Synthesis and Characterization of Poly(silyl urethane)s Derived from Glycol-Modified Silanes

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ABSTRACT: Hybrid composites are a class of material that have gained substantial recognition due to their highly sought-after properties of both organics and inorganics. A novel method for incorporating inorganic content into urethane materials is through the use of organically modified silicate cross-linkers. Glycol-modified silanes, in particular, allow for the facile preparation of highly cross-linked urethane materials with a wide range of bulk and surface characteristics including glass transition temperature (-40.4–$85.6°C$), storage modulus (0.7–1.62 GPa), and surface energy (19.0–62.4 dynes cm^{-1}). Importantly, control of the overall polymer properties remains achievable via the structural control of macrodiols and isocyanates. Additionally, incorporation of silicate cross-linkers into urethane systems provides these materials with a hydrolyzable character, which may be controlled by altering the bulk polymer composition, cross-link density, and surface energy. The unique nature of these systems also allows for the preparation of highly cross-linked urethanes in the absence of any heavy metal catalysts and depending on the composition, with the use of little to no solvent. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 161–173, 2013

INTRODUCTION

The desire for new functional materials for a variety of specialty applications, such as catalysis, green fuels, and functional coatings, has stimulated a great deal of research devoted to the development and characterization of hybrid composites.[1] Materials composed of both organic and inorganic components have been shown to possess the highly sought-after properties of each of their constituents, such as the flexibility, low-density, and processability of organics and the hardness, strength, and thermal stability of inorganics.[1–4] These characteristics make hybrid composite materials particularly interesting for applications ranging from optics and electronics to biotechnology and high-performance coatings.[3–8]

Although hybrid materials may exist in a number of different forms, they are typically grouped into Class I and Class II materials.[9] Class I hybrids exist in a state where weak bonds, such as hydrogen bonds, van der Waals interactions, or ionic bonds between organic and inorganic compounds are the unifying force between components.[9] Stronger chemical bonding (typically covalent in nature) characterizes the interactions between organic and inorganic constituents in Class II hybrids.[9]

The simplest example of Class I hybrids are blends of inorganic and organic materials in the absence of any strong interaction.[1]

Doping of sol–gel matrices by organic dyes or other small organic compounds is a prime example of this class of material.[1,10] Although there are numerous different methods for the preparation of such blends, the absence of any molecular tethers may result in the formation of heterogeneous materials. Although even weak interactions between components may facilitate distribution of lower molecular weight components throughout the matrix and prevent heterogeneity problems, the advantages of homogeneity and controlled size, composition, and architecture on material properties have stimulated the design and synthesis of Class II hybrids.[11]

The diversity of Class II hybrid composites has thrived recently due to advancements in sol–gel chemistry and controlled polymerizations.[11–13] Unique hybrid materials have been designed based on polymer brushes, organic/inorganic copolymers, functionalized particles, and countless other controlled molecular architectures.[11] Furthermore, material properties of these well-defined hybrid materials support further investigations into hybrid material development.

Recently, the development of hybrid polyurethane materials has come into favor due to the numerous promising characteristics of networks such as abrasion resistance, low-curing temperatures, and favorable impact strengths in addition to the plethora

Additional Supporting Information may be found in the online version of this article.

of potential applications for which urethanes may be used.[14–16] Polyhedral oligomeric silsesquioxane (POSS) and poly(dimethyl-siloxane) (PDMS)-modified urethanes have been prepared for applications ranging from biomaterials to ultraviolet-curable coatings and textile treatments among many others.[17–23] In general, the incorporation of these inorganic constituents into polymeric materials led to improved characteristics such as biostability, flexibility, water resistance, heat resistance, and strength compared to the individual components alone. Additionally, a variety of unique optical and electronic properties may be imparted into urethane composites via the incorporation of inorganic components, such as POSS, within the polymeric matrix.

Motivated by a historically important hybrid copolymer, tributyltin methacrylate, which possesses a unique self-polishing behavior that became extremely important for the marine coatings industry, we sought to develop an environmentally friendly alternative hydrolyzable hybrid composite material with potential uses in marine and other specialty coating applications. Herein, the synthesis of urethane hybrids with glycol-modified silicate crosslinkers is presented. The influence of both isocyanate and silicate structure on resulting material properties such as glass transition temperature (T_g), modulus, hydrolysis rates, and hardness is examined. The effect of tethered low-energy macrodiols on material properties is also investigated.

EXPERIMENTAL

Materials

Tetraethyl orthosilicate (TEOS), ethylene glycol, 1,4-butanediol, 4,4′-methylenebis cyclohexylisocyanate (HMDI), poly(ethylene glycol) (PEG, $M_n \sim$ 950–1050), terathane 1000 polyether glycol [polytetramethylene oxide (PTMO); $M_n \sim$ 1000], and hydroxyl-terminated polydimethylsiloxane ($M_n \sim$ 550) were purchased from Sigma-Aldrich (Milwaukee, WI) and used as received unless otherwise noted. Methyltrimethoxysilane (MTMOS) was purchased from Fluka (Buchs, Switzerland). Desmodur N 3600 polyisocyanate, a homopolymer of hexamethylene diisocyanate, was received from Bayer MaterialScience (Pittsburgh, PA). N,N-Dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Fisher Scientific.

Characterization

All ^{1}H and ^{13}C-NMR were performed in CDCl$_3$ on a Bruker AVANCE 300 MHz nuclear magnetic resonance spectrometer with a TMS internal standard. Chemical shifts are reported in units of parts per million downfield from TMS. Thermogravimetric analysis was performed on a TA Instruments Q50 TGA using heating rates of 10°C min^{-1} under N$_2$ atmosphere. Glass transition temperatures were measured using a TA Instruments Q20 differential scanning calorimetry (DSC), with heating and cooling rates of 20°C min^{-1}. Glass transition temperatures were identified as the inflection point of the endotherm. FTIR spectra were acquired using a Thermo Scientific Nicolet 6700 FTIR using attenuated total reflectance mode from 4000 to 400 cm^{-1}. Contact angles were measured using an AST Products VCA Optima goniometer. Surface energies were calculated using the Van Oss/Chaudhury/Good theory,[24] and contact angle values were obtained for 3× distilled water, diiodomethane, and hexa-

decane. A Perkin Elmer DMA 8000 Dynamic Mechanical Analyzer was used to measure polymer glass transitions and moduli and operated in tension mode with a frequency of 1 Hz, 15 μm amplitude, and a temperature range of −70–150°C. Glass transitions were recorded as the maximum of the loss modulus. Gel fractions of the poly(silyl urethane)s were determined by soaking samples in THF for 24 h at room temperature. After the removal of the solvent, the samples were dried overnight to remove residual THF, and the gel fraction (Q_g) was calculated as

$$Q_g = \frac{m_f}{m_i} \times 100\%$$

where m_i and m_f are the initial and final masses of the poly(silyl urethane) samples, respectively. Film tack and hardness were measured using a TA XTPlus Texture Analyzer. Hardness is reported as the force in grams required to penetrate 10% of the depth of the film. Tack values are the force required to pull away from the film after the probe has been held constant at 10% into the depth of the film for 10 s. Coating hydrolysis was quantified by comparing sample masses before and after soaking in aqueous solution at room temperature for designated time periods. Briefly, polymers with known mass were placed in sealed containers with 20 mL distilled water. At the designated time point, the polymers were removed from the container, rinsed gently with distilled water, and dried in a vacuum oven at 50°C for 2 days to remove any residual water within the matrix. The percent hydrolysis was then calculated by comparing the initial and final sample masses using the equation:

$$\%\text{Hydrolysis} = \frac{m_i - m_f}{m_i} \times 100\%$$

### General Procedure for the Synthesis of Glycol-Modified Silanes

Glycol-modified silanes were prepared in a manner similar to that reported previously in the literature.[25,26] Briefly, MTMOS or TEOS was mixed with diol (ethylene glycol or 1,4-butanediol) in either 1 : 3 or 1 : 4 molar ratios in a round-bottomed flask equipped with a short path still head with magnetic stirring. The mixture was slowly heated to 140°C under an inert atmosphere at which point the alcohol produced began to distill. After reacting for 16 h, the reaction was cooled to room temperature, and residual alcohol and unreacted starting materials were removed under reduced pressure to yield the products as optically transparent viscous liquids.

