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Novel Silicon-Containing Polyurethanes from Vegetable Oils as Renewable Resources. Synthesis and Properties

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Hydrosilylation of methyl 10-undecenoate (UDM) with phenyl tris(dimethylsiloxy)silane (PTDS) followed by a reduction of carboxylate groups was used to obtain a silicon-containing polyol with terminal primary hydroxyl groups (PSi194). Biobased silicon-containing polyurethanes, with a silicon content between 1.7% and 9.0%, were prepared from epoxidized methyl oleate-based polyether polyol (P184), PSi194, and 4,4′-methylenebis(phenyl isocyanate) (MDI). The thermal, mechanical, and flame-retardant properties of these materials were examined. The most notable change resulting from the incorporation of PSi194 is the appearance of melting endotherms of variable enthalpy and position and a downward shift in the T_g. The incorporation of silicon does not change the thermal stability but enhances the stability of the char under air atmosphere. Polyurethanes with higher silicon content no longer burn in ambient air without complementary oxygen, which suggests that these biobased materials are very interesting for applications that require fire resistance.

Introduction

Biomaterials, chemicals, and energy from renewable resources have been the object of considerable interest in recent years.[1] In the search for sustainable chemistry, considerable importance is being attached to polymers prepared from biological sources, and interest has focused on the use of cheap, biodegradable, and annually renewable starting materials such as starch, cellulose, carbohydrates, proteins, and vegetable oils for synthesizing a wide range of bioplastics.[2] The aim of this research is to reduce petroleum dependence, reduce the negative impact on the environment, and add value to existing agricultural products so that farming and industry can benefit. Vegetable oils are one of the cheapest and most abundant biological sources available in large quantities, and their use as starting materials has numerous advantages, for example, low toxicity, inherent biodegradability, and high purity.[3] They are considered to be one of the most important classes of renewable resources for the production of biobased thermosets.[4]

Polyols derived from vegetable oils are new raw materials from renewable resources and are essential in the preparation of any polyurethane product. For natural oils to be used as raw materials for polyol production, multiple hydroxyl functionality is required. Two different ways of preparing vegetable oil-based polyols have been successfully developed. In the first, polyols are formed by reaction at the double bond of the unsaturated fatty oil. For example, the epoxidation and further oxirane ring opening leads to polyols with secondary hydroxyl groups,[5−7] while the hydroformylation and the ozonolysis lead to polyols with primary hydroxyl groups.[8,9] In the second, a combined reaction at the double bonds and subsequent reduction of the carboxyl group yields the hydroxyl moieties.[10]

Polyurethane polymers are a versatile class of polymers which are used in a wide range of applications, and their structure can be tailored to specific requirements.[11] Depending on the hydroxyl value and other characteristics of the polyol, it can be applied in the development of adhesives, coatings, and flexible or rigid foams. In combination with isocyanates, vegetable oil-based polyols produce polyurethanes that can compete in many ways with polyurethanes derived from petrochemical polyols, and their preparation for general polyurethane use has been the subject of many studies.[5−10,12−15] Moreover, due to the hydrophobic nature of triglycerides, vegetable oils produce polyurethanes which have such excellent chemical and physical properties as enhanced hydrolytic and thermal stability.[16,17] Nowadays, it is a challenge to synthesize suitable diisocyanates via diamino compounds derived from vegetable oils, making it possible to produce polyurethanes completely from renewables. Like other organic polymeric materials, the flammability of these materials is a shortcoming in some applications. Major progress in the area of flame-retardant polyurethanes in recent years has been made in the field of phosphorus- or silicon-containing products.[18]

Some papers have appeared in recent years about the synthesis of siloxane-based polyurethanes with improved biostability and good mechanical properties.[19] Linear polyhedral oligomeric silsesquioxane (POSS)-containing polyurethanes have been reported for application as surface coatings.[20,21] Polyurethane networks incorporating POSS with enhanced glass transition temperatures, improved thermal stabilities, and flame retardance have been also reported.[22] Besides the interest in investigating the structural properties of the new silicon-containing polyurethanes, we believe that many of their features (for example, improved thermal stability, biostability, and biocompatibility, good mechanical properties, and fire resistance) can be exploited in the field of polyurethanes for specialized applications.

To further extend the applications of these renewable resources, our group has focused on converting vegetable oils into useful biopolymers. In a previous study, we described the synthesis of polyether polyols through the combination of cationic polymerization of epoxidized methyl oleate (EMO) and the reduction of carboxylate groups to hydroxyl moieties.[10] Polyols with different hydroxyl contents were obtained and reacted with MDI to yield polyurethanes that behave like hard

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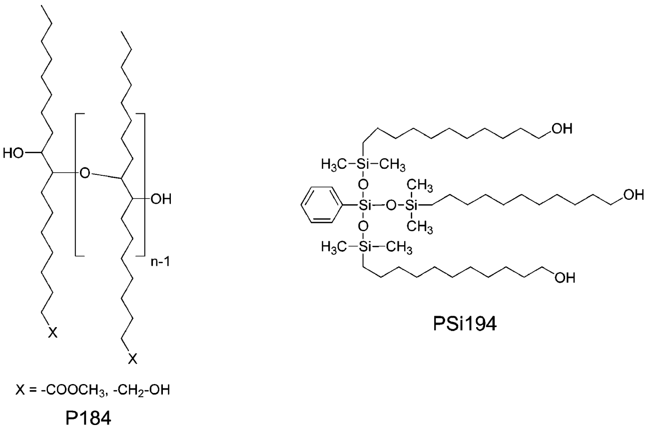
Chart 1. Chemical Structure of Polyols P184 and PSi194



rubbers or rigid plastics. We have also investigated the synthesis of new organic−inorganic hybrid materials via the hydrosilylation reaction in an attempt to find new applications for unsaturated fatty compounds. There has been considerable interest in these materials because of their unexpected properties.[23] After our efforts to functionalize vegetable oils so that they could act as components for biopolymeric materials, we investigated the synthesis of a silicon-containing polyol and its application in the synthesis of silicon-containing polyurethanes with enhanced flame retardance.

