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From multi-functional siloxane-based cyclic carbonates to hybrid polyhydroxyurethane thermosets

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ABSTRACT

In this study, various novel cyclic carbonate-siloxane monomers were synthesized by hydrosilylation and CO_2 carbonation of allyl glycidyl ether and epoxy-eugenol functions. Different structures were obtained from cyclic siloxane (D4) or linear PMHS-PDMS polymers with dangling cyclic carbonate functions. This hybrid route gives access to highly functional and low viscous cyclic carbonate monomers. Cyclic siloxane-carbonate monomers were reacted with 1,5-diamino-2-methylpentane (DYTEK-A) and 1,3-cyclohexanebis(methylamine) (CBMA) to afford polyhydroxyurethane (PHUs) thermosets as non-isocyanate polyurethanes (NIPUs) with high conversions and good reactivity. PHU thermosets were characterized to compare the thermal and mechanical properties of those different structures. The impact of the functionality was highlighted with different functional oligomers playing on cross-linking density of materials. D4 structure led to short and functional star shape monomers and afforded polymers with the highest mechanical properties. Eugenol, with an aromatic moiety, increased the stiffness and the thermal stability of PHU thermosets. Such hybrid PHU-siloxanes polymers combined flexibility of siloxanes with high mechanical performances of urethane groups.

Keywords: Cyclic carbonate; Polyhydroxyurethane; Siloxane; Thermoset; eugenol

INTRODUCTION

Polyurethanes (PUs) are one of the most widely used polymers in the world and ranked 6th with 18Mt of global production in 2016.[1] They are used in a broad range of applications such as aeronautics, clothing, coatings, adhesives, insulation, etc.[2]–[6] They are obtained by the reaction of isocyanates and alcohols to afford urethane (carbamate) groups. The use of isocyanates to synthetize PUs presents environmental and health issues due to the high toxicity of those monomers.[7] The substitution of isocyanates become therefore a social issue and a major concern. As a new design of non-isocyanate polyurethanes (NIPUs), PolyHydroxyUrethanes (PHUs) are promising solutions to replace PUs. The reaction between cyclic carbonates and amines leads to urethane function with an additional hydroxyl group. Several reviews have reported the synthesis of such less toxic pathway [8], [9] and some focused specifically on eco-friendly and biobased pathways.[10]–[13] One of the main routes to synthetize cyclic carbonates involve the CO_2 carbonation of epoxydes.[11], [14] Furthermore, as a cheap, non-toxic and renewable resource, CO_2 presents major advantages. However, the main drawback of this system remains the low reactivity and the low conversion of the carbonate/amine reaction.[15], [16] To obtain PHU thermosets with interesting properties in terms of solvent resistance, thermal and mechanical properties, hybrid pathways have been explored. Indeed, hybrid non-isocyanate polyurethanes (H-NIPUs) give access to isocyanate-free polyurethanes mixing properties and reactivities of different polymers. To achieve complete curing and higher conversion, PHU prepolymers synthesized with amine excess can be reacted with epoxy monomers[17]–[19] or acrylate monomers.[20] PHU prepolymers with trimethoxysilane end groups have also been used for coatings *via* sol-gel routes[21]. Furthermore, cyclic carbonates are responsible of an increase of viscosity. Few cyclic carbonates with high functional structures have been synthesized and their high viscosity or solid state can be critical for processing.[22] However high functional monomers are needed to obtain high performance thermosets. Consequently, we decided to prepare multicarbonates with siloxane moieties in order to obtain liquid and low viscous polycarbonate.

The polysiloxanes are silicon derivatives built from Si-O-Si linkage such as polydimethylsiloxane (PDMS). They form the family of silicones and are found in many applications thanks to their remarkable properties such as hydrophobicity, high flexibility and

high thermal stability.[23]–[25] They are often used as hybrid-polymers by tuning them with other polymers to enhance their properties and mainly their mechanical strength. For example, the modification of siloxanes with epoxy groups is often reported.[26]–[28] The use of isocyanates grafted on siloxane chains afforded hybrid PU-siloxane polymers of high performances.[29]–[34] The synthesis of organic/inorganic hybrid PHU materials is therefore a promising approach to get rid of the use of isocyanates. Such hybrid routes are also a great way to improve the properties of conventional PHUs. Siloxanes monomers are furthermore commercially available in a large range of structure and functionality. Firstly, PDMS-amine can be reacted with cyclic carbonates to obtain such hybrid structures.[21], [35] On the other hand, cyclic carbonates can be directly modified with siloxane moieties. Various cyclic carbonate monomers can therefore be synthesized from tunable siloxanes derivatives, mainly by the reaction of hydrosylilation between allyl glycidyl ether (AGE) and polymethylhydrosiloxane (PMHS) moieties. A simple CO_2 carbonation of epoxy functions leads to cyclic carbonate monomers. Aguiar *et al.* obtained bis(cyclic carbonate)poly(dimethylsiloxane) from epoxy-PDMS and reacted this monomer with amines and diamines for PHUs synthesis.[36] Blattman *et al*. synthesized multifunctional POSS cyclic carbonates for casting and coatings applications.[37] Hybrid PHU-siloxane coatings have also been performed by Liu *et al*.[38] They reacted AGE with linear PMHS-PDMS oligomers and obtained various cyclic carbonates from CO_2 carbonation. Zhenya et *al.* reached to graft directly cyclic carbonate functions on siloxane chains by reacting allyl carbonate with PMHS in heterogeneous mixture with acetonitrile. Dielectric properties and ionic conductivities of those polymers were finally discussed.[39] On the other hand, eugenol is an interesting candidate to graft aromatic and biobased structures on siloxane chains thanks to its allylic function.[40], [41] As a biobased phenol, eugenol is generally obtained either from cloves (of which the main product is clove oil: 80%w) or from lignin by enzymatic reactions and has been widely used to synthesize rigid thermosets with high thermal stability.[42], [43]

The aim of this study is to synthetize different cyclic carbonate structures with dangling functions from linear and cyclic siloxane moieties. This hybrid pathway mixes siloxanes structures and cyclic carbonates functions to access to highly functional carbonate monomers with low viscosity. Cyclic siloxane (D4) and linear siloxane chains (PMHS-PDMS) of different functionalities were reacted with AGE or epoxidized eugenol. CO_2 carbonation of those monomers have led to four cyclic carbonates structures. D4-carbonate and PDMS-

eugenol carbonate are novel structures. Hence, star-shape and aromatic siloxane carbonate monomers were reported for the first time (Figure 1). The chemical structures were characterized by ^{1}H-, ^{13}C-NMR and FTIR analyses. 1,5-diamino-2-methylpentane (DYTEK-A) and 1,3-cyclohexanebis(methylamine) (CBMA) was used as curing agents to synthetize PHU thermosets. Different functionalities are finally compared through thermal and mechanical properties of PHU thermosets as well as different structures, functions and lengths.

