disks with flat surfaces sufficient enough to obtain the contact angles would be formed and provide hydrophobicity data. Depending on the sample, the composites revealed themselves to be either to "pasty" upon applying pressure or to brittle with no bonding ability, falling apart instantly. A more promising approach will be to redissolve each sample in hot DMSO and dip a microscope slide into the resulting solutions. The slides will then be put into an oven under reduced pressure to remove the DMSO. This should leave a film of each composite on the slide ideal for contact angle testing.

Of course, once the higher molecular weight, functionalized silicone is prepared and reacted with starch in the appropriate ratios, all the analyses described above will be performed on those products including differential scanning calorimetry. The higher volume of silicone will hopefully impose T_g(s) upon the newly formed composites.

Finally, there are many alternative approaches one may take in the pursuit of biopolymer-silicone interactions. For example, beside the "linking" organic group method mentioned in this paper, it may be possible to attach an allyl group coupling agent to the carbohydrate first, and then perform hydrosilylation using hydride-terminated PDMS. There is precedence for this using tri-glucose units.[6]

Furthermore, though it has not been stressed in this report, a series of reactions is in the works in which the starch hydroxyl anion is formed using n-butyllithium.[39] To this intermediate, hydride-terminated PDMS has been added providing electrophilic terminal silicon atoms with the hope of having a H^- leaving group formally leave in the form of H_2 gas.

The avenue worth pursuing at this point, in my opinion, is the one which continues the anhydride-terminated silicone research, at least to the point of obtaining higher molecular weight starting materials and reacting this with starch (now completed with series-3). The chemistry has been proven and it may be found that the properties of the potential composites could be very exciting. In addition, a comparative study of T_g values, spectroscopic data, and contact angles will be much more revealing once all of the data is gathered.

Also, I believe it would be very beneficial to pursue the glycidyl ether-terminated silicone. This silicone has been made very easily using BOTH high and low molecular weight PDMS in very high yields. There is no reason we cannot react them with starch (Figure 16). In the past, attempts to "open" up the epoxide were done without catalytic help or raised temperatures. The reaction might proceed more easily if a catalyst is used. Each functional glycidyl ether group still presents one cross-linking unit but this time, the size of the silicone is more controllable without having to do the triflic acid reaction. It would be useful to study the hydrolytic stability of the α-hydroxyl ether linking group. The physical properties of the composites formed could also be informative. When the stoichiometric ratios of starch and silicone-linking-group are identical, are the physical characteristics of the product the same as the cyclic anhydride linking group or does the nature of the linking group influence the material and if so, to what extent?

Another line of research which would lead to hydrophilic-hydrophobic composites would involve the use of *mono*-functional, hydrophobic siloxane polymers.[40] Rather than using an α,ω-functionalized silicone which ultimately acts as a macro-crosslinking agent, one can conceive of a mono-functionalized silicone acting as a macro-protecting group. It would serve to hydrophobize hydrophilic biopolymers possibly allowing them to enter an organic media. Would the loss of any cross-linking attributes reduce the "plastic-like film" character leaving a more granular product with new and interesting hydrophobic properties? This approach is very feasible. The reactions leading to the proposed product (Figure 20) all have precedence[40] except for the functional group used.

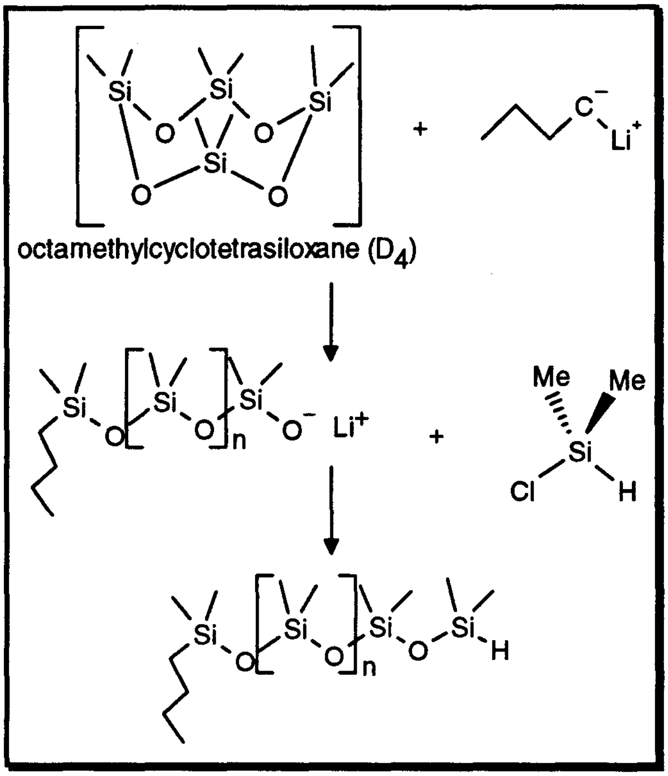


Figure 20

There is no precedence of a monofunctionalized silicone with the bicyclic anhydride terminus (Figure 21). However, there is precedence of the bifunctionalized silicone.[23,24]