The present study aims to develop novel, biobased silicon-containing polyurethanes from vegetable oils. We first investigated the hydrosilylation reaction of methyl 10-undecenoate (UDM), an *ω*-unsaturated fatty acid methyl ester which can be easily obtained from natural ricinoleic acid, with a trifunctional hydrosilylating agent, phenyltris(dimethylsiloxy)silane (PTDS), and the subsequent reduction of carboxylate groups to obtain a silicon-containing polyol (PSi194) with terminal primary hydroxyl groups. Silicon-containing polyurethanes were obtained from an EMO-based polyether polyol (P184), a silicon-containing polyol (PSi194) (Chart 1), and 4,4′-methylenebis(phenyl isocyanate) (MDI) as a cross-linking agent. The thermal properties of the polyurethanes prepared were studied by using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamomechanical analysis (DMTA), and the flame retardance was assessed by the limiting oxygen index (LOI) test.

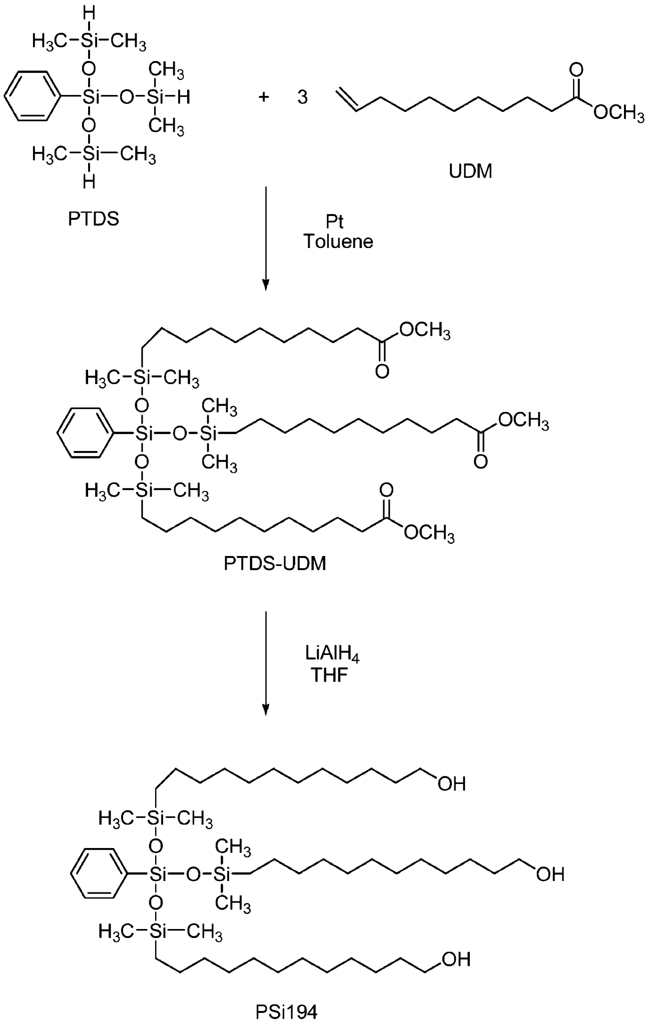
Experimental Section

Materials. The following chemicals were obtained from the sources indicated: phenyltris(dimethylsiloxy)silane, PTDS (95%, from ABCR), lithium aluminum hydride, $LiAlH_4$ (97%, from SDS), and 4,4′-methylenebis(phenyl isocyanate) (MDI, from Aldrich). They were all used as received. A platinum−divinyltetramethyldisiloxane complex with 3−3.5 wt % platinum in xylene (Aldrich) was dissolved in toluene to give a 274 ppm platinum concentration. The Pt solution was stored at 4 °C. Toluene and tetrahydrofuran (THF) were distilled from sodium immediately before use. Other solvents were purified by standard procedures.

Synthesis of Polyether Polyol P184. Epoxidized methyl oleate-based polyether polyol (P184) with OH number of 184 mg KOH/g was synthesized in our laboratory using the procedure described earlier.[10] This OH number corresponds to the equivalent weight of the polyol, 305, functionality, 3.8, and molecular weight, 1187. Methyl 10-undecenoate (UDM) was synthesized as previously described.[23]

Synthesis of Polyol PSi194. Silicon-containing polyol was synthesized in two steps: hydrosilylation of methyl 10-undecenoate (UDM) with phenyl tris(dimethylsiloxy)silane (PTDS) to obtain PTDS−UDM followed by a reduction of carboxylate groups to give primary hydroxyl groups in PSi194 (Scheme 1).