EXPERIMENTAL PART

Materials

Allyl glycidyl ether, Karstedt's catalyst (Pt 2%), Poly(dimethylsiloxane-co-methylhydrosiloxane) trimethylsilyl terminated ($M_n \approx 950$ g/mol, Si-H ≈ 6, noted "Si-6"), 1,5-diamino-2-methylpentane (DYTEK-A) and epichlorohydrin were purchased from Sigma-Aldrich. Sodium hydroxide, toluene and ethyl acetate (EtOAc) were supplied from VWR. α-xylene, eugenol and 2,4,6,8-Tetramethylcyclotetrasiloxane (D4H) were obtained from Alpha Aesar. Tetrabutyl ammonium bromide was purchased from Acros Organics. 1,3-cyclohexanebis(methylamine) (CBMA) was supplied by Mitsubishi Gas Chemicals. Poly(dimethylsiloxane-co-methylhydrosiloxane) trimethylsilyl terminated ($M_n \approx 1000$ g/mol, Si-H ≈ 3.5, noted "Si-3.5") was obtained from Elkem. All materials were used as received. Deuterated solvent $CDCl_3$ was obtained from Eurisotop for NMR studies.

Nuclear Magnetic Resonance analyses (NMR): Proton nuclear magnetic resonance (^{1}H NMR) analyses were performed in deuterated chloroform ($CDCl_3$) using a Bruker Avance 400 MHz NMR spectrometer at a temperature of 25 °C. NMR samples were prepared as follows: 10 mg of product for ^{1}H experiment in around 0.5 mL of $CDCl_3$. The chemical shifts were reported in part per million relative to tetramethylsilane.

Thermogravimetric Analyses (TGA) were performed using a TG 209F1 libra apparatus (Netzsch) at a heating rate of 20 °C/min. Approximately 10 mg of sample was placed in an alumina crucible and heated from room temperature to 600 °C under nitrogen atmosphere.

Differential Scanning Calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as the purge gas. Approximately 10 mg of sample was placed in perforated aluminum pans and the thermal properties were recorded between -100 °C and 200 °C at 20 °C/min to observe the glass transition temperature (T_g). The T_g values were measured on the second heating ramp to erase the thermal history of the polymer. All the reported temperatures are mean values.

Dynamic Mechanical Analyses (DMA) were carried out on Metravib DMA 25 with Dynatest 6.8 software. Samples were tested according to uniaxial tension mode while heating at a rate of 3 °C/min, at a frequency of 1 Hz with a fixed strain of 10^{-5} m.. Temperatures of

measurements were chosen to surround the *alpha* transition and fixed from ≈ T_g -100 °C to T_g +100 °C of the analyzed thermosets. These conditions were chosen to study the elastic behavior of the materials. All the analyses were performed two times on each materials.

Fourier Transform Infrared Spectroscopy (FTIR): Infrared (IR) spectra were recorded on a Nicolet 210 Fourier transform infrared spectroscopy spectrometer. The IR vibration bands absorptions mentioned in the text are reported in cm^{-1}. Materials analyses were recorded thanks ATR accessory. The conversions of PHU thermosets are calculated from areas of the urethane band (C=O, ≈1690 cm^{-1}) and the carbonate band (C=O, ≈1790 cm^{-1}), Equation 1.

Equation 1

$$Conversion = \left(1 - \frac{\int carbonate}{\int carbonate + \int urethane}\right) \times 100$$

Titration of the carbonate equivalent weight by ^{1}H-NMR: The Carbonate Equivalent Weight (CEW) is the amount of product needed for one equivalent of reactive carbonate function. It was determined by ^{1}H-NMR using an internal standard (benzophenone). A known weight of product and benzophenone was poured into an NMR tube and 500 mL of $CDCl_3$ were added. It was determined using the Equation 2 y comparing the integral of the protons of the benzophenone and the integral of the carbonate moiety.

Equation 2

$$AEW = \frac{\int PhCOPh * H_{carbonate}}{\int crabonate * H_{PhCOPh}} * \frac{m_{carbonate}}{m_{PhCOPh}} * M_{PhCOPh}$$

$\int_{PhCOPh}$: integration of the benzophenone protons; $\int_{carbonate}$: integration of the protons of the carbonate function; $H_{carbonate}$: number of protons of the carbonate function; H_{PhCOPh}: number of protons of the benzophenone; $m_{carbonate}$: weight of the product; m_{PhCOPh}: weight of the benzophenone; M_{PhCOPh}: molecular weight of the benzophenone

Cross-linking density: From rubber elasticity theory, the uniaxial stretching was studied on the rubbery plateau at T > T_α+50 (T = T_α+50 °C for all materials), and at very small deformations.[44] Under these hypotheses, the cross-linking density (υ'), can be obtained from Equation 3, where E' is the storage modulus (Pa), R is gas constant (8.314 $J.K^{-1}.mol^{-1}$) and T_α is the temperature, in K, of transition from vitreous to rubber domain of material determined at the maximum of the tan δ curve. Calculated values are given for information purposes and can only be compared.

Equation 3

$$\nu' = \frac{E'_{at\ T\alpha+50}}{3RT_{\alpha+50}}$$

Swelling Index (SI): Three samples of around 30 mg each were separately put in THF for 24 h. The swelling index was calculated using the Equation 4 where m_2 is the mass of the material after swelling in THF and m_1 is the initial mass of the material.

Equation 4

$$SI = \frac{m_2 - m_1}{m_1} \times 100$$

Gel Content (GC): After SI measurements, the three samples were dried in a ventilated oven at 70 °C for 24 h. The gel content was calculated using the Equation 5, where m_3 is the mass of the material after drying and m_1 is the initial mass of the material.

Equation 5

$$GC = \frac{m_3}{m_1} \times 100$$

Viscosity: Viscosities measurements were performed by rheological analyses at 25 °C on the AR-1000 rheometer (TA Instruments). A 40 mm diameter and 4° cone-plan geometry was used. Analyses in flow mode was performed with a gradient from 50 to 0.1 rad.s^{-1}. The maximum shear rate used was decrease for the most viscous monomers. Viscosity values are given as mean values.

Procedure for cyclic carbonates synthesis

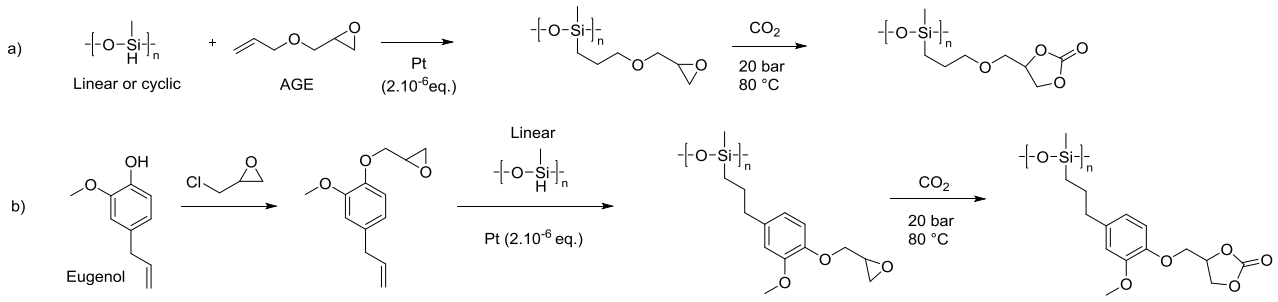

Figure 1. Syntheses of cyclic carbonates from AGE (a) and Eugenol (b)