Tetrakis(2-hydroxyethyl)orthosilicate: yield: 96%; ^{1}H-NMR (CDCl$_3$): 4.90–4.80 (OH), 3.93–3.90 (SiOCH_2), and 3.69–3.65 (CH_2OH). ^{13}C-NMR 65.67 and 63.68.

Tetrakis(4-hydroxybutyl)orthosilicate: yield: 94%; ^{1}H-NMR (CDCl$_3$): 4.80 (OH), 3.84–3.78 (SiOCH_2), 3.68–3.57 (CH_2OH), and 1.63–1.57 (CH_2). ^{13}C-NMR 61.91, 57.51, and 29.24.

1-Methyl-tris(2-hydroxyethoxy)silane: yield: 91%; ^{1}H-NMR (CDCl$_3$): 4.37–4.34 (OH), 3.90–3.73 (SiOCH_2), 3.70–3.58 (CH_2OH), and 0.20 (SiCH_3). ^{13}C-NMR 70.0, 69.6, and −1.8.

1-Methyl-tris(4-hydroxybutoxy)silane: yield: 95%; ^{1}H-NMR (CDCl$_3$): 4.63–4.57 (OH), 3.80–3.65 (SiOCH_2), 3.63–3.55
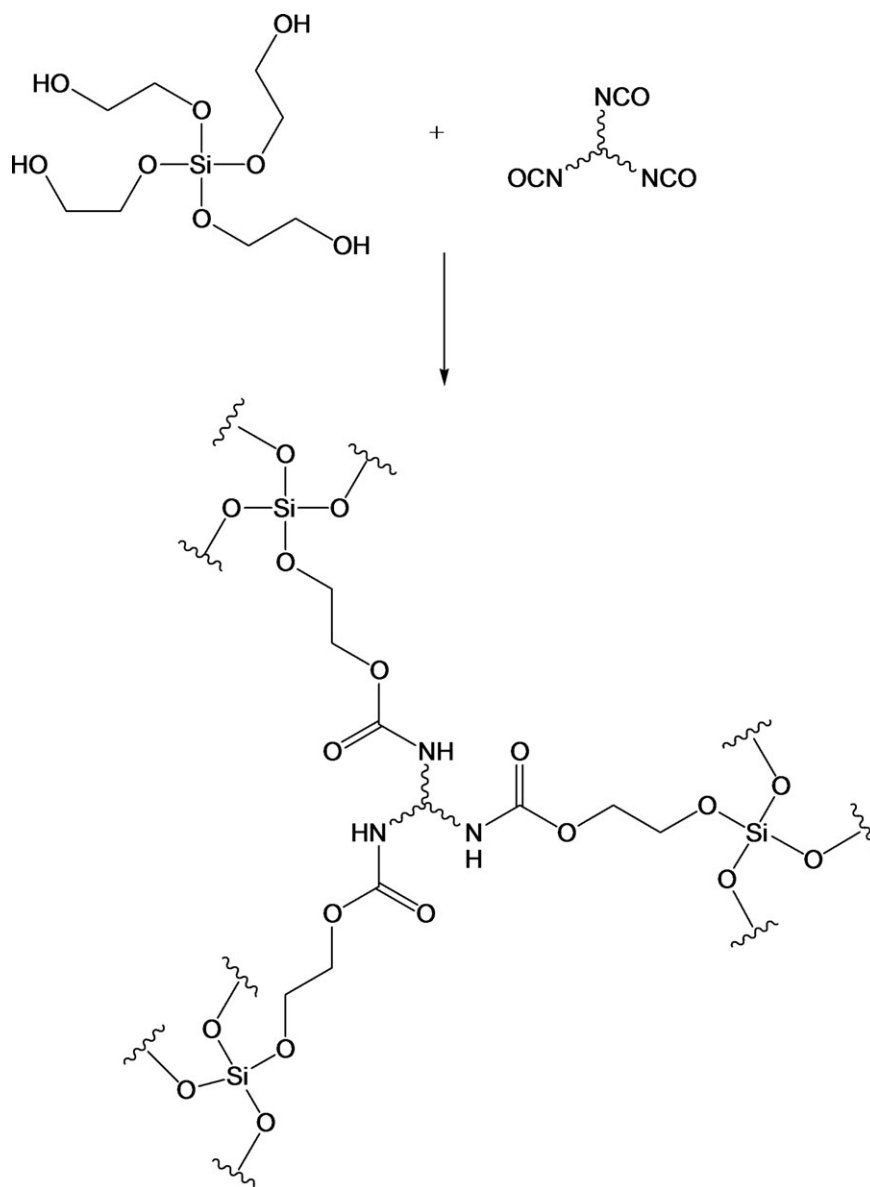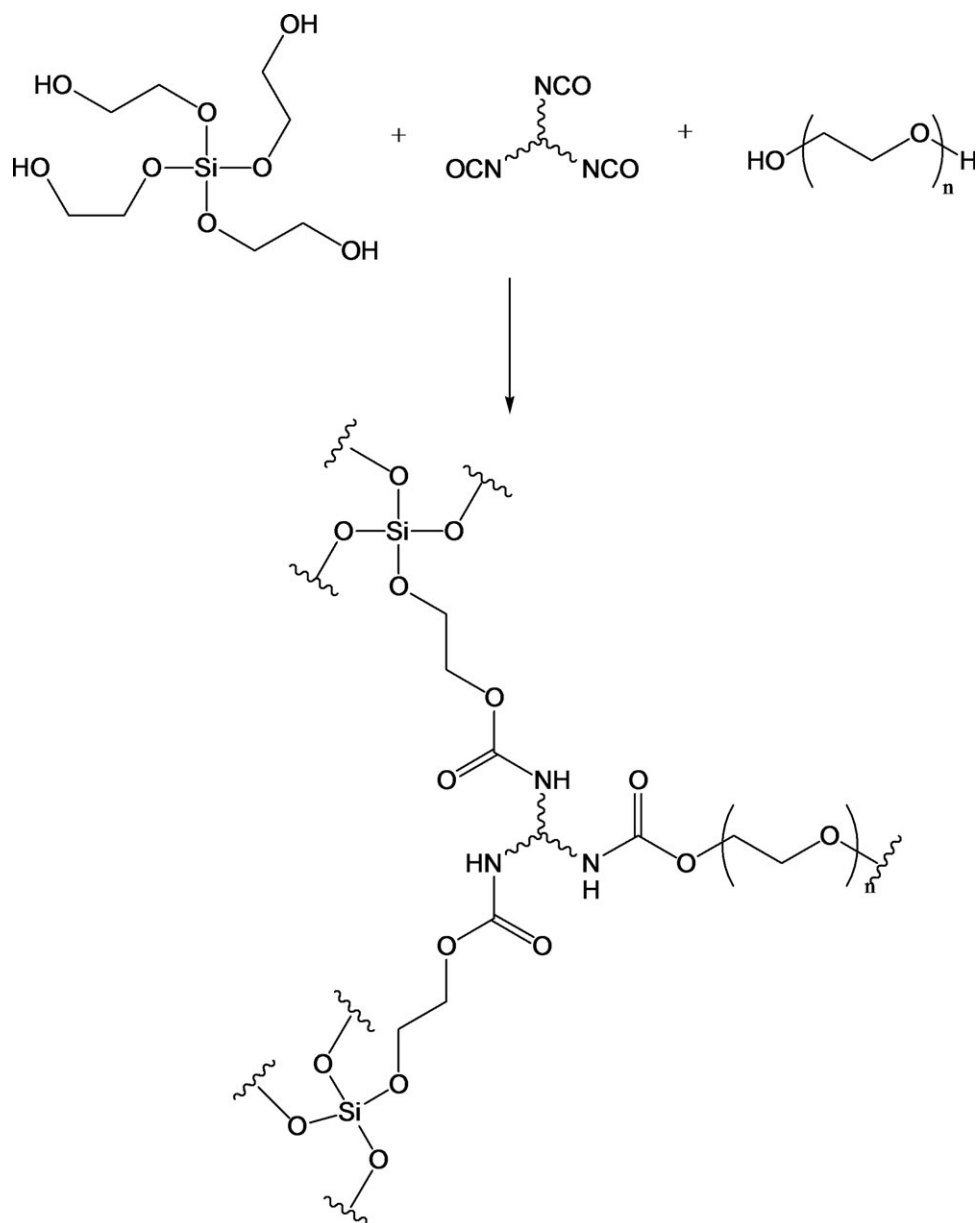
Figure 1. Representative synthesis of urethane network using tetrakis(2-hydroxyethyl)orthosilicate and Desmodur N 3600 polyisocyanate. *Note:* Desmodur is a proprietary homopolymer of hexamethylene diisocyanate.