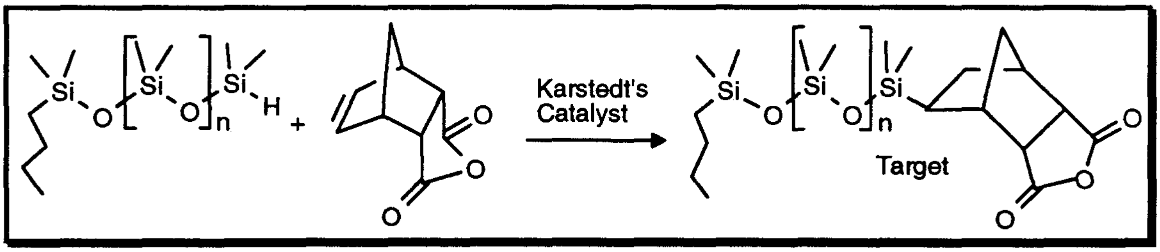


Figure 21

The route to the mono-hydride terminated silicone oligomer is also readily attainable[40,41] through the anionic ring opening polymerization of D_4. It is a living polymerization initiated by alkyl lithium in the presence of tiny amounts of promoters such as THF.[4] This system gives rise to controllable molecular weights.[40] To produce the desired terminus on the silicone, one adds an appropriately functionalized chlorosilane which, in this case, is the hydride functionalized dimethylchlorosilane (Figure 20).

Whether applying the approach of the macro cross-linker (α,ω-functionalized) or mono-terminated protecting group (Figure 21), one should most certainly begin to explore the use of functional groups other than the ones already explored. Using the redistribution approach shown in Figure 18, one can envision growing silicones with desired endgroups as long as the functionality is stable to either base or acid.[31] The potentially more challenging step would be to synthesize the 1,3-functionalized disiloxanes if they are not commercially available. The generic synthesis involves the condensation of chlorsilanes (Figure 22).[3]

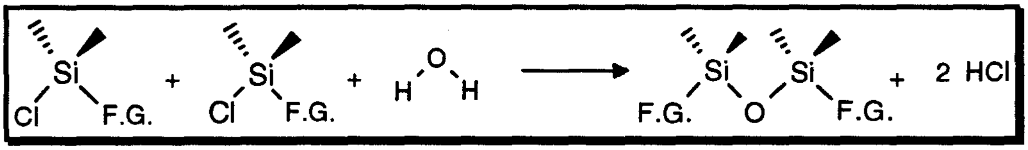


Figure 22

There is precedence for α,ω-terminated silicones with varying reactivities.[36] See Figure 23 for a few examples of these possible endgroups.

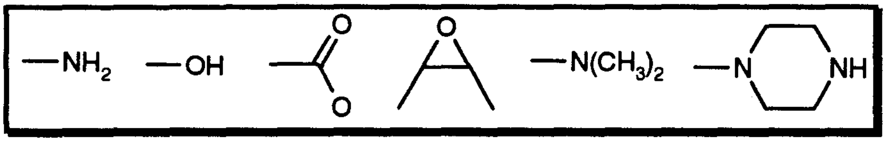
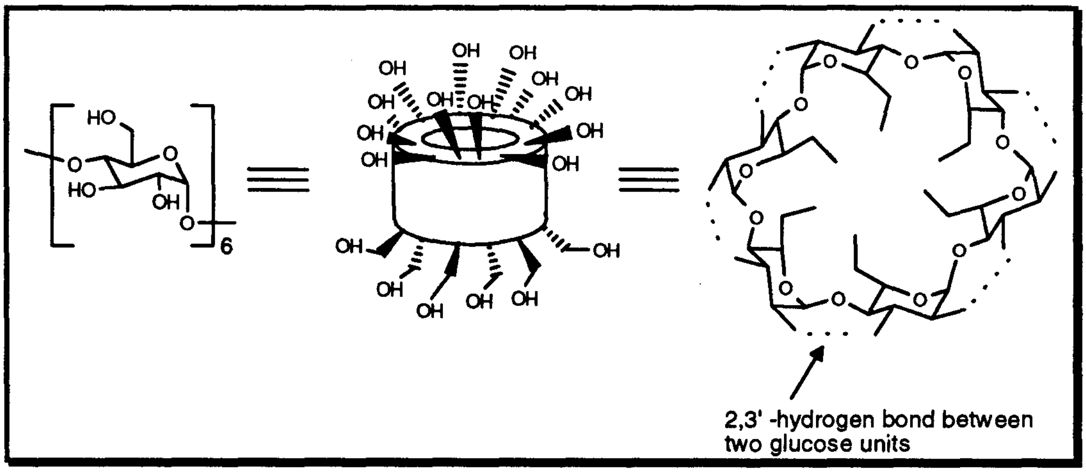


Figure 23

There are many conceivable applications for these silicones when their functionalities are altered. To follow one line of thinking as an example, one may foresee using silicones having electrophilic moieties that are susceptible to attack by polypeptide oligomers. A material could be formed that may lend itself to use in the fabrication of medical intra-venous IV bags.[42] This idea may solve the problem encountered with present day I.V. bags which are susceptible to chlorine leaching into the biomaterial. These bags are presently made from polyvinyl chloride (PVC).