Si-3.5 epoxy synthesis

In a round bottom flask, the PDMS-PMHS (Si-3.5, Si-H=3.5) (10 g, 1 eq.) and the allyl glycidyl ether (AGE) (3.72 g, 1 eq./Si-H) was solubilized in 20 mL of toluene. To eliminate any trace of moisture the solution was distilled at 50 °C under vacuum and a few amount of toluene was removed. The flask was poured under vacuum and then filled with argon gas (repeated 3 times). The reaction was finally stirred and conducted at 80 °C. The Karstedt's catalyst (Pt 2%w in xylene) was diluted 10 times in xylene before being added to the reaction (2.10^{-6} eq. of Pt). After 4 hours of reaction, activated charcoal and Na_2SO_4 were poured in the

solution and stirred for few hours. The solution was finally filtered on a fritted glass full of Na_2SO_4 and the solvent was removed under vacuum. A yellow viscous liquid was obtained with 85% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 0.1 ppm (m, Si-CH_3); 0.54 (m, Si-CH_2-) ; 1.65 (m, -CH_2-); 2.63 (m, -CH_2-O epoxy group); 2.81 (m, -CH_2-O epoxy group); 3.16 (m, -CH-O epoxy group); 3.37-3.53 (m, O-CH_2- and –O-CH_{2-}); 3.72 (d, O-CH_{2-}).

Si-6 epoxy synthesis

Si-6 epoxy was synthesized following the same hydrosilylation procedure using Si-6 (10 g, 1 eq.), AGE (7.6 g, 1 eq./Si-H), Karstedt's catalyst (2.10^{-6} eq. of Pt), and toluene (20 mL). (η = 93%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 0.07 ppm (m, Si-CH_3); 0.50 (m, Si-CH_2-) ; 1.61 (m, -CH_2-); 2.60 (m, -CH_2-O epoxy group); 2.78 (m, -CH_2-O epoxy group); 3.13 (m, -CH-O epoxy group); 3.34-3.50 (m, O-CH_2- and –O-CH_{2-}); 3.68 (d, O-CH_{2-}).

D4-epoxy synthesis

D4-epoxy was synthesized following the same hydrosilylation procedure using D4H (7.5 g, 1eq.), AGE (19.7 g, 1 eq./Si-H),), Karstedt's catalyst (2.10^{-6} eq. of Pt), and toluene (20 mL). (η = 83%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 0.08 ppm (m, Si-CH_3); 0.52 (m, Si-CH_2-) ; 1.62 (m, -CH_2-); 2.60 (q, -CH_2-O epoxy group); 2.79 (t, -CH_2-O epoxy group); 3.13 (m, -CH-O epoxy group); 3.34-3.50 (m, O-CH_2- and –O-CH_{2-}); 3.68 (d, O-CH_{2-}).

Si-eugenol epoxy synthesis

Eugenol was reacted with epichlorohydrin to yield to eugenol-epoxy monomer. The eugenol (10 g, 1 eq.), the epichlorohydrin (28.2 g, 5 eq.) and the catalyst TBABr (0.7 g, 0.05 eq.) were poured in a round bottom flash and stirred for 4 hours at 100 °C. The solution was then cooled down to room temperature and TBABr (0.7 g, 0.05 eq.) and a solution of NaOH 20%w (5 eq.) were added to the mixture for additional 2 hours. Ethyl acetate was finally added and the solution was washed 3 times with water and brine. The organic layer was finally dried with $MgSO_4$ and solvent was removed under vacuum to afford a yellow/green viscous liquid (η = 83%).

The Si-eugenol epoxy was synthesized from eugenol-epoxy monomer following the same hydrosilylation procedure using Si-3.5 (11.15 g, 1 eq.), eugenol-epoxy (8 g, 1 eq./Si-H), Karstedt's catalyst (2.10^{-6} eq. of Pt), and toluene (15 mL). (η = 86%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 0.06 (m, Si-CH_3); 0.54 (m, Si-CH_2-); 1.62 (m, -CH_2-); 2.53 (m, -CH_2-φ); 2.78 (m, -

CH_2-O epoxy group); 2.87 (m, -CH_2-O epoxy group); 3.36 (m, -CH-O epoxy group); 3.82 (m/s, O-CH_3); 4.01 (m, O-CH_2-); 4.17 (m, O-CH_2-); 6.58-6.90 (m, φ).

Carbonation procedure

The same procedure was applied for the four synthesized siloxane-epoxy monomers. The epoxy monomers was solubilized in ethyl acetate and poured in a autoclave reactor with 3%w of tetrabutylammonium bromide (TBABr). The reaction was conducted at 80 °C under pressure (P = 20 bar) for 3 days. The solution was then rediluted in ethyl acetate and washed with water (3 times) and brine. The organic layer was finally dried with $MgSO_4$ and solvent was removed under vacuum to afford a yellow viscous liquid.

Si-3.5 carbonate: ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 0.07 ppm (m, Si-CH_3); 0.50 (m, Si-CH_2-); 1.62 (m, -CH_2-); 3.46 (m, -CH_2-O); 3.58-3.74 (m, O-CH_2-); 4.39 (t, O-CH_2- carbonate); 4.50 (t,-CH_2- carbonate); 4.82 (m, O-CH- carbonate). ^{13}C NMR (101 MHz, $CDCl_3$, δ): -0.44 (Si-*C*H_3); 1.17 (*C*H_3-Si-*C*H_3); 1.88 (CH_2-Si-*C*H_3); 13.34 (CH_3-Si-*C*H_2); 23.10 (Si-CH_2-*C*H_2); 66.35 (CH_2 carbonate); 69.66 (O-*C*H_2-CH); 74.61 (O-*C*H_2-CH_2); 75.29 (CH carbonate); 155.08 (C carbonate). FTIR (cm^{-1}): 2960 (C-H aliphatic), 2871 (C-H aliphatic), 1791 (C=O carbonate), 1256 (Si-C), 1169 (C-O-C), 1005 (Si-O). (η = 82%).

Si-6 carbonate: ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 0.09 ppm (m, Si-CH_3); 0.50 (m, Si-CH_2-); 1.63 (m, -CH_2-); 3.46 (m, -CH_2-O); 3.55-3.73 (m, O-CH_2-); 4.38 (t, O-CH_2- carbonate); 4.49 (t,-CH_2- carbonate); 4.82 (m, O-CH- carbonate). ^{13}C NMR (101 MHz, $CDCl_3$, δ): -0.38 (Si-*C*H_3); 1.24 (*C*H_3-Si-*C*H_3); 1.93 (CH_2-Si-*C*H_3); 13.37 (CH_3-Si-*C*H_2); 23.17 (Si-CH_2-*C*H_2); 66.35 (CH_2 carbonate); 69.69 (O-*C*H_2-CH); 74.55 (O-*C*H_2-CH_2); 75.37 (CH carbonate); 155.14 (C carbonate). FTIR (cm^{-1}): 2958 (C-H aliphatic), 2874 (C-H aliphatic), 1790 (C=O carbonate), 1258 (Si-C), 1167 (C-O-C), 1009 (Si-O). (η = 80%).