Scheme 1. Synthesis of Silicon Polyol PSi194



Hydrosilylation of UDM. Methyl 10-undecenoate (UDM) (16 g, 80 mmol) was dissolved in anhydrous toluene (100 mL) under argon atmosphere in a 250 mL two-necked round-bottomed flask equipped with a refluxing condenser. A solution of Pt complex (2 mL, 0.54 ppm) was then injected into the solution using a syringe, and the mixture was stirred at room temperature for 5 min. The corresponding stoichiometric amount of phenyltris(dimethylsiloxy)silane (PTDS) (9.3 g, 26.7 mmol) was added, and the solution was warmed to 65 °C and stirred at this temperature for 2 h. After cooling, toluene was evaporated under reduced pressure, and the crude mixture was dissolved in CH_2Cl_2 and passed through a silica gel column to remove the Pt catalyst. Finally, the solvent was evaporated under vacuum, and the resulting product, PTDS−UDM, was obtained as a viscous oil (22.5 g, 91%).

^1H NMR ($CDCl_3$/TMS, δ (ppm)): 7.58−7.27 (m, H_{Ar}, 5H), 3.68 (s, $-OCH_3$, 9H), 2.32 (t, $-CH_2-CO$, 6H), 1.61 (m, CH_2-CH_2CO, 6H), 1.24 (m, $-CH_2-$, 42H), 0.53 (t, CH_2-Si, 6H), 0.08 (s, $Si-CH_3$, 18H).

^{13}C NMR ($CDCl_3$/TMS, δ (ppm)): 174.55 (s), 135.71 (s), 134.02 (d), 129.58 (d), 127.63 (d), 51.64 (q), 34.32 (t), 33.73 (t), 29.77 (t), 29.73 (t), 29.59 (t), 29.49 (t), 29.39 (t), 25.18 (t), 23.38 (t), 18.45 (t), 0.37 (q).

Reduction of PTDS−UDM. Lithium aluminum hydride (8.3 g, 219 mmol) was dispersed in 500 mL of anhydrous tetrahydrofuran (THF) in a 1 L, two-necked, round-bottomed flask under argon atmosphere. PTDS−UDM (22.5 g, 24.3 mmol), dissolved in anhydrous THF (50 mL), was added dropwise with stirring over a period of 30 min. After addition was complete, the mixture was stirred vigorously at room temperature for 1 h. After this, the excess $LiAlH_4$ was decomposed by adding 50 mL of ethyl acetate dropwise. Then, 10% H_2SO_4 aqueous solution was added, and the aqueous layer was extracted with ethyl acetate. The combined organic phase was washed with saturated sodium bicarbonate solution ($NaHCO_3$) until the pH was neutral and brine. The organic phase was dried over anhydrous magnesium sulfate, filtered, and the solvent was evaporated off yielding a viscous liquid (20.0 g, 98%). The titrimetically determined hydroxyl value of the product was 194 mg of KOH per gram.

^{1}H NMR ($CDCl_3$/TMS, δ (ppm)): 7.58−7.27(s, H_{Ar}, 5H), 3.61 (t, $-CH_2OH$, 6H), 1.55 (m, CH_2-CH_2OH, 6H), 1.23 (m, $-CH_2-$, 48H), 0.54 (t, $Si-CH_2-$, 6H), 0.07 (t, $Si-CH_3$, 18H).

^{13}C NMR ($CDCl_3$/TMS, δ (ppm)): 135.73 (s), 133.93 (d), 129.50 (d), 127.54 (d), 62.83 (t), 33.71 (t), 32.84 (t), 29.86 (t), 29.84 (t), 29.80 (t), 29.72 (t), 29.67 (t), 29.60 (t), 25.96 (t), 23.34 (t), 18.41 (t), 0.29 (q).

Synthesis of Polyurethanes. Polyurethanes were synthesized by reacting the appropriate amount of polyether polyol (P184), silicon polyol (PSi194), and MDI. The NCO/OH ratio was kept constant at 1.02. Polyols and MDI were mixed at 60 °C, and the mixture was poured into a preheated open mold at 60 °C and cured for 2 h at 60 °C and postcured at 110 °C overnight.

Characterization. The NMR spectra of the oil samples were recorded on a Varian Gemini 400 MHz spectrometer (400 MHz for ^{1}H and 100.57 for ^{13}C). The samples were dissolved in deuterated chloroform, and ^{1}H NMR and ^{13}C NMR spectra were obtained at room temperature using TMS as the internal standard. The IR spectra were recorded on a Bomem Michelson MB 100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated-total-reflection (ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma) was used to determine FTIR spectra.

Size-exclusion chromatography (SEC) analysis was carried out using a Waters 510 pump system equipped with a refractive index Shimadzu RID-6A. THF was used as the eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained using polystyrene standards.

Calorimetric studies were carried out on a Mettler DSC822e thermal analyzer with N_2 as the purge gas. The heating rate was 20 °C/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 as the purge gas at scanning rates of 10 °C/min.

Powder X-ray diffraction measurements were performed at room temperature on a Bruker AXS D8 Advance diffractometer. Cu anode, Kα radiation was used, and graphite was the secondary monochromator. In all experiments, the exit slit window was 0.5°, the antiscattering slit was 1.0 mm, and the divergence slit was 0.2 mm. The Bragg angle step was 0.05°, and the time per step was 5 s.

Mechanical properties were measured with a dynamic mechanical thermal analyzer (DMTA) (TA DMA 2928). Specimens 1.2 mm thick, 5 mm wide, and 10 mm long were tested in a three-point bending configuration. The various thermal transitions were studied between −100 and 140 °C at a heating rate of 5 °C/min and a fixed frequency of 1 Hz.

LOI values were measured on a Stanton Redcroft instrument, provided with an oxygen analyzer, on $100 \times 6 \times 4$ mm^3 polymer plaques prepared by molding.