Another application of interest for the above "silicone-protein" materials could be medical bandages. If the bandage were constructed from such materials, one may imagine two advantages. The first would be that the bandage will peel away without adhering to the wound because of repulsive hydrophobic-hydrophilic interactions. This would alleviate potential pain and/or discomfort. The second potential advantage might be in the biopolymeric portion. The hydrophilic portion should be attracted to the side of the wound. If the proteinaceous functionality contained a medicinal material, it might have medicinal benefits swelling or dissolving into the injured area.[42]

An additional avenue of research that could be pursued does not involve macromolecular, hydrophilic biopolymers. Therefore, it does not enter into the field of "materials science" or synthetic polymer-biopolymer interaction. The idea of hydrophobizing cyclodextrins seems to be one with interesting potentials.[43] Cyclodextrins are naturally occurring host molecules composed of a number of glucose units (in the case of α-cyclodextrin - 6) linked head to tail in an α-(1→4) relationship to form a ring called cycloamylose.[44] Below is a representation of α-cyclodextrin (Figure 24).



2,3' -hydrogen bond between two glucose units

Figure 24

It has a relatively inflexible doughnut-shaped structure. The top of the molecule has twelve secondary hydroxyl groups from positions 2 and 3 of the glucose units while the bottom has the six primary hydroxyl groups from position 6.[44] The outside of the cyclodextrin is consequently very hydrophilic while the inside is a rather hydrophobic cavity.

Because of these physical characteristics, the cavity can accommodate *guest molecules* which take advantage of the hydrophobic interactions to drive the system to form *inclusion complexes*. The size of the guest molecule is the determining factor for the formation of the complex. A benzene molecule is small enough to fit in a six glucose unit cyclodextrin. Applications include separation techniques and chemical derivatization of the guest molecule if the cyclodextrin is properly derivatized and the conditions are correct.

There are many possibilities for chemically derivatized cyclodextrins.[45,46] One might conceive of derivatizing cyclodextrins at either the α,ω-termini of a di-functionalized silicone or possibly even along the backbone in a multi-functionalized silicone. One could also imagine a "protected" cyclodextrin with a macro-organic moiety resulting from reaction with a mono-functionalized silicone such as the one portrayed in Figure 21. This system could lead to various uses which are situation specific. One example is to imagine using these silicone-cyclodextrin complexes at the interface of a subtle "oil-water" mixture such as ether and water. Just as water is slightly (6%) soluble in ether, there are some molecules which are primarily organic soluble but will also slightly dissolve in water. For a more full recovery of the organic compound, it is plausible to use this proposed complex at the water-ether interface when doing extractions. The silicone would anchor the complex in the organic phase while the cyclodextrins would dangle into the aqueous phase to "pull" small organic molecules into their organic cavity (Figure 25). Removal of the water and dissolution with excess organic solvent would liberate the desired molecules.

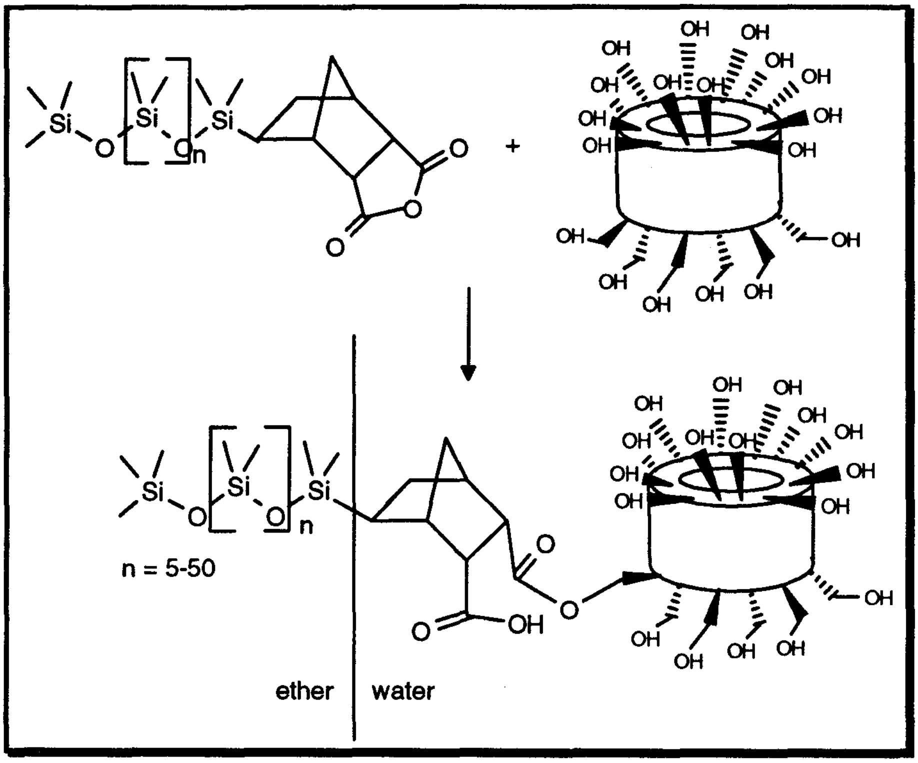


Figure 25

Experimental Section

General Procedures. All reagents used were taken directly from the bottle and used without further purification. Solvents used were purified before use. Dimethylsulfoxide was refluxed over and subsequently distilled from BaO, discarding the first 5% and the last 10% and stored over 4A molecular sieves. Cyclopentanol was refluxed over and subsequently distilled from CaH_2, discarding the first 5% and last 10% and then stored over 4A molecular sieves. All hydrosilylations were done neat in an open atmosphere. All other reactions were done under a dry nitrogen atmosphere.