(CH_2OH), and 0.17–0.13 ($SiCH_3$) ^{13}C-NMR 70.2, 69.7, 37.1, 36.3, and −1.8.

General Procedure for the Synthesis of Poly(silyl urethanes)

An oven-dried round-bottomed flask was charged with isocyanate followed by the addition of a stoichiometric (1 : 1 molar equivalent —NCO to —OH) amount of glycol-modified silane (Figure 1). The mixture was magnetically stirred at 55°C until optically transparent (∼ 4 h), at which point it was removed from stirring, poured into a mold or cast as a coating, and cured at 100°C for 24 h. Because of rapid gelation rates of certain combinations of isocyanates and silanes, some reactions were performed at room temperature in the presence of small amounts of DMF to promote miscibility of starting materials.

Poly(silyl urethanes) with macrodiols were synthesized by magnetically stirring isocyanate (4 mol eq) with a low-molecular weight (500–1000 g/mol) hydroxyl-terminated polymer [1 mol. eq.; PDMS, PTMO, or PEG] at 55°C (Figure 2). After 4 h, the isocyanate/macrodiol reaction was charged with the appropriate MTMOS-derived orthosilicate for polymers intended to be cross-linked via a trifunctional silane and stirred at 55°C until optically transparent. For materials cross-linked via a tetrafunctional silane, the isocyanate/surface modifier reaction was removed from heat after 4 h, diluted with a small amount of DMF, and cooled to room temperature for 1 h. A TEOS-derived orthosilicate in a small amount of DMF was then added to the reaction mixture and allowed to stir until optically transparent. When transparent, the reaction mixtures were poured into molds or cast as coatings and cured at 100°C for 24 h.

Figure 2. Representative synthesis of urethane network using tetrakis(2-hydroxyethyl)orthosilicate, Desmodur N 3600 polyisocyanate, and poly(ethylene glycol). *Note:* Desmodur is a proprietary homopolymer of hexamethylene diisocyanate.

RESULTS AND DISCUSSION

Synthesis and Characterization of Glycol-Modified Silanes and Poly(silyl urethanes)

The emergence of new technologies and applications requiring well-defined material specificity has stimulated the development of hybrid composite materials with a range of properties.[1,5] In this study, we examine the use of hydrolyzable silicate cross-linkers as a means to develop a range of hybrid urethane composites (Table 1) with varying material characteristics such as transition temperatures, surface energy, hydrolysis rate, and modulus. Although TEOS and MTMOS are widely used as precursors for the development of sol–gel materials,[9] due to their facile homopolymerization to form cross-linked siloxane-based materials, this study used them as starting materials for the development of hydrolyzable

cross-linkers for urethane materials. Transesterification of these silicates occurs readily in the presence of alcohols or glycols, provided that the low-molecular weight alcohol byproduct is removed to drive the reaction to completion. However, due to the bifunctionality of glycols, the opportunity arises for the formation of a mixture of products including bridged silane species when transesterification occurs at both glycol hydroxyl groups with two different silicon centers, ring structures when glycol hydroxyls are transesterified at the same silicon center, and finally the desired unbridged tris- and tetrakis-modified silanes (Figure 3, Supporting Information). Despite these possibilities, careful control of the reaction minimizes the formation of unwanted byproducts (Figure 4)

The synthesis of glycol-modified silane cross-linkers permitted the preparation of a range of highly cross-linked urethane materials
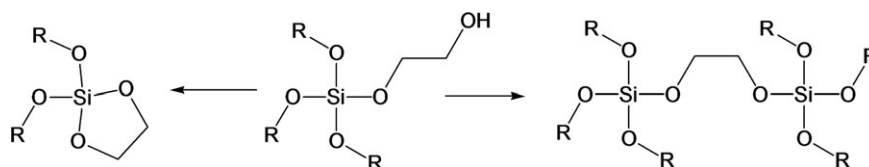
Figure 3. Potential side reactions of hydroxyl-terminated silicate cross-linkers.

via reaction with various polyisocyanates and macrodiols. Preliminary experiments indicated that the reaction of aromatic isocyanates with cross-linkers and macrodiols proceeded much more rapidly than that of aliphatic isocyanates, which was expected due to their well-known heightened reactivity compared to their aliphatic counterparts. However, the rapid and highly exothermic reactions involving the aromatic isocyanates resulted in the formation of undesirable urethane foams when large amounts of solvent were not used to control heat generation during the reaction, and therefore only aliphatic polyisocyanates were further investigated as potential-coating materials. After curing at 100°C for 24 h, the majority of the resulting products were optically transparent solids with the exception of some resins with PDMS macrodiols, which were white, opaque solids. Complete reaction of the starting materials was confirmed by monitoring the disappearance of the characteristic isocyanate peak at ~ 2270 cm^{-1} using FTIR (Figure 5) and further supported by polymer gel fractions ranging from 61.8 to 99.1% (Table II). Interestingly, reactions containing both

HMDI and tetrakis(2-hydroxyethyl)orthosilicate resulted in the formation of nonuniform coatings consisting of macroscopic crystalline solids randomly distributed in a partially cured resin even at prolonged curing times and higher temperatures. Furthermore, despite being able to form visually uniform materials, the combination of tetrakis(2-hydroxyethyl)orthosilicate with Desmodur polyisocyanate resulted in heterogeneous polymers with interspersed macroscopic rigid and flexible portions. This heterogeneity may result from the homopolymerization of the silicate cross-linkers to form highly cross-linked rigid silicon-rich domains leaving flexible urethane portions to polymerize in other macroscopic domains.