Scanning electron microscopy (SEM) was performed on a JEOL JSM 6400 scanning electron microscope, at an activation voltage of 15 kV. For the atomic mapping, an Oxford INCA Energy Dispersive X-ray Micro Analyzer was used. The polymeric samples were mounted on a sample holder and were sputter-coated under vacuum with graphite.

General Procedure for Unilever-Method Hydroxyl Value Determination.[24] To the amount of weighed sample in a round-bottom flask was added an accurately measured volume of acetic anhydride. After mixing, the flask was placed in an oil bath at 95−100 °C. After 1 h, the flask was cooled, and 1 mL of distilled water was added. After shaking, heating was continued for 10 min to convert the anhydride into acid. After cooling again, 5 mL of 95% ethanol was added, and the contents were titrated with ethanolic potassium hydroxide solution using phenolphthalein as indicator. A blank determination was carried out with a similar procedure.

Results and Discussion

Synthesis and Characterization of Polyols. Silicon-containing polyol was synthesized in two steps: hydrosilylation of methyl 10-undecenoate (UDM) with phenyl tris(dimethylsiloxy)-silane (PTDS) to obtain PTDS−UDM followed by a reduction of carboxylate groups to give primary hydroxyl groups in PSi194 (Scheme 1).

The chemistry of the hydrosilylation of olefins has been extensively studied,[25] but only a few studies on fatty compounds have been published.[23,26−28] The reaction proceeds when, after the hydrosilane has been activated, it undergoes addition across the carbon−carbon multiple bond. This reaction usually needs a catalyst; the most commonly used are transition metal complexes.

According to our previous results,[23] the hydrosilylation of UDM with PTDS was carried out using Karstedt's catalyst (catalyst/C=C mol ratio 3.5×10^{-5}/l) at 65 °C. FTIR spectroscopy was used to follow the reaction's progress, monitoring the disappearance of the characteristic stretching vibration peaks of $-CH=CH_2$ and Si−H groups at 1640 and 2168 cm^{-1}, respectively. ^{1}H and ^{13}C NMR analysis of the obtained product showed the characteristic signals at 0.5 and 18.4 ppm, respectively, which confirms the covalent $-CH_2-$Si linkage between the fatty acid chain and the silicon core. Double-bond isomerization to internal positions (signal at 5.4 ppm) was hardly observed. Since Si−H coupling side reactions have been described for the hydrosilylation reaction,[29,30] SEC analysis of the product was carried out to confirm the absence of undesired compounds. The molecular weight determination showed a monomodal molecular weight distribution that implies the absence of these coupling products.

PTDS−UDM was used as the starting material for the reduction of the carboxylate groups to synthesize a triol with primary hydroxyl groups. The reduction was carried out using lithium aluminum hydride ($LiAlH_4$) as reducing agent in THF solution, and the expected product was characterized by spectroscopic techniques. The FTIR spectrum showed that the ester carbonyl band at 1750 cm^{-1} had disappeared. Figure 1 shows the ^{1}H and ^{13}C NMR spectra of PSi194 with the signal assignments. The hydroxyl content value (HV) of the PSi194 was determined with the Unilever method.[24] The result (194 mg KOH/g) was very close to the theoretical value of 200. The characteristics of PSi194 are listed in Table 1. The DSC plots for PSi194 exhibit a main peak at −20 °C and smaller ones at −12 and −31 °C. Multiple peaks in PSi194 can be ascribed to different crystalline forms.

Synthesis and Characterization of Polyurethanes. In this study, novel biobased polyurethanes were prepared from epoxidized methyl oleate-based polyether polyol (P184) with OH number of 184 mg KOH/g, silicon-containing triol (PSi194), and 4,4′-methylenebis(phenyl isocyanate) (MDI) as a cross-linking agent. As has been previously described,[10] P184 was obtained from methyl oleate by the epoxidation of carbon double bonds, cationic oligomerization of the resulting epoxy fatty acid ester, and partial reduction of the ester groups. The characteristics of this polyether polyol are summarized in Table 1.

A series of five different polyurethanes with silicon content between 1.7% and 9.0% was prepared from the above-mentioned

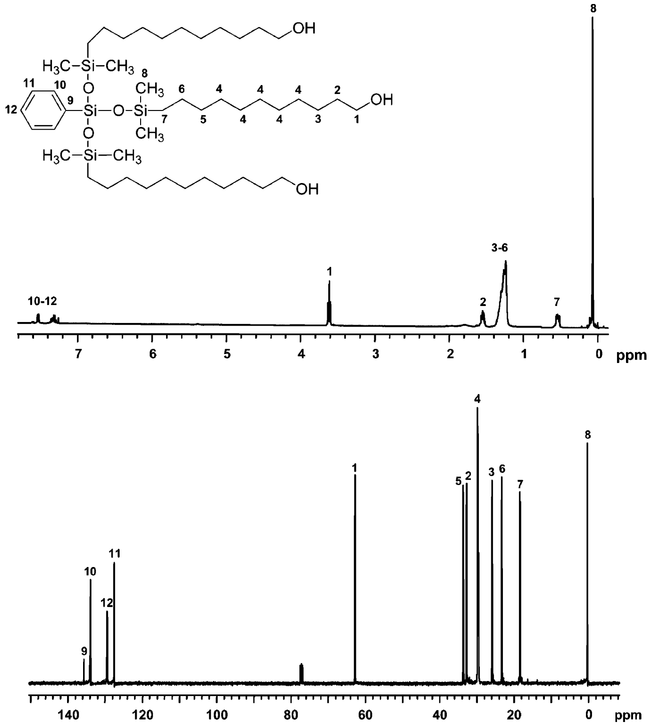


Figure 1. ^{1}H and ^{13}C NMR spectra of silicon containing polyol PSi194 ($CDCl_3$, 400 MHz).