^1H NMR were performed on either a Bruker AC-200 (200.13 MHz), a Bruker AC-300 (300.13 MHz) or a Bruker AM-500 (500.13 MHz) spectrometer. All natural-abundance ^{13}C NMR were performed on either a Bruker AC-200 (at 50.32 MHz), a Bruker AC-300 (at 75.03 MHz) or a Bruker AM-500 (at 125.78 MHz) spectrometer. ^{13}C NMR spectra were recorded with broad-band proton decoupling. Solid state ^{13}C NMR was performed on a Bruker AC-100 (100 MHz). ^{29}Si NMR were performed on a Bruker AC-300 spectrometer. Infrared spectra (IR) were recorded on a Bio-Rad FTS-40. Mass spectrometry was performed using either electron impact (EI) or chemical ionization (CI) techniques. This was accomplished using a VG ZAB-E mass spectrometer.

The molecular weight distributions of the oligomers were analyzed using a Waters Gel Permeation Chromatograph equipped with a Waters 410 Differential Refractive Index detector. Two Jordi Mixed bed columns in series were utilized with 1,1,1-trichloroethane as solvent flowing at 1.5 mL/min. Narrow molecular weight polystyrene standards from Polymer Laboratories were used for calibration of the chromatographic system.

Preparation of Polydimethylsiloxane(allyl glycidyl ether)$_2$. To a solution of benzene (5 mL) containing allyl glycidyl ether (0.14 mL, 1.15 mmol) was added hydrogen-terminated polydimethylsiloxane (PDMS) [500 centistokes] (5.2 mL, 0.57 mmol). The mixture was stirred at room temperature under a dry nitrogen atmosphere for 2 min. before 3 drops of platinum-divinyltetramethyldisiloxane solution in toluene (Karstedt's catalyst) was added. The mixture was allowed to stir for 36 h at room temperature during which time the clear solution became pale yellow in color. To remove the platinum catalyst, 0.3 g of activated DARCO G60 charcoal was added to the mixture and heated at 90°C for 5 min. After cooling the charcoal was filtered off and washed with cold benzene 3 times.

Upon removal of benzene under reduced pressure, a clear viscous liquid remained (3.24 g, 0.18 mmol, 65 %). ^{1}H NMR: (CDCl3, 200 MHz) δ (ppm) = -0.07 (s, 6H), 0.47 (t, 2H), 1.59 (tt, 2H), 2.57 (m, 1H), 2.76 (m, 1H), 3.17 (tt, 1H), 3.43 (m, 3H), 3.70 (dd, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 0.0, 0.9, 14.0, 23.4, 44.1, 50.7, 71.9, 74.2. ^{29}Si NMR ($CHCl_3$, 300 MHz) δ (ppm) = -22.5, -21.9, 7.2. IR (neat) ν = 2963, 2906, 1945, 1412, 1261, 1075, 1021, 799, 500 cm^{-1} **NOTE:** The characteristic signals for the Si-H bond vibrations at 2128 cm^{-1} and the C=C double bond vibrations at 1647 cm^{-1} for the respective starting materials were not present in the product.

Preparation of Acid Catalyzed Benzylamine Opening of Allyl glycidyl Ether Epoxide (5). To allyl glycidyl ether (2 mL, 16.9 mmol) was added benzylamine (9.2 mL, 84.3 mmol). This was followed by the addition of acetic acid (0.10 mL, 1.6 mmol). The mixture was stirred overnight at room temperature. The crude product mixture was distilled under vacuum (12 mm Hg). Colorless fractions distilled at 78°C (excess benzylamine) and 190°C, leaving an orange-brown paste-like impurity in the round bottom flask.

The clear, viscous fraction at 190°C was determined to be pure product (2.41 g, 10.9 mmol, 64%). ^{1}H NMR: ($CDCl_3$, 200 MHz) δ (ppm) = 1.93 (s, 1H), 2.64 (m, 2H), 3.37 (d, 2H), 3.57 (s(br), 1H), 3.74 (s, 2H), 3.85 (m, 1H), 3.87 (d, 2H), 5.16 (dd, 1H), 5.17 (dd, 1H), 5.80 (m, 1H). Calc. for $C_{13}H_{19}NO_2$, m/e 221; found, 222.

Preparation of Benzyl-Hydrogen Maleate. To benzyl alcohol (5.17 mL, 0.05 mol) was added maleic anhydride (5 g, 0.05 mol). The mixture was stirred overnight at 80°C under a dry nitrogen atmosphere. The reaction was monitored by TLC (silica, eluting solvent-ether, UV detection) and indicated that the crude product mixture contained more than one compound. Isolation of the desired product was performed using radial chromatography (fraction 1: hexane; fractions 2: hexane/ether (55:45); fractions 3-7: ethyl acetate).

The desired product was obtained as a white solid (0.71 g from a 1 g aliquot, 3.45 mmol, 71%). ^{1}H NMR: ($CDCl_3$, 200 MHz) δ (ppm) = 5.13 (s, 2H), 6.22 (s, 1H), 6.23 (s, 1H), 7.25 (s, 5H), 9.91 (s, 1H). ^{13}C NMR: ($CDCl_3$, 50 MHz) δ (ppm) = 67.7, 128.4

(intense), 130.1, 132.0, 134.3, 166.1, 167.3. IR (KBr pellet) ν = 3066, 2926, 1731, 1641, 1455, 1413, 1259, 1216, 1167, 754, 699 cm^{-1}.