D4-carbonate: ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 0.06 ppm (m, Si-CH_3); 0.49 (m, Si-CH_2-); 1.57 (m, -CH_2-); 3.44 (m, -CH_2-O); 3.53-3.70 (m, O-CH_2-); 4.35 (t, O-CH_2- carbonate); 4.48 (t,-CH_2- carbonate); 4.79 (m, O-CH- carbonate). ^{13}C NMR (101 MHz, $CDCl_3$, δ): -0.70 (Si-*C*H_3); 1.87 (CH_3-Si-*C*H_2); 23.00 (Si-CH_2-*C*H_2); 66.27 (CH_2 carbonate); 69.61 (O-*C*H_2-CH); 74.30 (O-*C*H_2-CH_2); 75.36 (CH carbonate); 155.12 (C carbonate). FTIR (cm^{-1}): 2930 (C-H aliphatic), 2871 (C-H aliphatic), 1784 (C=O carbonate), 1260 (Si-C), 1165 (C-O-C), 1040 (Si-O). (η = 55%).

Si-eugenol carbonate: ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 0.06 ppm (m, Si-CH_3); 0.53 (m, Si-CH_2-); 1.62 (m, -CH_2-); 2.53 (m, -CH_2-φ); 3.80 (m/s, O-CH_3); 4.16 (m, O-CH2-); 4.59 (m, O-CH2- carbonate); 4.97 (m, O-CH- carbonate); 6.58-6.90 (m, φ). ^{13}C NMR (101 MHz, $CDCl_3$, δ): -0.25 (Si-*C*H_3); 1.27 (*C*H_3-Si-*C*H_3); 1.92 (CH_2-Si-*C*H_3); 17.43 (CH_3-Si-*C*H_2); 25.30 (Si-CH_2-*C*H_2); 39.24 (CH2-*C*H2- φ); 55.94 (O-*C*H3); 66.52 (CH_2 carbonate); 69.73 (O-*C*H_2-CH); 74.60 (CH carbonate); 112.85-144.55 (φ); 150.24 (C carbonate). FTIR (cm^{-1}): 2960 (C-H aliphatic), 2926 (C-H aliphatic), 1795 (C=O carbonate), 1589 (C-H aromatic), 1513 (C-H aromatic), 1256 (Si-C), 1166 (C-O-C), 1013 (Si-O). (η = 73%).

Procedure for PHUs syntheses

Several formulations were carried out using synthesized carbonate monomers and different amines. In order to prepare the materials, the mass of amine was calculated using the Equation 6. The amine hydrogen equivalent weight (AHEW) and the carbonate equivalent weight (CEW) represent the amount of product needed for one equivalent of reactive function.

Equation 6

$$m_{amine} = \frac{AHEW_{amine} \, x \, m_{carbonate}}{CEW}$$

The materials were synthesized with a molar ratio carbonate/amine of 1/1. Indeed, one carbonate function react with one hydrogen of the primary amine. This ratio was evaluated by DSC studies. The amine and the carbonate were stirred using a SpeedMixer™ under vacuum and then the homogeneous mixture obtained was put in a silicon mold for 80 °C, 4 hours and 100 °C, 1 hour for all materials.

RESULTS AND DISCUSSION

I. Monomers synthesis

Four cyclic carbonate-siloxane monomers were obtained by hydrosilylation synthesis using Karstedt catalyst. First of all epoxy-siloxane monomers were synthesized *via* AGE grafting onto linear PMHS-PDMS oligomers leading to dangling epoxy functions. Two siloxane oligomers were chosen with two different PMHS functionality (Si-H ≈ 3,5 or 6). The number of siloxane moieties (m + n + 2 = Si-O ≈ 14) is similar for both oligomers and functionalities can thus be compared. The tetramethylcyclotetrasiloxane (D4H) were reacted with AGE to build star shape epoxy monomer from a cyclic siloxane. Finally, eugenol was reacted with epichlorohydrin and grafted onto Si-3.5 PMHS-PDMS oligomer. These four epoxy monomers were finally converted into cyclic carbonate monomers by CO_2 carbonation with tetrabutylammonium bromide (TBABr) as catalyst. Carbonation reactions were conducted in autoclave reactor at 80 °C under pressure (P = 20 bar). The structure of cyclic carbonates bearing by PMHS-PDMS chains was previously described by Liu *et al.*[38] and have been synthesized for this study to be compared with the novel structures with D4 and eugenol. The structures of synthesized cyclic carbonates and amines are shown Figure 2.

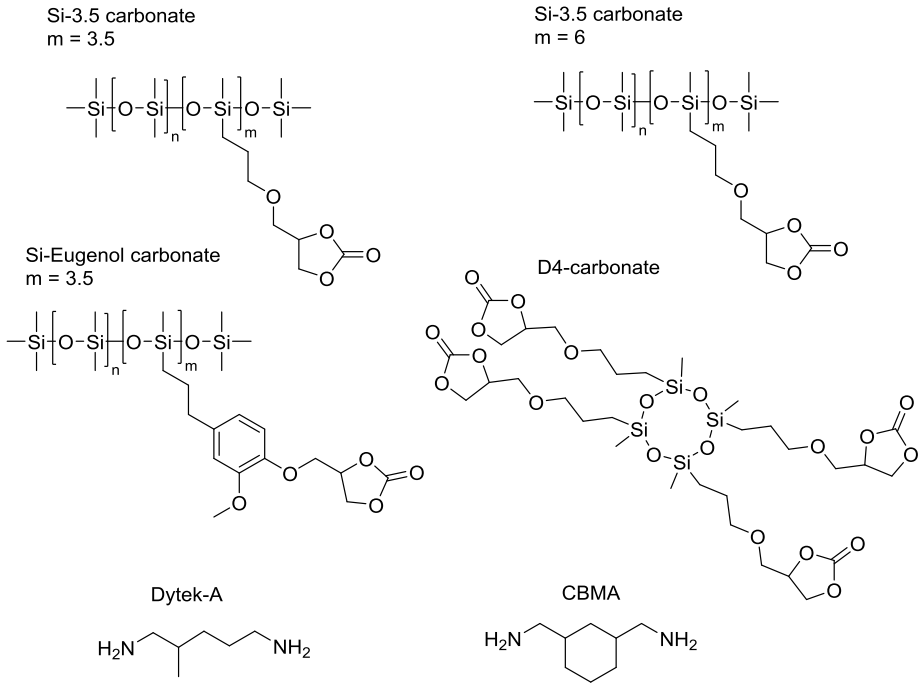

Figure 2. Structures of synthesized siloxane-carbonates and amine cross-linkers

The reactions were monitored by ^{1}H-NMR analyses to control the conversion of double bonds into epoxy functions and then of epoxy functions into carbonates. The ^{1}H-NMR spectra of the different Si-epoxy intermediates are presented in SI-Figure 1,6,11,16. All the final structures were analyzed and controlled by NMR analyses: ^{1}H, COSY, ^{13}C and HMQC (SI-Figure 1-20). FTIR analyses were also performed to confirm the structures. The appearance of the carbonyl (C=O) band at 1790 cm^{-1} is characteristic of the presence of the cyclic carbonate function. All the FTIR spectra of cyclic carbonate monomers are shown in SI-Figure 21-24.