Table 1. General Properties of the Polyols

polyol	HV[a] (mg KOH/g)	EW[b] (g/equiv)	Mn (SEC) (g/mol)	Mw/Mn (SEC)	functionality[c]
P184	184	305	1187	1.59	3.8
PSi194	194	295	870	1.12	2.9

[a] Hydroxyl content values. [b] Equivalent weight calculated from the HV. [c] Functionality was obtained by dividing the experimental molecular weight (Mn) by the EW.

Table 2. Melting Points (T_m), Melting Enthalpies (ΔH_m), and Glass Transition Temperatures (T_g) of Polyurethanes from DSC and DMTA

	molar		DSC			DMTA
	ratio[a]	Si (%)	T_m (°C)	ΔH_m (J/g)	T_g[b] (°C)	tan δ_{max}[c]
PU-0	1/0	0			39	63
PU-1.7	0.75/0.25	1.7			25	50
PU-3.8	0.49/0.51	3.8	54	1.0	20	43
PU-6.2	0.24/0.76	6.2	58	5.4	16	41
PU-9	0/1	9.0	93	22.4	9	31

[a] Molar ratio of P184/PSi194. [b] From the second heating of DSC measurements with a heating rate of 20 °C/min. [c] Maximum value of the tan δ–temperature curve from DMTA.

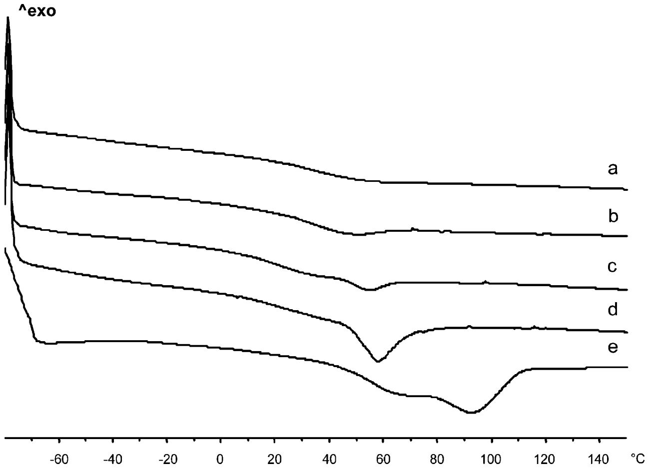


Figure 2. DSC thermograms (20 °C/min) of polyurethanes PU-0 (a), PU-1.7 (b), PU-3.8 (c), PU-6.2 (d), and PU-9 (e).

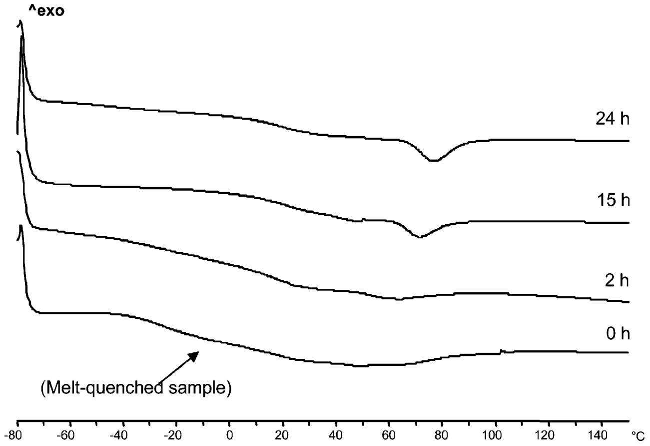


Figure 3. DSC thermograms (20 °C/min) of the melt-quenched PU-6.2 samples, which were annealed at 50 °C for different periods of time.

polyols and MDI by varying the P184/PSi194 molar ratio: PU-0, PU-1.7, PU-3.8, PU-6.2, and PU-9 (see Table 2). The NCO/OH molar ratio was kept constant at 1.02, and reactants were mixed at 60 °C and cured at this temperature for 2 h and postcured at 110 °C overnight to give the polyurethanes. The conversion of the reaction was monitored by FTIR spectroscopy. The disappearance of the absorption band at 2240 cm^{-1} assigned to the isocyanate group indicated that the reaction was complete. The materials containing P184 remained flexible, while polyurethane PU-9, which does not contain this polyol, behaved like a rigid material. All the polyurethanes synthesized were characterized by FTIR. Their urethane structure was demonstrated by absorption bands at around 3412 cm^{-1} (N–H stretching), 1530 cm^{-1} (N–H deformation), and 1725 cm^{-1} (C═O). Other peaks at 1270 (Si–CH_3) and 1060 (Si–O–Si) cm^{-1} confirmed the siloxane structure of PSi194-based polyurethanes.

The thermal behavior of the materials obtained was investigated with DSC (Figure 2). PU-0 exhibited a T_g at 39 °C. The most notable result of incorporating PSi194 is the appearance of melting endotherms of variable enthalpy and position and a downward shift in the T_g. The samples with no crystallinity are transparent, while those semicrystalline are white. The rather low melting points seem to be indicative of small domains. The lower T_g values of the silicon-containing polyurethanes can be related by the presence of Si–O and Si–C units in the backbone.