Preparation of Diels-Alder Adduct: Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic-anhydride (or the Bicyclic Anhydride) (2). Dicyclopentadiene (70 mL) was decomposed to the cyclopentadiene monomer by heating at 176 °C.

To an ethyl acetate (15 mL) solution (requires heating for dissolution) of maleic anhydride (3.2 g, 0.033 mol) was added ligroin, b.p. 60-90°C (10 mL). The solution was cooled thoroughly in an ice bath. Cyclopentadiene (3.2 mL, 0.047 mol) was added and the flask was swirled vigorously before being returned to the ice bath. The white spear-shaped crystals formed were obtained by filtration and washed 3 times with cold ligroin. Yield of the adduct: (4.1 g, 0.025 mol, 76%; m.p. = 164-166 °C). ^1H NMR: ($CDCl_3$, 200 MHz) δ (ppm) = 1.65 (dd, 2H), 3.50 (d(br, m), 4H), 6.28 (t, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 46.1, 47.0, 52.7, 135.5, 171.3. IR (KBr pellet) ν = 3602, 2981, 2880, 1854, 1172, 1663, 1466, 1335, 1297, 1232, 1090, 907, 736, 608.

Preparation of Low Molecular Weight Polydimethylsiloxane(allyl glycidyl ether)$_2$ (3). To allyl glycidyl ether (5.37 mL, 0.047 mol) was added hydrogen-terminated polydimethylsiloxane (PDMS) [1~2 centistokes] (9.06 g, 0.023 mol) neat. The mixture was stirred at room temperature under a dry nitrogen atmosphere for 1 min. before 3 drops of platinum-divinyltetramethyldisiloxane (Karstedt's catalyst) was added. The mixture was allowed to stir for 24 h at room temperature during which time the clear solution became pale yellow in color. To remove the platinum catalyst, anhydrous diethyl ether and activated DARCO G60 charcoal (0.3 g) were added to the mixture and heated at reflux for 5 min. After cooling, the charcoal was filtered off using cold ether to wash 3 times. The ether was removed by rotary evaporation. The product was a clear, more viscous liquid (15.37 g, 0.022 mol, 99 %). ^{1}H NMR: (CDCl3, 200 MHz) δ (ppm) = 0.01 (s, 6H), 0.44 (m, 4H), 1.55 (m, 4H), 2.54 (s(br), 2H), 2.72 (s(br), 2H,), 3.08 (s(br), 2H), 3.36 (m, 6H), 3.66 (d, 2H, ^{1,3}J=11.3 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz) δ (ppm) = 0.0, 0.9, 14.0, 23.4, 44.1, 50.7, 71.9, 74.2. ^{29}Si NMR ($CHCl_3$, 300 MHz) δ (ppm) = -22.3, -21.7, 7.4. IR (neat) ν = 2960, 2872, 1480, 1413, 1340, 1260, 1089, 1035, 910, 800, 705 cm^{-1}.

Preparation of Polydimethylsiloxane(Bicyclic Adduct)$_2$ (4). To the bicyclic adduct (4.26 g, 0.026 mol) was added hydrogen-terminated polydimethylsiloxane [1~2 centistokes] (5.02 g, 0.013) neat. The mixture was stirred at room temperature under a dry nitrogen atmosphere for 1 minutes before 3 drops of platinum-divinyltetramethyldisiloxane (Karstedt's catalyst) was added. The mixture was allowed to stir for 24 h at room temperature during which time the clear solution became pale yellow in color. The reaction was monitored by ^{1}H NMR and depending on whether the Si-H proton of the silicone (δ = 4.6 ppm) or vinyl protons of the anhydride (δ = 6.29 ppm) persisted, a minute amount of the corresponding reagent was added with 1 drop of catalyst until both signals disappeared.

To remove the platinum catalyst, anhydrous diethyl ether and activated DARCO G60 charcoal (0.3 g) were added to the mixture. The flask was then heated at reflux for 5 min. After cooling, the charcoal was filtered off using cold ether and washed 3 times with ether. The ether was removed by rotary evaporation. The product was a clear, viscous liquid (7.83 g, 0.011 mol, 84%). ^{1}H NMR: ($CDCl_3$, 300 MHz) δ (ppm) = 0.04, 0.07 (s, 6H), 0.64 (t(br),1H), 1.54 (m(br), 2H), 1.64 (m(br), 2H), 2.80 (d(br), 2H), 3.38 (m, 2H).

^{13}C NMR: ($CDCl_3$, 75 MHz) δ (ppm) = -0.7, 1.1, 25.8, 26.7, 40.8, 41.2, 41.6, 49.6, 52.7, 172.1, 172.3. ^{29}Si NMR (CDC13, 250 MHz) δ (ppm) = -21.8, -20.5 (more intense), -3.2. NOTE: The 'proton coupled' silicon NMR was also run and the terminal Si in the silicone was a septet as opposed to the doublet of septets seen for H-$\underline{Si}$-$(CH_3)_2$- in the starting material. IR (neat) ν = 2962, 2877, 1859, 1782, 1411, 1261, 1224, 1083 (br), 908, 801, 591 cm^{-1}.