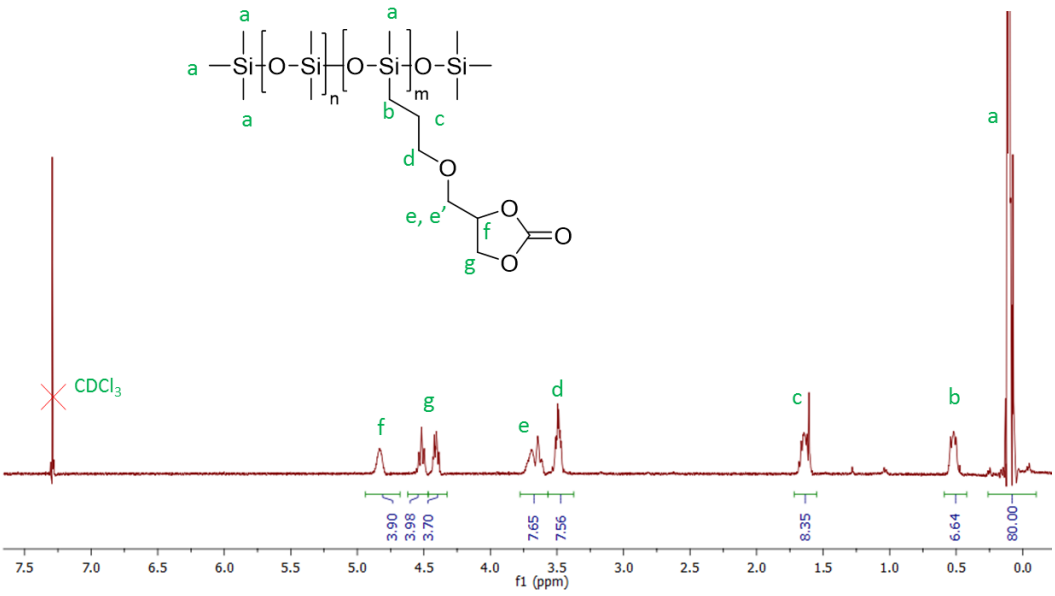

Figure 3. ^{1}H-NMR ($CDCl_3$) spectrum of Si-3.5 carbonate monomer

The ^{1}H-NMR analysis of the Si-3.5 carbonate monomer was performed in deuterated chloroform ($CDCl_3$), Figure 3. The carbonate function is confirmed by the presence of the proton *f* at 4.82 ppm and protons *g* at 4.33-4.55 ppm. The protons *e* are observed at 3.57-3.75 ppm. The grafting onto siloxane oligomer is confirmed by the disappearance of the double bond and is observed by the presence of protons *b* (0.5 ppm), *c* (1.63 ppm) and *d* (3.49 ppm). The protons *a* that correspond to the methyl groups on silicon atoms are localized at 0.1 ppm.

Both ^{1}H-NMR spectra of Si-6 and Si-3.5 carbonate monomers are similar (respectively Figure 3 and SI-Figure 7). The only differences lies in the values of integration of protons.

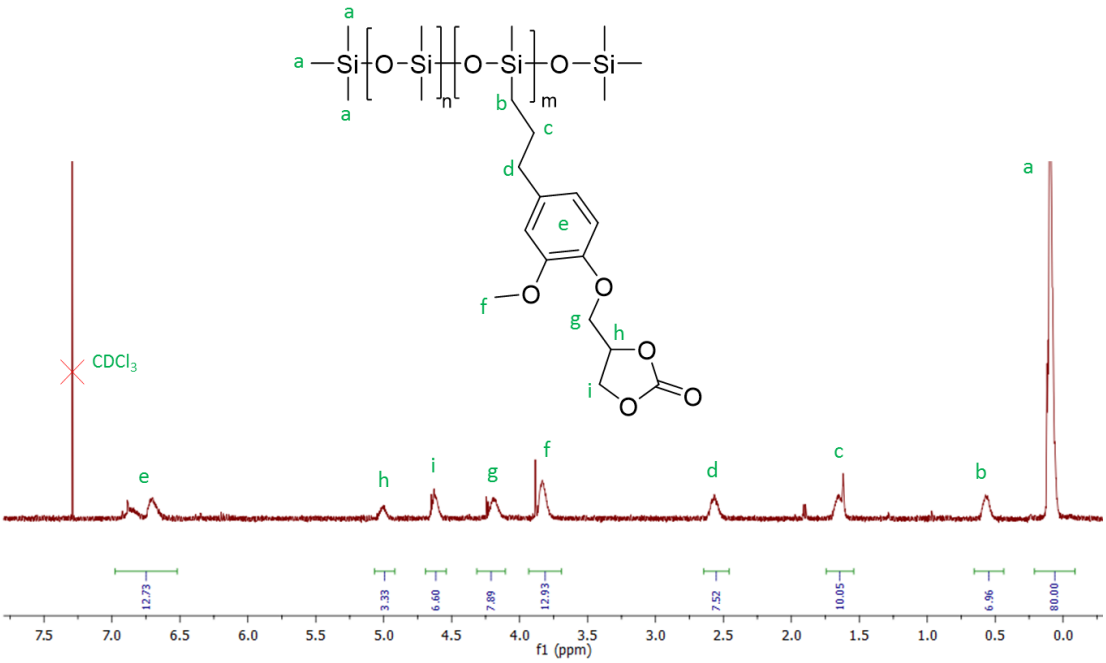

Figure 4. ^{1}H-NMR ($CDCl_3$) spectrum of Si-Eugenol carbonate monomer

Similarly, Figure 4 shows the ^{1}H-NMR spectrum of Si-eugenol carbonate monomer. In this spectrum, the signal at 0.6 ppm is assigned to the protons *a* of the methyl groups on silicon atoms. The protons *b*, *c* and *d* at respectively 0.53, 1.61 and 2.54 ppm are assigned to the chain between the siloxane oligomer and the aromatic group of the eugenol. The protons *f* of the methoxy group of eugenol are observed at 3.80 ppm whereas protons *e* of the aromatic group are observed from 6.56 to 6.92 ppm. Finally the presence of the cyclic carbonate function is confirmed by the protons *g* (4.16 ppm), *h* (4.97 ppm) and *i* (4.58 ppm).

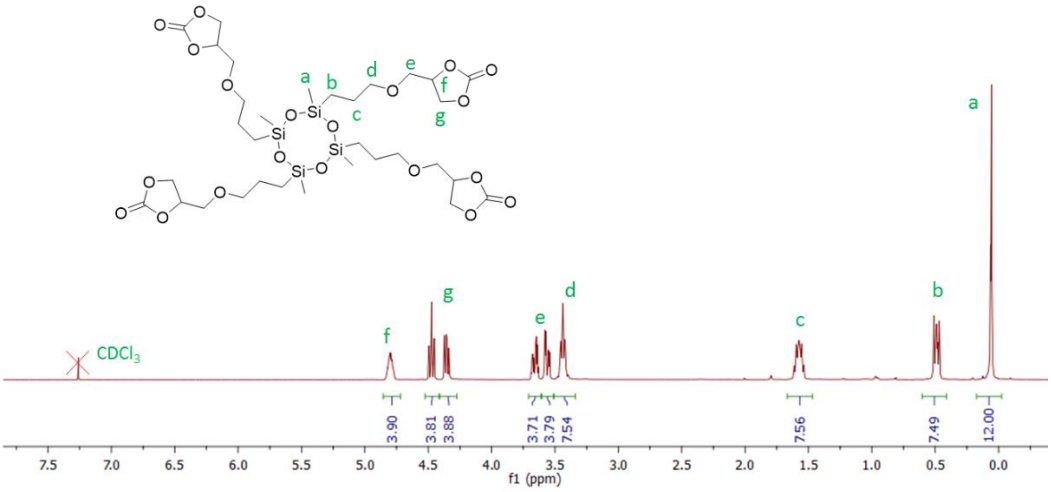

Figure 5. ^{1}H-NMR ($CDCl_3$) spectrum of D4-carbonate monomer

Finally, the ^{1}H-NMR spectrum of D4-carbonate is shown Figure 5. The protons *a* of the methylsiloxane are localized at 0.05 ppm. The allyl function were grafted onto Si-H function

of D4H. The corresponding protons *b*, *c*, *d* are observed at respectively 0.49, 1.57 and 3.43 ppm. The cyclic carbonates function are characterized by the presence of the proton *f* at 4.79 ppm, the protons *g* from 4.30 to 4.53 ppm and the protons *e* from 3.50 to 3.72 ppm.