As expected, the cross-linked urethane materials exhibited a wide range of thermal properties due to differences in the cross-link density and polymer composition (Table II).[27] Networks containing Desmodur N 3600 as the isocyanate displayed glass transition temperatures markedly lower than their counterparts composed of HMDI as a result of the increased rotational
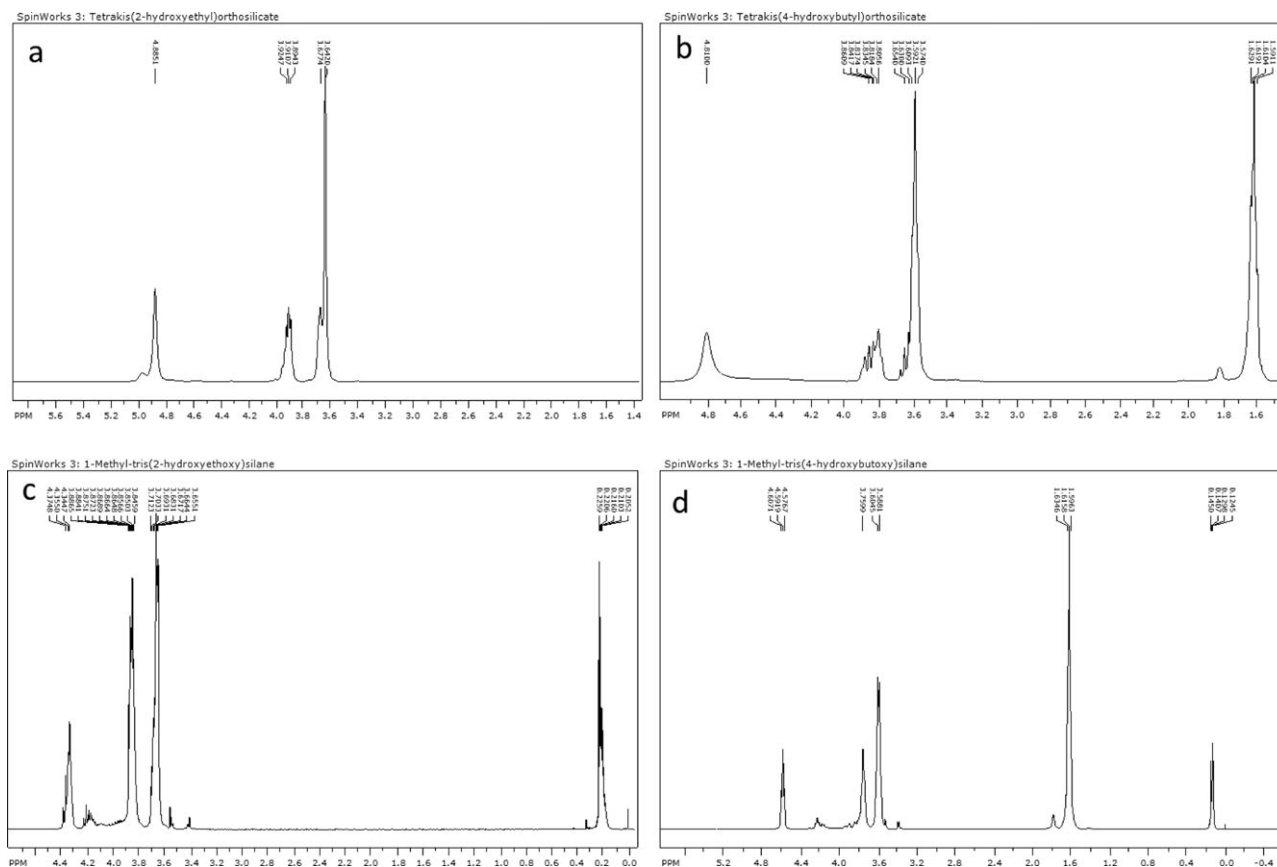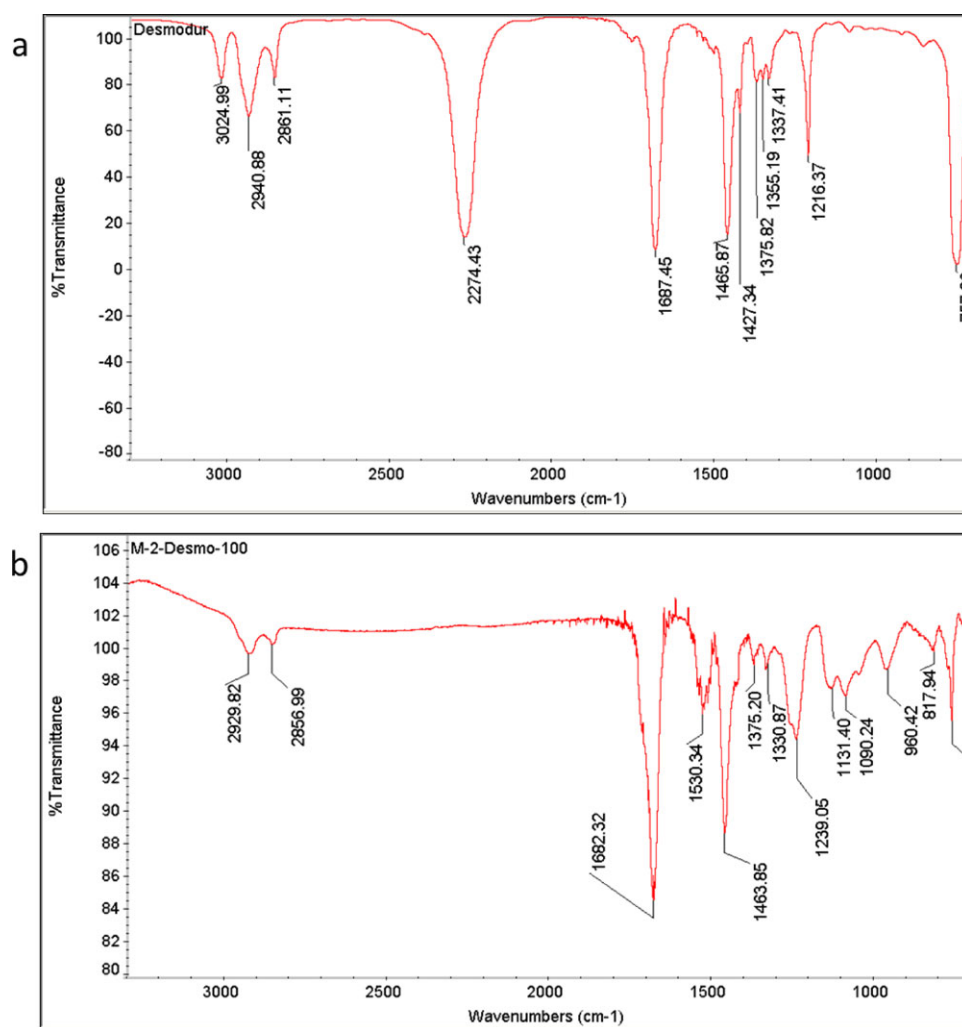

Figure 4. ^{1}H-NMR spectra of (a) tetrakis(2-hydroxyethyl)orthosilicate, (b) tetrakis(4-hydroxybutyl)orthosilicate, (c) 1-methyl-tris(2-hydroxyethoxy)silane, and (d) 1-methyl-tris(4-hydroxybutoxy)silane.

Figure 5. FTIR spectra of (a) Desmodur N 3600 polyisocyanate and (b) M-2-desmo-100 polyurethane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degrees of freedom associated with the linear, albeit trifunctional isocyanate, compared to the more rigid, primarily cyclic HMDI.[28] For example, the glass transition temperatures observed for T-4-cyclo-100 and M-4-cyclo-100 were 72.5°C and 52.1°C, respectively, while their counterparts composed of Desmodur were 10.3 (T-4-desmo-100) and 15.7°C (M-4-desmo-100) [Table II, Figure 6(a)]. The molar reactivity of the cross-linkers also influenced the transition temperatures as the incorporation of a trifunctional silicate cross-linker decreased the observed glass transition temperatures compared to a polymer composed of a tetrafunctional cross-linker (52.1°C for M-4-cyclo-100 compared to 72.5°C for T-4-cyclo-100).[28] Further influencing the glass transition temperature of the cured resins was the alkyl content of the silicate cross-linkers. The increasing alkyl content of the silicate cross-linkers derived from 1,4-butanediol allows for more rotational degrees of freedom (enhanced flexibility) than those derived from ethylene glycol as evidenced by a comparison of T_g for M-2-cyclo-100 and M-4-cyclo-100 (85.6°C vs. 52.1°C) as well as M-2-desmo-100 and M-4-desmo-100 (42.6°C vs. 15.7°C) [Table II, Figure 6(b)]. Importantly, material homogeneity has a substantial influence on the thermal

behavior of resulting materials, as those composed of heterogeneous materials (i.e., T-2-desmo-100), exhibit glass transitions for their respective softer domains, while transitions were not able to be observed for the more rigid silicon-rich domains. As a result, glass transition values of these materials are erroneously low compared to homogeneous materials (M-2-desmo-100).