Preparation of Hydrolyzed Polydimethylsiloxane(Bicyclic Adduct)$_2$. To a solution of acetone containing PDMS(bicyclic anhydride)$_2$ (0.30 g, 0.41 mmol) was added distilled water (0.015 mL, 0.83 mmol) and 1/2 pellet of KOH. The mixture was allowed to stir for 24 h at which time dilute HCl was added to neutralize (pH = 5) the solution. The desired product was extracted from diethyl ether, which was dried using anhydrous magnesium sulfate. The solvent was removed by rotary evaporation. The product was a viscous, clear and colorless liquid (0.11 g, 0.14 mmol, 32%). ^{13}C NMR: (DMSO-D_6, 50 MHz) δ (ppm) = -0.9, 1.0, 22.5, 26.4,45.6, 48.8, 104.3, 107.2, 173.2, 173.5. ^{29}Si NMR (DMSO, 300 MHz) δ (ppm) = -21.3, -14.9, 7.23. IR (neat) ν = 3199 (br), 2962, 1716, 1414, 1263, 1026, 860, 799, 694 cm^{-1}.

Preparation of Polydimethylsiloxane(Bicyclic Anhydride-Cyclopentane-Ester-Acid)$_2$ (6). To a solution of distilled cyclopentanol (0.25 mL, 2.75 mmol) containing catalytic dimethylaminopyridine (33.6 mg, 0.28 mmol) was added polydimethylsiloxane(bicyclic anhydride)$_2$ (1 g, 1.38 mmol). The mixture was stirred at room temperature under a dry nitrogen atmosphere for 48 h. The reaction was monitored for disappearance of cyclic anhydride carbonyl signals at 1178 cm^{-1} and 1854 cm^{-1} as well as the development of a new ester carbonyl signal at 1733 cm^{-1} and a new acid carbonyl signal at 1710 cm^{-1}. Isolation of the purified desired product was performed using positive pressure (flash) chromatography (aliquot = 0.57g, height = 18 cm, width = 2 cm; fractions 1-7; hexane; fractions 8-32: hexane/ethyl acetate (50:50); fractions 33-40: ethyl acetate).

The desired product was obtained as a very viscous, sticky, clear and colorless liquid (0.88 g, 0.94 mmol, 68%). ^{1}H NMR: ($CDCl_3$, 200 MHz) δ (ppm) = 0.04 (s, 6H), 1.36 (m (br), 1H), 1.66 (m (br), 8H), 2.47 (m (br), 2H), 2.57 (m (br), 2H), 2.84 (m (br), 2H), 3.06 (m (br), 2H), 5.11 (m (br), 1H). ^{13}C NMR: (CDC13, 50 MHz) δ (ppm) = -0.9. 1.1, 23.7, 26.7, 32.1, 32.6, 39.1, 40.5, 41.5, 46.3, 47.7, 109.1, 172.3, 178.7. ^{29}Si NMR ($CHCl_3$, 300 MHz) δ (ppm) = -22.2, -21.8, 6.4. IR (neat) ν = 3102 (br), 2961, 2876, 2664, 1734, 1708, 1419, 1343, 1259, 1164, 1089(br), 1033(br), 905, 799, 698 cm^{-1}.

Preparation of Series-1 Starch-Silicone(Bicyclic Anhydride)$_2$ Composite. The general protocol without specific amounts is presented here. The ratios of the reactants and exact amounts are indicated in (Table 6). To a solution of distilled dimethylsulfoxide (DMSO) containing powdered, refined starch and dimethylaminopyridine (DMAP) (7% mole ratio w.r.t. glucose units in starch) was added α,ω-(bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic-anhydride)polydimethylsiloxane (**4**). The mixture was stirred at 80 °C under a dry nitrogen atmosphere for 1h. The DMSO was then removed by kugelrohr distillation (70 °C / 4 mm Hg). The resulting physical properties for each of the respective starch-silicone composites varied according to the relative ratio between anhydride (A) unit attached to the silicone and glucose (G) units in starch.

Table 6: Composition of Silicone versus Starch for Series-1 Composites

Ratio of Reactants	Amount of Silicone	Moles of Silicone	Amount of Starch	Moles of Starch according to

(A:G)	(g)	(mmol)	(g)	Glucose Units (mmol)
1:0.3	1.0	1.37	0.16	0.94
1:1	1.0	1.37	0.47	2.76
1:5 kugelrohred	1.0	1.37	2.30	13.53
1:5 not kugelrohred	0.5	0.69	1.15	6.76
1:20	0.2	0.27	1.87	11.00
1:50	0.1	0.14	2.34	13.76

Infrared spectroscopy was performed for each composite via KBr pellet formation. Liquid N_2 was poured over a 50 mg aliquot of each respective sample in mortar. The resulting brittle sample was crushed as finely as possible before the sample became amorphous again.

The 1A:0.3G composite product was a colorless, tacky-waxy film on the side of the flask (quantitative yield by mass). IR (KBr pellet) ν = 3416 (br), 2962, 2880, 1860, 1783, 1744 (less prominent), 1652, 1415, 1261, 1224, 1085, 1030, 946, 908, 798, 590 cm^{-1}.

The 1A:1G composite product was a transparent, colorless solid film adhered to side of the flask (quantitative yield by mass). ^{13}C CP/MAS (1.5 second recycle, 1 millisecond contact, 100 MHz) δ (ppm) = 1.7, 26.1, 40.5, 50.0, 72.7, 102.6, 173.7 (all signals broad). IR (KBr pellet) ν = 3424 (br), 2924, 1734, 1651, 1558, 1437, 1262, 1152, 1080, 1022, 953, 799, 668 cm^{-1}.