When samples were run a second time after melting, no melting peaks were observed. This is probably the result of the miscibility of the P184 and PSi194 fragments above the melting point. High viscosity and low mobility due to cross-linking makes crystallization upon cooling difficult. Sample PU-6.2 was annealed at 50 °C for several hours and left to cool slowly to room temperature to promote phase separation and crystallization. Figure 3 illustrates the DSC thermograms of the PU-6.2 samples after annealing at 50 °C for different periods of time. We found that a small endotherm appearing in the vicinity of the annealing temperature shifted to a higher temperature and increased in enthalpy as the annealing time increased. Therefore, better miscibility of PSi194 segments with the P184 phase raises T_g, and the sample displays higher crystallinity.

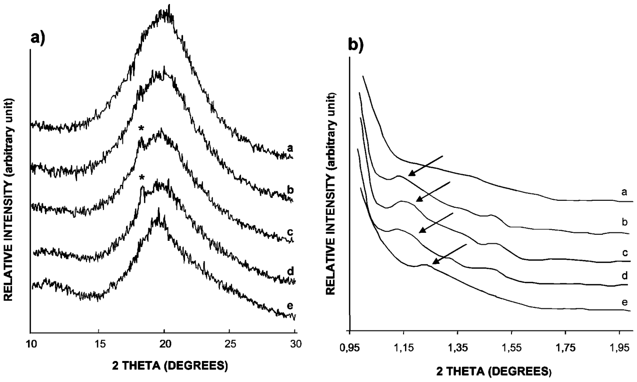


Figure 4. WAXS diffractograms (a) and zoom-in plot of scattering profiles at small angles (b) of polyurethanes PU-0 (a), PU-1.7 (b), PU-3.8 (c), PU-6.2 (d), and PU-9 (e).

Wide-angle X-ray diffraction experiments confirmed calorimetric findings. The WAXD pattern of the PU-0 sample shows a broad halo characteristic of amorphous substances with the maximum at about $2\theta = 20°$ (Figure 4a). As the PSi194 content increases, the WAXD curve essentially shows the same pattern, but the peak becomes narrower, and a crystalline peak can be observed at $2\theta = 18°$ (marked with * in Figure 2) for PU-3.8 and PU-6.2, suggesting a slight increase in crystallinity. Scattering profiles at small angles are used to check phase-separated structures. If a maximum appears at small angles, this would be the conclusion of the coexistence of two separated phases, an amorphous-rich phase and a crystalline-rich phase. Figure 4b shows the scattering profiles at small angles of the synthesized polyurethanes. As can be seen, PU-0 does not show an appreciable scattering on the detector indicating the presence of homogeneous phase. However, samples which contain PSi194 show peaks at small angles (marked with arrows in Figure 4b) that may be evidence of microphase formation.[31]

The dynamomechanical behavior of the polyurethanes has been investigated. Figure 5a shows the elastic modulus as a function of the temperature. As can be seen, materials containing P184 behave like cross-linked polymeric networks with respect to E' curves. At low temperatures, there is a glass state with E' at a high modulus plateau, and at higher temperatures, there is a rubbery state with a lower E'. Figure 5b shows the dissipation factor tan δ curves as a function of temperature. The location of the tan δ peak is dependent on silicon content and shifts to low temperature when the PSi194 content increases. The glass transition temperatures determined from the peaks of tan δ curves are higher than those determined by DSC (see Table 2), which can be related to the heat transporting hysteresis for large-scale samples in DMA. The magnitude of tan δ is also affected by the PSi194 content, and as can be seen, it increases for the silicon-free PU-0 and the lower silicon content of PU-1.7 and PU-3.8. This suggests that the PSi194 incorporation makes the PU more viscous. However, the peak value of tan δ for PU-6.2 is lower even though its Si content is higher. This can be explained by the presence of microcrystalline domains in the polymer, as has been observed by DSC, which restricts the chain mobility. Moreover, a β transition can be observed, more clearly for the PU-1.7. The origin of this peak is not known, but it may be related to the rotational motions of the short units in the fatty acid chain.[9] PU-9 shows a different dynamomechanical behavior. As a semicrystalline material, the α relaxation peak is associated to the melting of the crystalline phase. Moreover, a β relaxation, related to the glass transition, can be observed. The magnitude of tan δ for this relaxation is much lower than the ones previously described, according to a lower mobility and a higher degree of crystallinity.