Table 1. Properties of synthesized cyclic carbonate- siloxane monomers

Carbonates	**CEW (g/eq.)**	**Viscosity (Pa.s)**
Si-3.5 Carbonate	454	0.5
Si-6 Carbonate	298	4
D4 Carbonate	218	12
Si-Eugenol Carbonate	605	61

The viscosity of synthesized monomers was evaluated through rheological analyses in flow mode. The results are summarized Table 1 and measurements are shown in SI-Figure 28. Due to a higher functionality, Si-6 carbonate (4 Pa.s) is more viscous than the Si-3.5 carbonate (0.5 Pa.s). The D4 carbonate (12 Pa.s) has the higher ratio of carbonate functions compare to siloxane chains and is therefore more viscous than Si-3.5 and Si-6 carbonates. The eugenol-based carbonate has the highest density in carbonate function (CEW) and present also the highest viscosity (61 Pa.s). The cyclic carbonate function confers rigidity to polymers due to the creation of numerous physical bonds. Therefore, cyclic carbonates increase a lot the viscosity of monomers while siloxanes are low viscous polymers. For process issue this high viscosity is a major drawback. Hence, to perform cyclic carbonates of high functionality and low viscosity is a true challenge. For comparison, classical short and functional cyclic carbonates such as glycerol-, pentaerythritol- and trimethylolpropane- based cyclic carbonates have a dynamic viscosity at 25 °C of respectively, 213 Pa.s, 13000 Pa.s and 133 Pa.s.[22] The hybrid pathway employed in this study is therefore an access to high functional cyclic carbonates of low viscosity.

II. Synthesis and characterizations of PHU-siloxane thermosets

In order to synthetize various PHU thermosets the four carbonate monomers were reacted with two different amines, the 1,5-diamino-2-methylpentane (DYTEK-A) and the 1,3-cyclohexanebis(methylamine) (CBMA). Firstly, long aliphatic amines such as Priamine (Croda®) and a PDMS amine-terminated ($M_n \approx 2{,}500$ g/mol) were reacted with siloxane-carbonate monomers but have presented strong miscibility issues. These mixtures did not afford cross-linked and solid materials but only viscous and biphasic gels. Therefore,

DYTEK-A and CBMA were chosen as short and aliphatic amines to avoid miscibility issues with carbonate moieties.

Determination of optimized formulations and curing process

To synthetize PHU thermosets, the theoretical ratio for the carbonate/NH_2 couple is 1:1 *ie* one carbonate function for one amine function. In order to confirm the theoretical value and to follow the best formulation ratio, the optimum stoichiometry between carbonate monomers and amines was determined by DSC (maximum glass transition temperature of cured materials). The highest glass transition temperature (T_g) of materials is obtained for the optimum network, which has the highest cross-linking density and thus the less unreacted free functions. This study was performed for Si-eugenol carbonate monomer with DYTEK-A as the cross-linker. Five different ratios were chosen around 1:1 and materials were cross-linked at 80 °C for 4 hours and at 100 °C for 1 hour to achieve the complete conversion. The variation of the T_g, measured during the second DSC run, is plotted versus the Carbonate/Amine ratio in Figure 6.

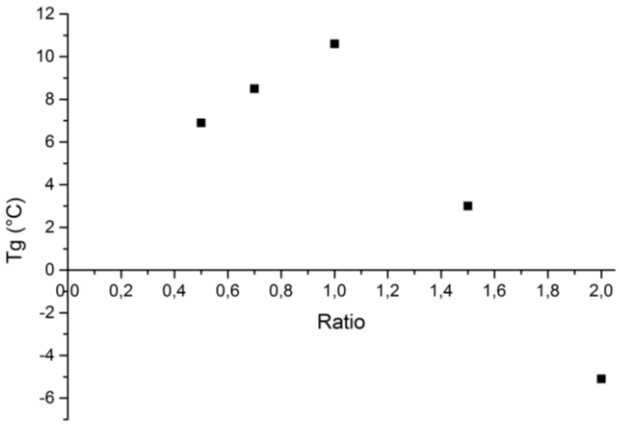

Figure 6. T_g values measured by DSC of materials Si-Eugenol/Dytek-A at different stoichiometric ratios carbonate/NH_2

The optimum ratio measured with DSC analysis corresponds to the maximum of T_g. This experimental result is similar to the theoretical ratio of 1:1. Therefore, all the following materials were formulated according to this ratio.

The thermosets were prepared in solvent free and catalyst free conditions according to the following procedure: the cylocarbonate monomers and amines were first mixed under vacuum with a SpeedMixer™ to perform homogeneous mixture and to avoid the presence of bubbles. The mixture was then pulled in a silicon mold and cured in an oven at 80 °C for 4 hours and 100 °C for 1 hour.

Structural characterizations

Table 2. Formulations of PHU-siloxane thermosets

Material names	Carbonate	Amine	FTIR Conversion (%)	SI (%)	GC (%)
Si-3.5-D	Si-3.5 C5	Dytek A	89	259	92
Si-3.5-C		CBMA	85	162	90
Si-6-D	Si-6 C5	Dytek A	94	118	98
Si-6-C		CBMA	87	128	97
Eug-D	Si-Eugenol C5	Dytek A	98	218	94
Eug-C		CBMA	94	217	93
D4-D	D4 C5	Dytek A	86	112	100
D4-C		CBMA	96	105	100

CEW: Carbonate Equivalent Weight (determined by NMR titration); SI: Swelling index (THF); GC: Gel Content (THF)

The conversion of cyclic carbonate functions is evaluated from FTIR analyses (SI-Figure 25) and results are summarized Table 2. The cyclic carbonate functions react with amine functions and lead to urethane groups formation. The conversions were calculated according to the band area ratio between the carbonate group and the sum of carbonate groups and urethane groups, Equation 1. High conversions were obtained with all PHU materials with values from 85% to 96%. The conversion of the carbonate/amine reaction is known to be limited, partly due to the presence of hydrogen bonds and high viscosity of the growing polymer.[15], [16], [45] Values above 90% are very high for solvent- and catalyst-free systems. High temperature are also used to overcome this limit but side-reactions are also promoted. These good results could be explained by the use of high functional monomers as well as the low viscosity of the siloxane monomers which could allow to give mobility to growing species that reached higher conversions.