The 1A:5G composite product which was kugelrohr distilled to remove the DMSO was a hard, brittle off-white material (quantitative yield by mass). IR (KBr pellet) ν = 3415 (br), 2959, 2923, 1734, 1648, 1566, 1439, 1409, 1261, 1154, 1048, 1027, 953, 799, 576 cm^{-1}.

The 1A:5G composite product which was not kugelrohr distilled to remove the DMSO was a transparent and homogeneous (if undisturbed) gel (quantitative yield by mass). IR (KBr pellet) ν = 3362 (br), 2913, 1732, 1438, 1409, 1313, 1260, 1152, 1057, 1029, 955, 801, 702, 670, 577 cm^{-1}.

The 1A:20G composite product was a rubbery, white material (quantitative yield by mass). IR (KBr pellet) ν = 3370 (br), 2916, 1734, 1438, 1409, 1316, 1261, 1153, 1083, 1027, 953, 856, 799, 761, 705, 575 cm^{-1}.

The 1A:50G composite product was a rubbery, white material a little more brittle than the 1A:20G material (quantitative yield by mass). IR (KBr pellet) ν = 3413 (br), 3195, 2923, 1717, 1647, 1608, 1467, 1418, 1384, 1261, 1147, 1036, 962, 850, 806, 673 cm^{-1}.

Redistributed Polydimethylsiloxane(Bicyclic Adduct)$_2$ (1500 g mol^{-1}) (7). To polydimethylsiloxane(bicyclic adduct)$_2$ (1.0 g, 1.37 mmol) was added seven equivalents (2.99 mL, 9.62 mmol) of octamethylcyclotetrasiloxane (D_4). The desired molecular weight was an average molecular weight of 1500 g mol^{-1}. To achieve this, 10-15% excess D_4 was added to account for unreacted cyclics. The mixture was stirred at room temperature for 1 minute before 3 drops of trifluoromethylsulfonic acid (triflic acid) was added. The mixture became cloudy reddish-brown in color after 5 minutes. It was allowed to stir for 4 hours before being quenched with magnesium oxide (equivalent mole ratio w.r.t. triflic acid). The quenched mixture was left to stir overnight leaving a clear product with the reddish-brown triflate salts adhered to the flask. The silicone was dissolved in hexane and decanted into a 25 mL round bottom flask. The hexane was removed by rotary evaporation. The mixture was then distilled at reduced pressure (heated to 120 °C, 1 mm Hg) to remove low molecular weight cyclics.

The desired product was obtained as a slightly viscous, clear colorless liquid (1.34 g, 0.89 mmol, 65 %). ^{1}H NMR: ($CDCl_3$, 200 MHz) δ (ppm) = 0.04, 0.07 (different mol. wt.) (s, 6H), 0.64 (t (br),1H), 1.54 (m (br), 2H), 1.64 (m (br), 2H), 2.80 (d (br), 2H), 3.38 (m, 2H). ^{13}C NMR: ($CDCl_3$, 75 MHz) δ (ppm) = -0.7, 1.1, 25.8, 26.7, 40.8, 41.2, 41.6, 49.6, 52.7, 172.1, 172.3. ^{29}Si ($CHCl_3$, 300 MHz) δ = -22.3, -21.8, 5.2. IR (neat) ν = 2963, 2904, 1860, 1784, 1412, 1261, 1224, 1089 (br), 1021 (br), 908, 865, 800, 701, 591 cm^{-1}. Gel Permeation Chromatography: (polystyrene calibration) Mn/Mw = 1450 g mol^{-1}. It is important to note that all spectroscopic data is identical with the lower molecular weight starting material except for GPC and 1H NMR integration which indicates a molecular weight of approximately 3500 g mol^{-1}.

Preparation of Series-2 Starch-Silicone(Bicyclic Anhydride)$_2$ Composite. The general protocol without specific amounts is presented here. The ratios of the reactants and exact amounts are indicated in Table 7. To a solution of distilled dimethylsulfoxide (DMSO) containing powdered, refined starch and dimethylaminopyridine (DMAP) (7% mole ratio w.r.t. glucose units in starch) was added polydimethylsiloxane (1100 MW)-α,ω-(bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic-anhydride)$_2$ (**7**). The mixture was stirred at 80 °C under a dry nitrogen atmosphere for 1h. The DMSO was then removed by kugelrohr distillation (70 °C / 4 mm Hg). The resulting physical properties for each of the respective starch-silicone composites varied according to the relative ratio between anhydride (A) unit attached to the silicone and glucose (G) units in starch.

Table 7: Composition of Silicone versus Starch for Series-2 Composites

Ratio of Reactants (A:G)	Amount of Silicone (g)	Moles of Silicone (mmol)	Amount of Starch (g)	Moles of Starch according to Glucose Units (mmol)
1:1	0.5	0.45	0.16	0.91
1:5	0.5	0.45	0.77	4.53
1:20	0.5	0.45	3.10	18.2
1:50	0.1	0.09	1.54	9.06

As for series-1, infrared spectroscopy was performed for each composite using KBr pellets and sample crushed by the liquid N_2 technique.