The incorporation of macrodiol property modifiers into the urethane resin systems also significantly influenced the thermal behavior of these materials (Table II). Despite low-molar content of macrodiols polymerized into the resin (25% terminal hydroxyl content), the relatively high-molecular weight compared to the other resin components allowed the macrodiols to be the dominant component in the resulting thermal behavior of the polymer. As expected due to high correlation between glass transition temperatures of polyurethanes and their prepolymer derivatives,[29] the majority of these macrodiol-modified polymers exhibited glass transition temperatures well below room temperature. Observed T_g values for all network polymers with PEG 1000 components were between −15.3 and −40.4, which, although much higher than the value for PEG 1000 alone were substantially less than

Table I. Composition of Crosslinked Poly(silyl urethane) Network Polymers

Composition	Silane	Diol	Isocyanate	Macrodiol
T-2-cyclo-100	TEOS	EG	HMDI	None
T-2-desmo-100	TEOS	EG	Desmodur	None
T-4-cyclo-100	TEOS	BD	HMDI	None
T-4-desmo-100	TEOS	BD	Desmodur	None
M-2-cyclo-100	MTMOS	EG	HMDI	None
M-2-desmo-100	MTMOS	EG	Desmodur	None
M-4-cyclo-100	MTMOS	BD	HMDI	None
M-4-desmo-100	MTMOS	BD	Desmodur	None
T-2-cyclo-100-PDMS-500	TEOS	EG	HMDI	PDMS-500
T-2-cyclo-100-PTMO-1000	TEOS	EG	HMDI	PTMO-1000
T-2-cyclo-100-PEG-1000	TEOS	EG	HMDI	PEG-1000
T-2-desmo-100-PDMS-500	TEOS	EG	Desmodur	PDMS-500
T-2-desmo-100-PTMO-1000	TEOS	EG	Desmodur	PTMO-1000
T-2-desmo-100-PEG-1000	TEOS	EG	Desmodur	PEG-1000
M-2-cyclo-100-PDMS-500	MTMOS	EG	HMDI	PDMS-500
M-2-cyclo-100-PTMO-1000	MTMOS	EG	HMDI	PTMO-1000
M-2-cyclo-100-PEG-1000	MTMOS	EG	HMDI	PEG-1000
M-2-desmo-100-PDMS-500	MTMOS	EG	Desmodur	PDMS-500
M-2-desmo-100-PTMO-1000	MTMOS	EG	Desmodur	PTMO-1000
M-2-desmo-100-PEG-1000	MTMOS	EG	Desmodur	PEG-1000
T-4-cyclo-100-PDMS-500	TEOS	BD	HMDI	PDMS-500
T-4-cyclo-100-PTMO-1000	TEOS	BD	HMDI	PTMO-1000
T-4-cyclo-100-PEG-1000	TEOS	BD	HMDI	PEG-1000
T-4-desmo-100-PDMS-500	TEOS	BD	Desmodur	PDMS-500
T-4-desmo-100-PTMO-1000	TEOS	BD	Desmodur	PTMO-1000
T-4-desmo-100-PEG-1000	TEOS	BD	Desmodur	PEG-1000
M-4-cyclo-100-PDMS-500	MTMOS	BD	HMDI	PDMS-500
M-4-cyclo-100-PTMO-1000	MTMOS	BD	HMDI	PTMO-1000
M-4-cyclo-100-PEG-1000	MTMOS	BD	HMDI	PEG-1000
M-4-desmo-100-PDMS-500	MTMOS	BD	Desmodur	PDMS-500
M-4-desmo-100-PTMO-1000	MTMOS	BD	Desmodur	PTMO-1000
M-4-desmo-100-PEG-1000	MTMOS	BD	Desmodur	PEG-1000

those of the parent polymers synthesized without macrodiols. The influence of the degree of crosslinking on transition temperature is particularly noticeable for the PEG 1000 modified materials in that the glass transition range decreases noticeably when comparing materials of similar gel fraction. Specifically, the transition temperature range decreases from 29.7°C to 14.4°C when polymers with gel fractions under 70% are excluded from comparison. This influence is also particularly evident when comparing M-4-cyclo-100-PEG-1000 and M-4-desmo-100-PEG-1000, whose observed glass transitions are −40.4 and −20.7°C, respectively. Despite possessing, the more rigid isocyanate M-4-cyclo-100-PEG-1000 has a much lower observed glass transition temperature as a result of its substantially lower gel fraction (61.8%) than that of M-4-desmo-100-PEG-1000 (97.8%). This incorporation of physically dispersed as opposed to covalently bound low-T_g components predictably results in a significant reduction in glass transition temperatures observed.

In general, PTMO-modified urethanes possessed slightly higher T_g values than similar PEG-modified versions in accordance with previous observations that greater oxygen atom spacing in polyether diols results in higher transition temperatures.[30] Similar to the PEG-modified materials, the PTMO network polymer with a comparatively low-gel fraction (M-4-cyclo-100-PTMO-1000) also extended the range of measured transition temperatures for this group of materials. In this instance, however, the less crosslinked material possessed a higher temperature transition than its more cross-linked counterparts. This behavior may be attributed to spatial heterogeneity of the cured material resulting in samples with PTMO rich and PTMO poor regions, resulting in a material with an overall broad glass transition. This hypothesis of sample heterogeneity is further supported by the comparatively high-glass transition measured for M-2-desmo-100-PTMO-1000 (7.1°C), despite its high-gel fraction (98.7%) compared to other samples containing PTMO macrodiols.

Table II. Bulk Material Properties of Poly(silyl urethanes) Cured for 24 h at 100°C

| Sample	Gel fraction (%)[a]	T_g (°C)[b]	T_g (°C)[c]	Storage modulus at 25°C (MPa)[c]	Degradation onset (°C)[d]
T-2-cyclo-100	e	e	e	e	e
T-2-desmo-100	96.6	−1.6	f	f	235
T-4-cyclo-100	98.7	72.5	74.2	1620.0	248
T-4-desmo-100	95.9	10.3	−4.1	6.70	249
M-2-cyclo-100	77.7	85.6	f	f	221
M-2-desmo-100	97.8	42.6	57.7	956.5	235
M-4-cyclo-100	63.5	52.1	70.3	287.5	262
M-4-desmo-100	99.1	15.7	23.0	16.0	260
T-2-cyclo-100-PDMS-500	e	e	e	e	e
T-2-cyclo-100-PTMO-1000	e	e	e	e	e
T-2-cyclo-100-PEG-1000	e	e	e	e	e
T-2-desmo-100-PDMS-500	95.9	14.9	23.6	1.6	244
T-2-desmo-100-PTMO-1000	94.8	−5.7	f	f	251
T-2-desmo-100-PEG-1000	96.9	−29.7	f	f	260
M-2-cyclo-100-PDMS-500	81.2	g	124.3	1150.0	236
M-2-cyclo-100-PTMO-1000	98.1	−6.3	44.3	117.9	252
M-2-cyclo-100-PEG-1000	81.8	−19.5	f	f	260
M-2-desmo-100-PDMS-500	95.5	1.3	4.3	1.6	224
M-2-desmo-100-PTMO-1000	98.7	7.1	6.6	7.9	252
M-2-desmo-100-PEG-1000	84	−20.5	−12.3	0.7	256
T-4-cyclo-100-PDMS-500	93.5	g	f	f	260
T-4-cyclo-100-PTMO-1000	81.2	−18.2	23.9	16.9	264
T-4-cyclo-100-PEG-1000	67.2	−38.2	6.4	11.3	278
T-4-desmo-100-PDMS-500	98.8	16	f	f	269
T-4-desmo-100-PTMO-1000	94.3	−18.9	−19.6	4.9	254
T-4-desmo-100-PEG-1000	90.8	−15.3	−26.3	3.3	248
M-4-cyclo-100-PDMS-500	96.7	g	f	f	243
M-4-cyclo-100-PTMO-1000	65.1	12.2	27.1	79.6	275
M-4-cyclo-100-PEG-1000	61.8	−40.4	14.7	45.6	305
M-4-desmo-100-PDMS-500	90.9	12.9	f	f	259
M-4-desmo-100-PTMO-1000	98.1	−10.2	−0.5	5.4	280
M-4-desmo-100-PEG-1000	97.8	−20.7	−4.4	4.5	295

[a]Quantified as insoluble material after 24-h solvent exposure, [b]Based on DSC analysis, [c]Based on DMA analysis, [d]Based on TGA analysis, temperature corresponds to 10% mass loss, [e]Uniform samples could not be produced, [f]Could not be determined using DMA analysis due to material brittleness or softness, [g]Could not be determined using DSC analysis due to lack of a measurable transition.