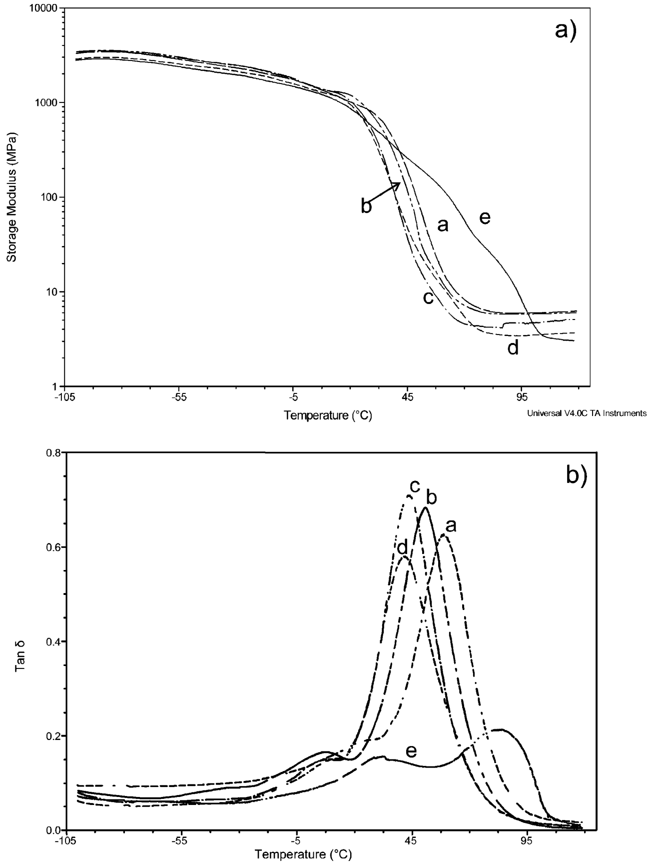


Figure 5. Storage modulus (E') and loss factor (tan δ) of polyurethanes PU-0 (a), PU-1.7 (b), PU-3.8 (c), PU-6.2 (d), and PU-9 (e) as a function of temperature.

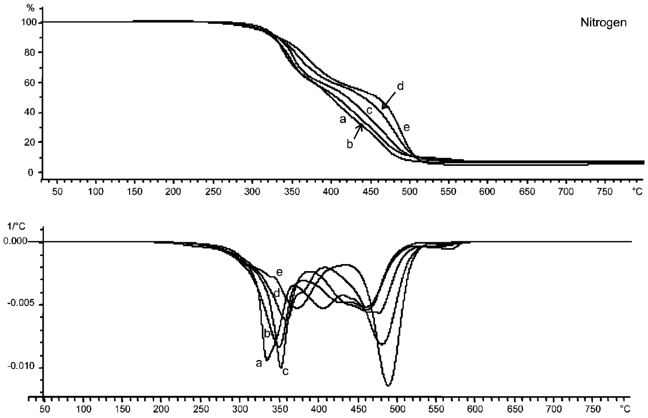


Figure 6. TGA plots (10 °C/min) and first derivative curves of polyurethanes PU-0 (a), PU-1.7 (b), PU-3.8 (c), PU-6.2 (d), and PU-9 (e) under nitrogen atmosphere.

The reported thermogravimetric analysis of polyurethanes based on petroleum-based polyols suggests that thermal stability is poor.[16,32,33] The onset of urethane bond dissociation is somewhere between 150 and 220 °C, depending upon the type of the isocyanate or polyol. Thermal decomposition of the polyurethanes obtained was investigated by TGA under nitrogen and air atmospheres. Figures 6 and 7 show the TGA and the corresponding derivative curves under both atmospheres, and Table 3 summarizes the thermogravimetric data. As can be seen, onset decomposition temperatures do not show significant

Table 3. Thermogravimetric Data and Limiting Oxygen Indices (LOI) of Polyurethanes

		TGA (N_2 atmosphere)			TGA (air atmosphere)			
	Si (%)	$T_{10\%\ \mathrm{loss}}$[b] (°C)	T_{max}[c] (°C)	$\mathrm{yield}_{800\ °C}$[d] (%)	$T_{10\%\ \mathrm{loss}}$[b] (°C)	T_{max}[c] (°C)	$\mathrm{yield}_{800\ °C}$[d] (%)	LOI
PU-0	0	329	332/404/460	3	322	337/403/565	0	18.2
PU-1.7	1.7	325	349/420/460	7	314	346/432/569	0	19.0
PU-3.8	3.8	330	351/470	6	320	349/469/580	2	20.4
PU-6.2	6.2	330	359/481	7	322	350/482/585	2	22.1
PU-9	9.0	331	371/487	5	333	363/485/600	5	23.6

[a] Molar ratio of P184/PSi194. [b] Temperature of 10% of weight loss. [c] Temperature of the maximum weight loss rate. [d] Char yield at 800 °C.

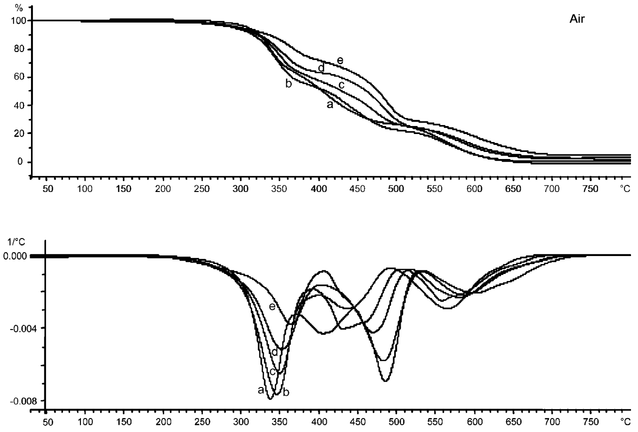


Figure 7. TGA plots (10 °C/min) and first derivative curves of polyurethanes PU-0 (a), PU-1.7 (b), PU-3.8 (c), PU-6.2 (d), and PU-9 (e) under air atmosphere.