The series-2 1A:1G composite product was plastic-like, but opaque in nature. Upon removal of DMSO, the material seemed to still have an oily texture distinguishing the longer chained silicone and/or unreacted silicone (see IR assignments). The number of cross linkages was not at its limit using series-1 as a measuring stick (quantitative yield by mass). IR (KBr pellet) ν = 3415(br), 2964, 1860 (weak), 1780 (weak), 1738, 1710, 1414, 1360, 1262, 1090, 1021, 862, 799, 701 cm^{-1}.

The series-2 1A:5G composite product was a transparent, colorless solid plastic-like material (quantitative yield by mass). IR (KBr pellet) ν = 3429 (br), 2963, 2923, 1737 (br), 1648, 1567, 1441, 1413, 1262, 1153, 1085, 1027, 954, 801, 574 cm^{-1}.

The series-2 1A:20G composite was a soft, not quite gooey translucent material like warmed cellophane (quantitative yield by mass). IR (KBr pellet) ν = 3382, 2965, 2915, 1733 (br), 1647, 1440, 1413, 1262, 1153, 1084, 1026, 953, 800, 705, 575 cm^{-1}.

The series-2 1A:50G composite was an orange-yellow gummy material (quantitative yield by mass). IR (KBr pellet) ν = 3325 (br), 2915, 1733 (weak, br), 1648, 1438, 1408, 1317, 1262, 1153, 1083, 1026, 952, 801, 761, 706, 575 cm^{-1}.

Redistributed of Polydimethylsiloxane(Bicyclic Adduct)$_2$ (10 000 g mol^{-1}) (8). To polydimethylsiloxane(bicyclic adduct)$_2$ (2.0 g, 2.75 mmol) was added 38 equivalents (34.0 mL, 0.11 mol) of octamethylcyclotetrasiloxane (D_4). The desired molecular weight was an average molecular weight of 10 000 g mol^{-1}. To achieve this, 10-15% excess D_4 was added to account for unreacted cyclics. The mixture was stirred at room temperature for 1 minute before 3 drops of trifluoromethanesulfonic acid (triflic acid) was added. The mixture became cloudy reddish-brown in color after 5 minutes. It was allowed to stir for 48 hours before being quenched with magnesium oxide (equivalent mole ratio w.r.t. triflic acid). The quenched mixture was left to stir for 1 hour causing the mixture to become a cloudy white in color. The mixture was dissolved in cyclohexane and the triflate salts were filtered off using Celite. Cyclohexane was removed from the filtrate by rotary evaporation. The mixture was then distilled at reduced pressure (heated to 210 °C, 1 mm Hg) to remove low molecular weight cyclics.

The desired product was obtained as a very viscous, clear colorless liquid (20.41 g, 2.27 mmol, 83 %). ^{1}H NMR: ($CDCl_3$, 200 MHz) δ (ppm) = 0.04, 0.07 (s, 6H), 0.64 (t (br),1H), 1.54 (m (br), 2H), 1.64 (m (br), 2H), 2.80 (d (br), 2H), 3.38 (m, 2H). ^{13}C NMR: ($CDCl_3$, 75 MHz) δ (ppm) = -0.7, 1.1, 25.8, 26.7, 40.8, 41.2, 41.6, 49.6, 52.7, 172.1, 172.3. ^{29}Si ($CHCl_3$, 300 MHz) δ (ppm) = -22.3, 5.3. IR (neat) ν = 2963, 2904, 1860, 1784, 1412, 1261, 1224, 1089 (br), 1021 (br), 908, 865, 800, 701, 591 cm^{-1}. Gel Permeation Chromatography: (polystyrene calibration) Mn/Mw = 30 000 g mol^{-1}???. It is important to note that all spectroscopic data is identical with the lower molecular weight starting material except for GPC and ^{1}H NMR integration which indicates a molecular weight of approximately 9000 g mol^{-1}.

Appendix

Differential Scanning Calorimetry

The point at which a linear polymer changes from a glassy substance to a rubbery material is known as the glass transition temperature (T_g).[47] When heated above the T_g, amorphous polymers pass successively through rubbery, gum-like, and finally liquid states with no clear boundary between the different phases. The T_g is known as a "second-order transition".[15] This transition is characteristic of a particular polymer in much the same way that a melting point is characteristic of corresponding low-molecular weight compounds. Exactly how different molecular features affect the glass transition temperature is still not fully understood. From what is understood to date, it must be noted that there is a close relationship between the T_g and the flexibility of a polymer chain. Flexibility depends more on rotation or torsion of chemical bonds in the backbone of a polymer and not on changes in bond angles. It is the "unwinding" of the randomly coiled polymer chain rather than bond angle distortion that has been found to affect glass transition temperature. Thus, flexibility depends on what is referred to as "torsional mobility".[47] Generally, the greater the torsional mobility, the lower the T_g.

The inherent flexibility of the backbone is, however, only one contributing factor to the glass transition temperature of a polymer. Torsional mobility is also affected by the side groups. Larger or charged side groups on a the same backbone may repel or attract each other causing lower chain mobility.[48] This would lead to higher T_g values.

Differential Scanning Calorimetry is one of the most convenient techniques for the measurement of glass transition temperatures. This process operates using two small metal containers. One contains the polymer sample, the other contains a control. The two are subjected to individual electric heaters with heat sensors that monitor each temperature. When the sample absorbs heat during a transition, the change is detected by the sensor which initiates greater current flow to compensate for the loss.[47] The greater current flow is translated into a transition temperature.

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