Interestingly, the T_g values for the PDMS-modified networks were not consistently less than those of their PEG and PTMO-modified counterparts, despite PDMS being an extremely low-T_g material itself. Although some of these cured resins were flexible at room temperature and possessed glass transition temperatures in the range of 1.3–16.0°C, others formed extremely hard materials for which glass transition temperatures could not be determined via DSC suggesting material crystallinity. As the average molecular weight of the PDMS used was only ∼ 500 g/mol, the diverse bulk properties of these materials may occur as a result of component incompatibility (much like hard/soft incompatibility in traditional linear polyurethanes) combined with the inability of the macrodiol to self-segregate due to

extremely short chain lengths (an estimated six to eight monomer units long) and the high content of hard-segment domains.[20,31] The opaque character of all the PDMS-modified materials supports this hypothesis. Current investigations are underway regarding macrodiol chain lengths required to generate elastomeric PDMS-modified urethanes with predictable transitions.

Similar to the transition temperatures of the cross-linked urethane materials, the storage moduli of these thermosets at room temperature were also extremely diverse. The structural variability of the urethane resins provided moduli ranging over three orders of magnitude (1.62 GPa–0.7 MPa), with the materials
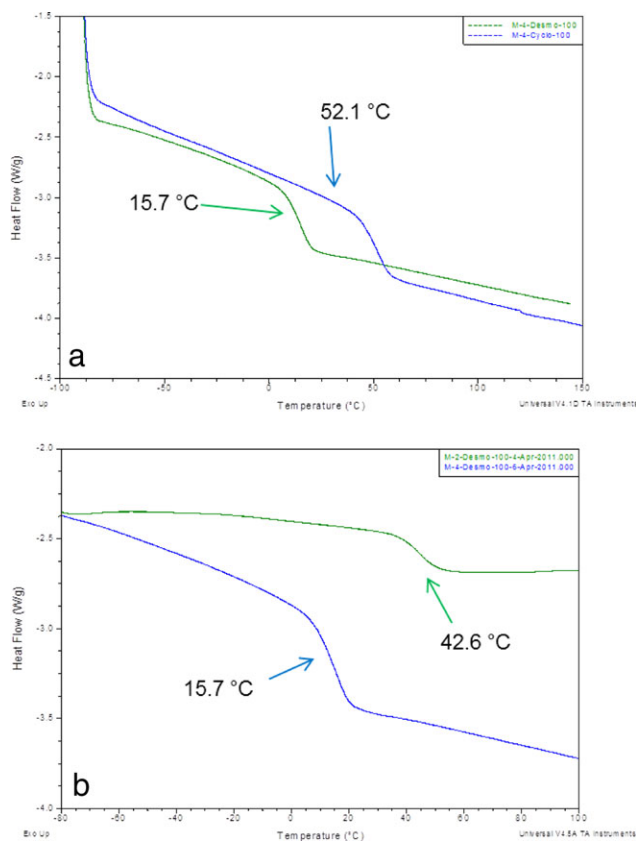
Figure 6. DSC thermograms showing structural dependence of silicate crosslinkers on urethane glass transition temperatures. (a) M-4-cyclo-100 (blue line) and M-4-desmo-100 (green line) and (b) M-2-desmo-100 (green line) and M-4-desmo-100 (blue line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

containing HMDI having substantially higher moduli than their counterparts composed of Desmodur (Table II, Figure 7). For example, M-4-cyclo-100 has a modulus of 287.5 MPa, while M-4-desmo-100 has a modulus of only 16.0 MPa. Ethylene glycol-modified silicate cross-linkers also imparted much higher storage moduli than the butanediol-modified versions in resins without any macrodiols (the storage moduli for M-2-desmo-100 and M-4-desmo-100 are 956.5 and 16.0 MPa, respectively). For most compositions, inclusion of a macrodiol into the urethane matrix resulted in a decrease in the observed modulus values resulting from the decrease in overall density of cross-links. Despite this importance of macrodiols, the specific moduli values of macrodiol modified materials seemed to be more highly dependent on the isocyanate rather than the macrodiol, as the polyurethanes that differed only in the structure of the macrodiol have moduli on the same order of magnitude, while those that differed in the structure of the isocyanate possessed moduli spanning one to two orders of magnitude. In these instances, moduli of macrodiol-modified resins were higher for materials containing HMDI than those with desmodur. In general, the moduli observed followed trends of glass transitions observed, as materials with higher glass transition temperatures exhibited higher moduli than those materials with lower transition temperatures. Interestingly, for materials with extremely

low-gel fractions (and resulting low-cross-link density) such as M-4-cyclo-100-PTMO-1000 and M-4-cyclo-100-PEG-1000, the observed moduli were higher than expected compared to similar materials with high gel fractions. This modulus elevation likely results from increased rigidity of the cross-linked portion of the matrix despite having high weight percent of uncross-linked macrodiols present. Finally, PDMS-modified materials that showed semicrystalline behavior and were not too brittle to measure using DMA (i.e., M-2-cyclo-100-PDMS-500) possessed higher modulus values compared to similar compositions due to the stabilization afforded by the crystalline domains compared to materials with simple amorphous characteristics.

Despite differences in orthosilicate and isocyanate structures, the urethane resins without any macrodiol modifiers exhibited markedly similar static water contact angles with a range of only 15°. Exclusion of M-4-cyclo-100, which had a comparatively low-gel fraction, narrows the distribution even further to only 12°. This similarity of surface properties among this group is not surprising due to the structural resemblance between all the orthosilicate cross-linkers, and the relatively hydrophobic nature of both of the isocyanates used. Predictably, the inclusion of macrodiol modifiers into the urethane matrices showed a great impact on the surface characteristics of these materials. The contact angle range without macrodiols was only 15°, whereas the derivatives containing macrodiols possessed a contact angle range of almost 60°. In general, the macrodiol dictated the resulting urethane contact angle of the resulting derivatives with PDMS > PTMO > PEG, with the only exceptions arising from low-gel fraction materials. Low-gel fraction urethanes likely upset this trend by having greater matrix reorganization due to fewer tethering cross-links and local heterogeneity of the surfaces.