The gel content (GC) corresponds to the residual mass of materials after immersion in THF and drying in an oven. Values of GC are summarized Table 2. The values above 90% highlight the high conversion of materials. The network is fully cross-linked and no free species remain in the network. The completion of the curing is also confirmed by the absence of remaining enthalpy of reaction regarding to DSC analyses on cured materials. No difference of T_g is neither observed between the first and the second heating ramp.

Thermal properties

Table 3. Physico-chemical properties of PHU-siloxane thermosets

Materials	ATG		DSC	DMA			
	$Td_{5\%}$ (°C)	**Char % (°C)**	**T_g (°C)**	**T_α (°C)**	**E'_{glassy} (GPa)**	**$E'_{rub.}$ (MPa)**	**υ' (mol/m^3)**
Si-3.5-D	315	3	-12	-15	1.3	5.7	886
Si-3.5-C	300	0	4	2	1.2	5.0	729
Si-6-D	308	5	14	15	1.6	10	1392
Si-6-C	312	6	31	33	2.0	10	1310
Eug-D	304	14	11	14	1.5	3.3	461
Eug-C	309	14	26	26	1.5	3.6	482
D4-D	312	5	37	40	2.3	13	1665
D4-C	308	5	60	66	2.3	10	1183

$Td_{x\%}$: degradation temperature at x%w; E'_{glassy}: storage modulus on the glassy domain (at T_α-50 °C); $E'_{rubbery}$: storage modulus on the rubbery domain (at T_α+50 °C); υ': cross-linking density (at T_α+50 °C)

Thermogravimetric analyses (ATG) were performed on all PHU materials from 25 °C to 600 °C under nitrogen atmosphere. The ATG thermograms are plotted Figure 7 and results are summarized Table 3. The curves present a profile in two steps. A first degradation is observed from 300 °C and a second from 400 °C. The second degradation is attributed to the siloxane part of materials. Indeed the shape of this degradation is similar between the materials which all possessed similar siloxane chains. As the major variable element in these structures, the first degradation is attributed to the cyclic carbonate moiety grafted into the siloxane chain *ie* the carbon chain. The Si-6 monomer has a higher functionality and thus more cyclic carbonate moiety than the Si-3.5 monomer. Therefore, its first degradation presents a higher gap. This observation is also confirmed by D4-based materials thermograms. Indeed the D4-carbonate present the lower ratio of siloxane to carbon atoms and thus the higher gap. The aromatic ring of the Si-eugenol carbonate monomer confers more thermal stability to the material and its first degradation is therefore lower. This higher thermal stability also explain the higher value of residues content. Indeed, aromatic rings increase the char yield. Finally, no differences are observed between the two amine.

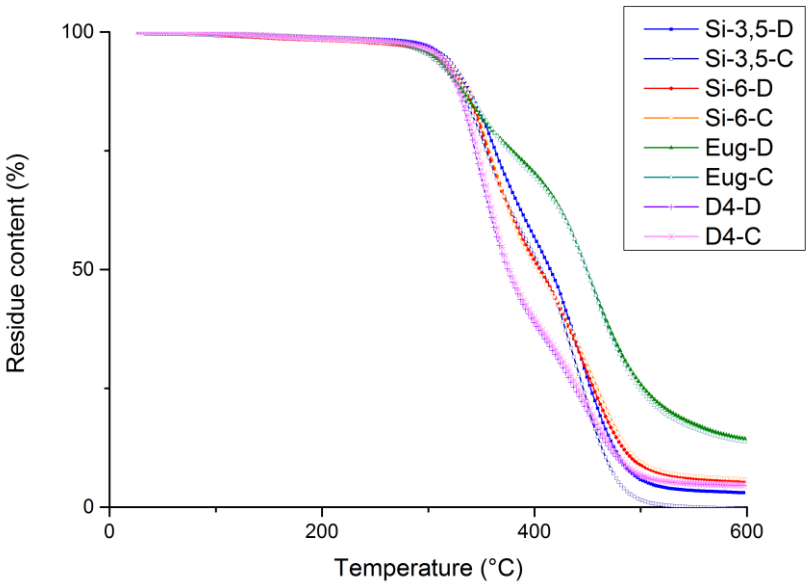

Figure 7. ATG thermograms of PHU-siloxane thermosets

The thermal properties of materials were analyzed by DSC analyses, SI-Figure 26-27. The results are summarized Table 3. The synthesized materials exhibit glass transition temperature from -12 °C to 60 °C, modulated by the different structures of carbonates and amines used. The glass transition temperature is linked to the chain mobility and depends on the structure and the cross-linking density of materials. The CBMA brings more rigidity to the network than the DYTEK-A due to presence of the aliphatic ring and its lower mobility. The T_g of materials cured with CBMA are therefore 15 °C higher than those cured with DYTEK-A. The higher gap (23 °C) with D4-carbonate is explained by the higher conversion and thus the higher cross-linking density of the network. As shown by Si-3.5 and Si-6 based materials T_g results, the higher the cross-linking density is, the higher the T_g is. Si-6 monomer has a higher functionality in cyclic carbonate functions and thus a higher cross-linking density and less space between the nodes. Therefore this monomer increased the T_g by 26 °C compare to the Si-3.5 monomer. Indeed, the functionalities can be compared provided that the length of the siloxane chains is the same. A difference of 20 °C in T_g values is also observed for eugenol-based materials compare to Si-3.5-based materials. Both are based on siloxane chain of same length and functionality. The stiffness and the weak mobility of the aromatic ring of eugenol increased the T_g of materials. Note that the use of eugenol has the same impact for T_g values than the increase of functionality with Si-6 carbonate when compare to Si-3.5-based materials. Finally, the high functionality compare to its short length gives to the D4-carbonate materials the highest T_g.

Thermo-mechanical properties

Thermo-dynamical properties of materials have been evaluated *via* dynamical mechanical analysis (DMA) and the results are summarized Table 3. The storage modulus and the tan δ of each materials are plotted versus the temperature Figure 8 and Figure 9. The maximum of the tan δ curve determines the temperature of the *alpha* transition, mechanical manifestation of the glass transition temperature. T_α follows for each materials the same trend than T_g and values of T_α and T_g are very close. Those transitions are modulated by the structure of the amine and the density of the network. The shape of the tan δ pic gives information on homogeneity of materials. The narrow peak observed Figure 10 for D4-based materials especially, indicates a very good homogeneity due to its well-defined structure compare to oligomers based materials. The storage modulus E' is an indication of the stiffness of materials. First of all no major influences are highlighted depending on the amine used and values of $E'_{rubbery}$ for DYTEK-A- and CBMA-based materials are close, contrary to the T_g and T_α values. The comparison of thermo-dynamical properties of materials according to the cyclic carbonate used presents different trends between $E'_{rubbery}$ and T_α values. Indeed the cross-linking density seems to have a strong impact on the stiffness of materials. Furthermore, the nodes of the network are urethane functions; an increase of cross-linking density is also an increase of urethane functions, known to increase the mechanical properties and the stiffness. The higher functionality of Si-6 carbonate compare to Si-3.5 carbonate increase the cross-linking density and thus the stiffness of the network and the $E'_{rubbery}$ values (5,7 MPa against 10 MPa with the DYTEK-A). The length of carbon chain of the eugenol carbonate increases the space between the nodes and therefore decrease the cross-linking density. Despite the rigidity of the aromatic ring, this lower cross-linking density is responsible of lower stiffness for the eugenol-based materials compare to the Si-3.5-based materials (3.3 MPa against 5.7 MPa with the DYTEK-A). Although the D4-carbonate materials present the highest T_α, the values of $E'_{rubbery}$ are not much above those of others materials (13 MPA and 10 MPa with DYTEK-A and CBMA respectively). According to the theory of rubber elasticity, the molecular weight between the cross-linking nodes of a cured network is proportional to its storage modulus in the rubbery domain.[44] Therefore the cross-linking density υ' is calculated by equation 3. Those values are in agreement with the space between the nodes discussed earlier and affected by the length of carbon chain between the siloxane and the cyclic carbonate and the functionality of monomers. Furthermore, those values follow the

same trend than the swelling index. The SI is proportional to the amount of solvent able to penetrate the network and therefore the space between the nodes.