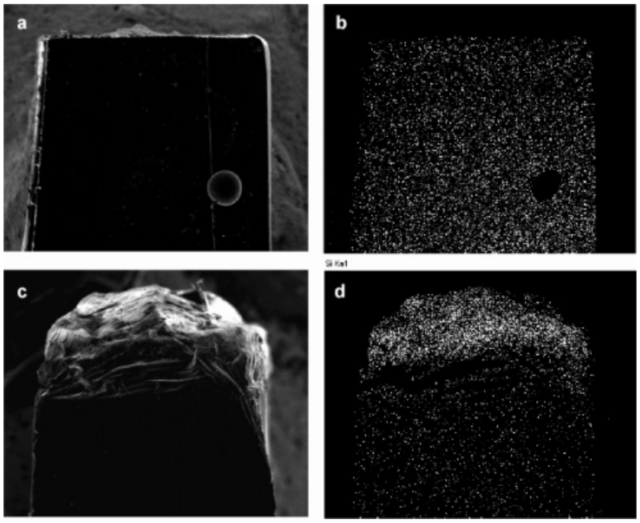


Figure 8. SEM and SEM-EDX Si mapping micrographs of sample PU-9 before (a,b) and after (c,d) burning LOI test: (left) SEM, and (right) SEM-EDX micrographs.

differences among the samples, suggesting that the incorporation of silicon does not change the thermal stability under air or nitrogen. From the derivative curves, it can be seen that in both nitrogen and air more than one process occurs during thermal degradation. Petrovic et al.[16] observed a similar behavior in the case of vegetable oil-based polyurethanes. They showed that poly(oxypropylene) (PPO)-based polyurethanes degrade in a single step, whereas vegetable oil-based polyurethane show a two-step decomposition. The derivative curves in our study revealed that the temperature corresponding to the maximum weight loss rate increases and the maximum weight loss rate decreases as the silicon content increases. This degradation step, which takes place at temperatures between 330 and 370 °C, can be associated with the decomposition of urethane bonds, which takes place through the dissociation to isocyanate and alcohol, the formation of primary amines and olefins, or the formation of secondary amines.[18] Two more degradation steps can be observed for the silicon-free PU-0 or the lower silicon content PU-1.7, which can be attributed to the polyether polyol decomposition. PU-3.8, PU-6.2, and PU-9 show only one degradation process at higher temperatures that has to be ascribed to the decomposition of silicon units which produced volatile cyclic oligomers.[34]

In air, the thermooxidative degradation takes place at temperatures higher that 550 °C. Again, the silicon content influences the temperature of the maximum weight loss rate and the maximum weight loss rate. Char yields under nitrogen do not show significant differences among the polymers, while in air, silicon-containing polymers show a slight increase in the char yield.

Silicon has proven to be one of the first choices as a flame-retardant element. The silicon dependence of the limiting oxygen index (LOI) has been investigated in several families of silicon-containing polymers.[35] LOI measures the ease at which materials can be extinguished and is the minimum percent of oxygen in an oxygen/nitrogen atmosphere that will just sustain combustion in a candle-like configuration of a top-ignited vertical test specimen. The LOI values obtained for our polyurethanes are listed in Table 3. As soon as a silicon-containing polyol was introduced (from 1.7 wt % Si), the LOI improved slightly and reached an index of 19. LOI increased with the PSi194 ratio and was maximum for neat PSi194 polyurethane. The significance of this result is that polyurethanes PU-6.2 and PU-9 (whose LOI values are higher than 21) no longer burn in ambient air if there is no supplementary oxygen and are therefore very interesting materials for applications that require fire resistance.

To understand the role of silicon in the enhancement of flammability, scanning electronic microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) images were made of samples before and after the burning test. Figure 8a,c represents the surface SEM image of the PU-9 sample before and after the LOI test, respectively. The Si-mapping profile before the combustion test (Figure 8b) showed a homogeneous distribution of silicon, while the mapping after combustion (Figure 8d) showed that the burned surface was covered with char layers containing silicon atoms in very high densities. The relatively high oxygen density and low carbon density in the top burned surface (O and C mapping profiles are not shown) demonstrated that the residue contained a certain amount of silica (SiO_2). These observations are in accordance with the mechanism of improved fire performance via silicon modification. Incorporating silicon into the polymers enhanced flame retardancy because it produced continuous layers of silica that retarded the oxidation of the char.[36]

Conclusions

A novel silicon polyol (PSi194), based on methyl 10-undecenoate (UDM) and phenyl tris(dimethylsiloxy)silane (PTDS), was synthesized. A series of five different polyurethanes with a silicon content between 1.7% and 9.0% was prepared from the above-mentioned polyol, epoxidized methyl oleate-based polyether polyol (P184), and MDI by varying the molar ratio of the polyols. The most notable change from the incorporation of PSi194 is the appearance of melting endotherms of variable enthalpy and position and a downward shift in the T_g. These polyurethanes have T_g's ranging from 9 to 39 °C. As the PSi194 content increases, partial crystallinity and phase separation were detected using WAXD data. The samples with no crystallinity are transparent, while those with crystallinity are white. Polyurethanes containing P184 exhibit a dynamomechanical behavior typical of cross-linked polymeric networks, while PU-9 behaves like a semicrystalline material; there is a soft rubbery phase with a glass transition temperature of 31 °C and a hard crystalline phase with a melting transition of 90 °C. All polyurethanes are thermally stable over 250 °C. Char yields under nitrogen do not show significant differences among the polymers, but in air, the char yield for silicon-containing polymers increases slightly. The limiting oxygen index (LOI) increases with the PSi194 ratio and reaches values higher than the atmospheric oxygen index for PU-6.2 and PU-9. From the SEM-EDX analysis before and after burning tests, the improved fire performance can be explained by the production of continuous layers of silica that retarded the oxidation of the char. These novel biobased polyurethanes were prepared using 49−70 wt % of biorenewable materials, which shows that it is possible to exploit renewable resources to manufacture original and useful materials.

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