As surface energies are calculated using contact angle values, these materials exhibited surface energy trends similar to those of the contact angle measurements (Table III). Resins without macrodiols possessed a narrow surface energy range (excluding M-4-cyclo-100) of only ~ 10 dynes cm^{-1}, which was expanded
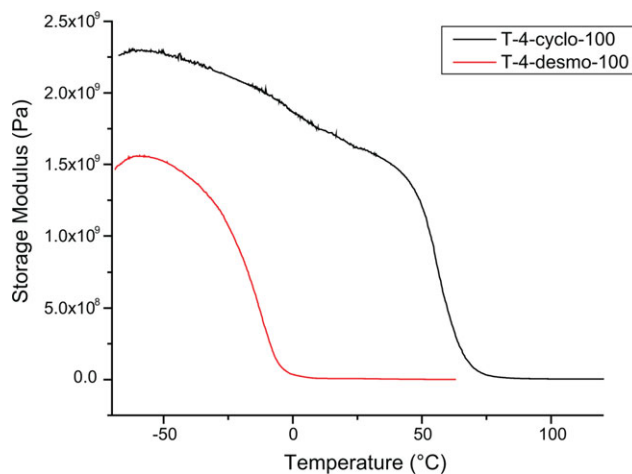
Figure 7. Storage modulus comparison between T-4-cyclo-100 and T-4-desmo-100. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table III.** Surface Properties of Poly(silyl urethanes) Cured for 24 h at 100°C

Sample	Contact angle (°)[a]	Surface energy (dynes cm^{-1})[b]	Tack (g)[c]	Hardness (g)[d]
T-2-cyclo-100	[e]	[e]	[e]	[e]
T-2-desmo-100	76.1 ± 3.1	42.8	[f]	[f]
T-4-cyclo-100	87.3 ± 1.1	41.5	0.62 ± 0.03	952.35 ± 3.53
T-4-desmo-100	77.2 ± 1.5	43.4	368.48 ± 317.04	532.59 ± 51.12
M-2-cyclo-100	85.1 ± 1.3	41.8	0.87 ± 0.36	400.82 ± 2.60
M-2-desmo-100	88.3 ± 1.7	31.8	[f]	[f]
M-4-cyclo-100	74.2 ± 1.5	46.1	0.83 ± 0.16	1349.96 ± 14.83
M-4-desmo-100	81.7 ± 2.5	37.3	30.91 ± 10.08	383.64 ± 28.41
T-2-cyclo-100-PDMS-500	[e]	[e]	[e]	[e]
T-2-cyclo-100-PTMO-1000	[e]	[e]	[e]	[e]
T-2-cyclo-100-PEG-1000	[e]	[e]	[e]	[e]
T-2-desmo-100-PDMS-500	94.9 ± 1.0	27.2	0.64 ± 0.04	583.46 ± 68.91
T-2-desmo-100-PTMO-1000	82.1 ± 2.8	39.1	[f]	[f]
T-2-desmo-100-PEG-1000	78.3 ± 1.8	43.3	82.85 ± 10.85	417.04 ± 34.32
M-2-cyclo-100-PDMS-500	94.3 ± 1.2	23.5	0.58 ± 0.01	717.98 ± 91.89
M-2-cyclo-100-PTMO-1000	83.6 ± 1.0	39.1	3.87 ± 0.56	923.06 ± 15.55
M-2-cyclo-100-PEG-1000	76.5 ± 1.7	43.8	[f]	[f]
M-2-desmo-100-PDMS-500	97.0 ± 2.3	29.7	0.63 ± 0.05	807.04 ± 191.03
M-2-desmo-100-PTMO-1000	76.7 ± 3.9	41.3	128.97 ± 20.67	287.86 ± 46.00
M-2-desmo-100-PEG-1000	95.3 ± 2.3	26.8	[f]	[f]
T-4-cyclo-100-PDMS-500	103.2 ± 2.1	19.3	0.71 ± 0.05	711.06 ± 3.53
T-4-cyclo-100-PTMO-1000	92.5 ± 1.2	40.4	289.70 ± 33.55	522.50 ± 5.24
T-4-cyclo-100-PEG-1000	95.9 ± 2.1	32.7	131.25 ± 25.20	495.09 ± 40.36
T-4-desmo-100-PDMS-500	97.9 ± 1.9	24.8	[f]	[f]
T-4-desmo-100-PTMO-1000	77.2 ± 1.6	44.1	143.43 ± 8.09	397.99 ± 51.56
T-4-desmo-100-PEG-1000	77.4 ± 0.6	40.3	[f]	[f]
M-4-cyclo-100-PDMS-500	103.7 ± 2.1	18.5	0.72 ± 0.03	700.63 ± 4.42
M-4-cyclo-100-PTMO-1000	78.7 ± 3.0	44.6	84.74 ± 14.71	467.91 ± 21.44
M-4-cyclo-1000-PEG-1000	44.8 ± 2.6	62.4	[f]	[f]
M-4-desmo-100-PDMS-500	101.6 ± 1.9	19.0	66.58 ± 14.63	392.08 ± 30.33
M-4-desmo-100-PTMO-1000	67.5 ± 7.2	[g]	[f]	[f]
M-4-desmo-100-PEG-1000	63.3 ± 1.9	[g]	30.89 ± 31.22	290.70 ± 33.60

[a]Average of at least six measurements; water as the wetting liquid, [b]Calculated by the Van Oss/Chaudhury/Good theory using average contact angle values for water, diiodomethane, and hexadecane as wetting liquids, [c]Maximum value on mass/time tack plot, [d]Force required to penetrate 10% thickness of coating with a 1″ stainless steel probe, [e]Uniform samples could not be produced, [f]Measured values outside of the instrumental accuracy range, [g]Could not be calculated due to complete wetting of one or more test liquids.

by the inclusion of the macrodiols. As expected, PDMS-modified materials showed the lowest observed surface energies (18.5–29.7 dynes cm^{-1}), while those with PEG or without any macrodiol possessed the highest (up to 62.4 dynes cm^{-1}). Again, low-gel fraction materials did not always behave in accordance with this observed trend.

Compositional differences of the cured resins accounted for large ranges for tack and hardness values. Unmodified urethanes possessed tack values spanning orders of magnitude in large part to their wide range of glass transition temperatures. It has previously been established that polymer tack is strongly related to the viscoelastic properties of materials, with tack increasing drastically above the polymer glass transition temperature compared to below it.[32] The synthesized materials follow these observed trends as the unmodified urethanes that have T_g values below room temperature had tack values of 368.48 ± 317.04 g (T-4-desmo-100) and 30.91 ± 10.08 g (M-4-cyclo-100) compared to values below 1.0 g for polymers with glass transition temperatures above room temperature. Although there remains a wide tack range for the macrodiol-modified urethanes, the correlation between low-glass transition temperatures and elevated tack values unfortunately does not hold true, as all the surface-modified urethanes capable of being analyzed had glass transitions below room temperature. The tack differences for
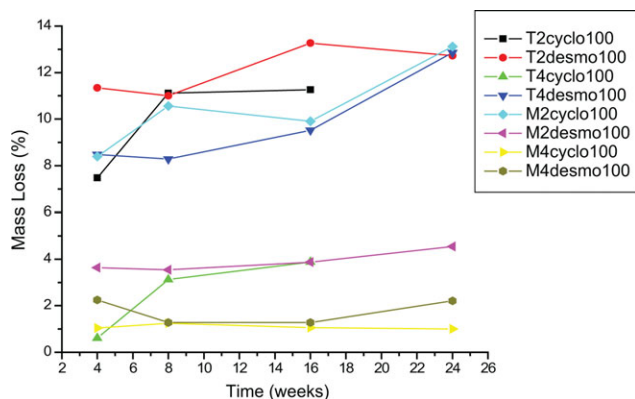
Figure 8. Mass loss of poly(silyl urethane) polymers in water at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