Finally, a small *beta* transition is observed for Si-3,5 and Si-Eug based materials. This transition is characterized by the decrease of E' on the glassy domain and a slight peak on tan δ curves between -75 and -50 °C. This transition depends on the cross-linking density and the mobility of short segments in the network. The higher functionality of Si-6 and the cyclic structure of the D4-C5 monomers block this mobility and no *beta* transition are observed with these monomers.

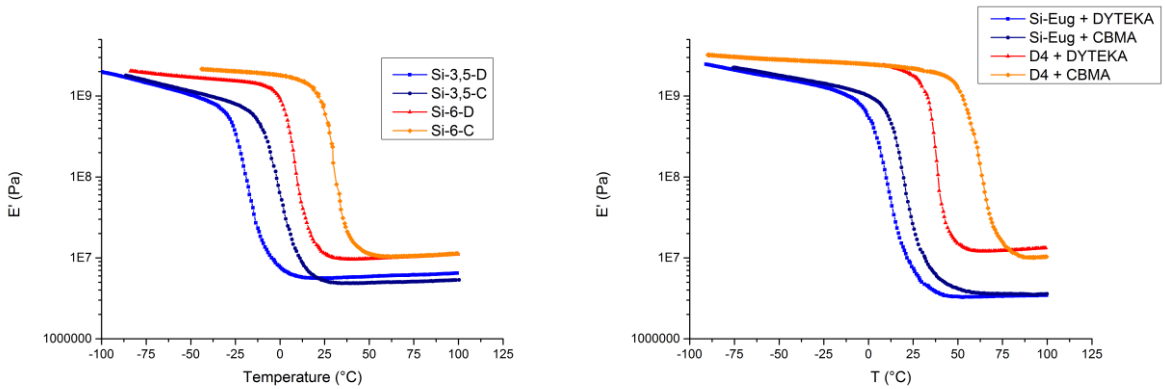

Figure 8. Storage modulus (E') versus temperature of PHU thermosets (left: Si-3.5 and Si-6; right: Si-Eugenol and D4)

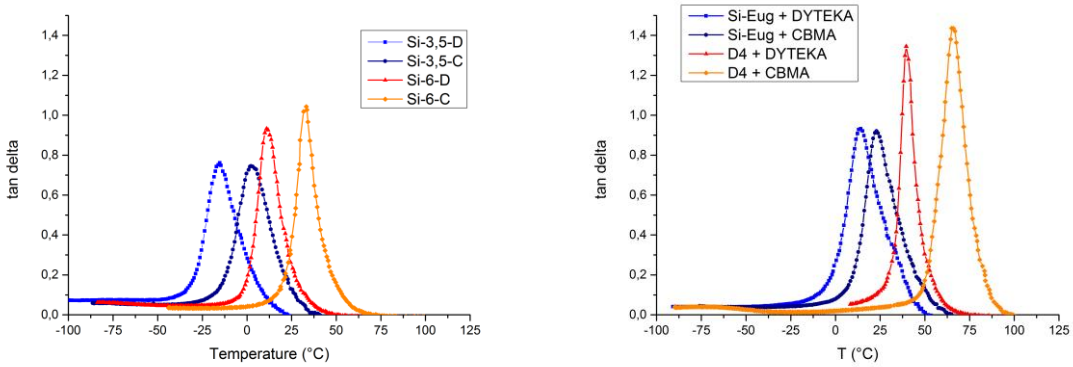

Figure 9. Tan delta versus temperature of PHU thermosets (left: Si-3.5 and Si-6; right: Si-Eugenol and D4)

The variations of the T_α values have been plotted versus the ratio of number of siloxane functions to number of carbonate functions (Si-3.5 = 4; Si-6 = 2.33; D4 = 1) for each amine used. As shown by the curves, the variation of T_α values is linear with the siloxane/carbonate ratio. Furthermore, the addition of eugenol has the same impact on T_α values than the increase of functionality with Si-6 compare to Si-3.5.

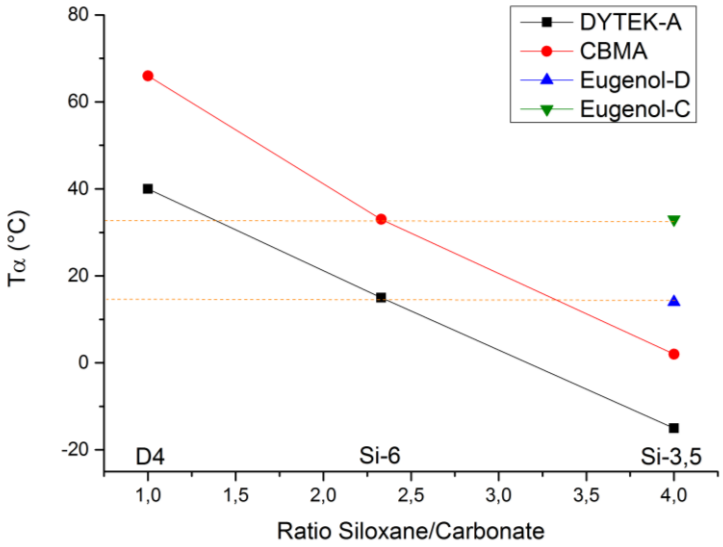

Figure 10. T_α values of thermosets versus the ratio siloxane/carbonate functions

CONCLUSION

In order to develop hybrid non-isocyanate polyurethane thermosets, new cyclic carbonate-siloxane monomers were designed by hydrosilylation and CO_2 carbonation reactions leading to dangling cyclic carbonates grafted on siloxane chains. The use of such hybrid structures enhanced properties of final materials by mixing high thermo-mechanical properties of PHUs with flexibility of siloxanes. Furthermore, cyclic carbonates of high functionality and low viscosity were obtained. The use of oligomers and highly functional monomers gave also access to high conversions. The thermoset characterizations were conducted as a comparative study highlighting the role of the functionality, the structure of the siloxane chain, the nature of the grafted cyclic carbonate and the choice of the amine as curing agent. A difference of +15 °C was observed with materials cured with CBMA instead of DYTEK-A for the T_g values but no major difference in term of stiffness (E') was observed. The difference of functionality between Si-3.5 and Si-6 monomers had a strong impact for T_g and E' values due to the higher cross-linking density conferred by Si-6 monomer. Eugenol has led to partially biobased materials and stiffness was increased thanks to its aromatic ring. The highest performances were obtained with D4-carbonate monomer build as a short star shape monomer of high functionality and high reactivity.

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The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.