these materials may however be explained using another tack correlation based on incomplete bond formation.[32] Although, there is a wide range of polymer gel fractions for the macrodiol-modified urethanes, tack values seem to be more dependent on the structure of the macrodiol surface modifier. Specifically, PTMO-modified materials, which are capable of forming hydrogen bonds, possessed higher tack values than PDMS-modified materials, in which hydrogen bonding is largely absent.[33] In this case, the PTMO ethers are likely acting as incomplete bonds due to their ability to form hydrogen bonds, which in turn increases tack values compared to the PDMS-modified materials. This theory also explains the inability to generate accurate tack data for a large number of the PEG-modified materials as PEG is known to have higher hydrogen-bonding capabilities than PTMO due to the increased ether content. As a result, the tack measurements for many of the
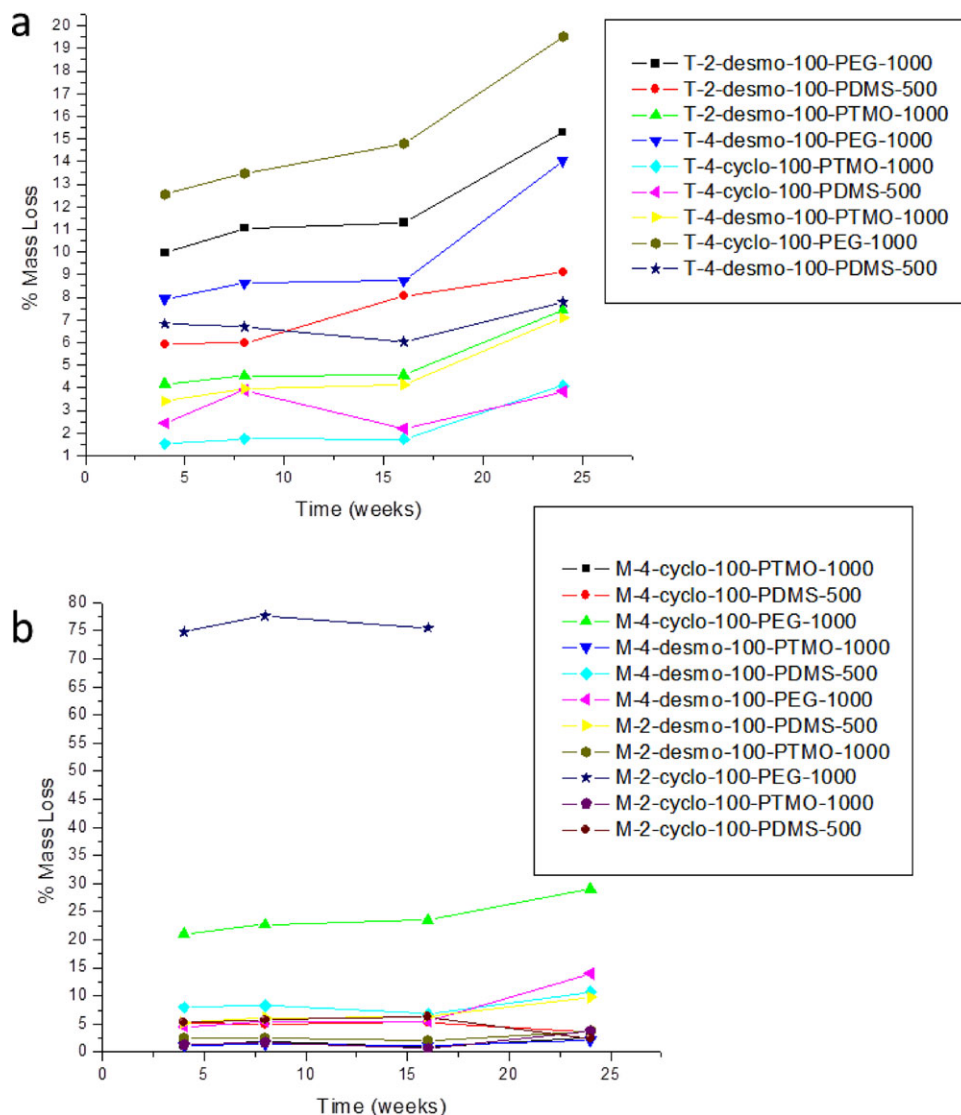
Figure 9. Mass loss of macrodiol-modified poly(silyl urethane)s with (a) tetrafunctional silicate cross linkers and (b) trifunctional silicate cross-linkers in water at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PEG-modified materials were outside the effective range for the instrument.

Hardness is a property of materials that is commonly used to measure the resistance to deformation at a polymer surface. Numerous factors influence the hardness of a material including the modulus, tensile strength, and work hardening among many others. Unfortunately, due to the diverse properties of these urethane materials, specific trends were not observed as a function of the alteration of structural features. Furthermore, hardness values did not seem to be influenced predominantly by any one thermal or mechanical characteristic such as the glass transition, modulus, or gel fraction of the material. Despite this, all these materials may be classified as hard based on an external comparison to previous reports of cross-linked polymeric materials, which had hardness values in the range of 51–93 g.

The utilization of polyfunctional silicates as crosslinkers for urethane-based oligomers allowed for the synthesis of hydrolyzable hybrid composite materials. As would be expected, the structure of both the crosslinker and the urethane oligomers provides control over the coating hydrolysis by mediating water uptake into the bulk material and the resulting hydrolysis of the Si—O bond. Interestingly, the trifunctional cross-linkers derived from MTMOS imparted greater hydrolytic stability than did the tetrafunctional cross-linkers (Figure 8). In general, this is attributed to greater hydrophobicity of MTMOS compared to TEOS; however, other factors including gel fraction and glass transition temperatures also seem to influence rates of hydrolysis. For example, the rate of hydrolysis of M-2-cyclo-100 is greatly accelerated compared to that of the other materials cross-linked with a trifunctional silicate due to the relatively low-gel fraction of that material compared to the other urethanes. This provides an increased opportunity for water uptake into the bulk material and, as a result, greater hydrolysis. Additionally, T-4-cyclo-100 had a much greater stability to hydrolytic conditions than other materials composed of the tetrafunctional cross-linker, which is attributed to its high-glass temperature and resulting enhanced resistance to water uptake compared to materials with lower glass transitions.

Upon incorporation of macrodiols into the urethane polymers, the hydrolytic stability of the resulting materials varied greatly (Figure 9). As would be expected based on the incorporation of a hydrophilic component, PEG-based materials resulted in much greater hydrolysis than materials composed of any other variation of components. Specifically, M-2-cyclo-100-PEG-1000 lost over 70% of its initial mass after only 4 weeks of submersion in water, whereas the highest mass loss for a material without PEG was only 12% (T-2-desmo-100). With PEG derivatives in particular, cross-linking with the tetrafunctional compounds was also found to have a significant influence on the overall hydrolysis of the material compared to those with trifunctional cross-linkers. This behavior arises from the reduced swelling and water uptake possible with the more highly cross-linked materials compared to more loosely cross-linked coatings. This difference in hydrolysis was not evident with other macrodiol compositions as all samples containing PTMO and PDMS did not have large variability in overall hydrolysis. The hydrophobic nature of these macrodiols did however increase the hydrolytic

stability, which is likely the result of decreased water uptake of the polymers. The hydrolytic stability of PDMS-containing urethanes is particularly interesting due to the fact that some compositions exhibited semicrystalline characteristics (such as T-4-cyclo-100-PDMS-500) and, as a result, exhibited slower than expected hydrolysis rates compared to similar compositions that did not crystallize. This behavior also occurs as a result of the decreased water uptake of the semicrystalline coatings compared to their amorphous counterparts. Interestingly, all materials experienced initial rates of hydrolysis at the first time point that were much faster than those at subsequent times. This indicates that in addition to hydrolysis, extraction of soluble materials is likely accounting for a large portion of the initial mass loss of each material. Furthermore, rapid initial mass loss followed by much slower hydrolysis over time suggests that nonhydrolyzable cross-links (i.e., allophanate or biuret linkages and incorporation of a trifunctional isocyanate) are providing enhanced hydrolytic stability to the material. Although this characteristic does slow polymer hydrolysis, it also likely prevents complete material hydrolysis. As such, formulations containing cross-links only via hydrolyzable silicate moieties may be necessary and are currently under further investigation.

CONCLUSIONS

Glycol-modified silanes are a group of novel polyurethane cross-linking agents that provide controlled hydrolysis to urethane materials with various compositions. These cross-linkers show compatibility with numerous different systems including those with and without macrodiol property modifiers (such as PEG, PTMO, and PDMS). Overall, high degrees of cross-linking may be achieved, while material properties remain predominantly dictated by the structure of remaining material components such as isocyanates and macrodiols. Furthermore, the ability to generate highly cross-linked materials in the absence of heavy metal catalysts and minimal solvent provides a promising avenue for the preparation of new environmentally friendly hydrolyzable materials for applications in areas such as marine and other types of functional protective coatings.

ACKNOWLEDGMENTS

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