Emerging Polyhydroxyurethanes as Sustainable Thermosets: A Structure−Property Relationship

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ABSTRACT: Polyhydroxyurethanes (PHU), obtained from CO_2-based cyclic carbonates (CC) and polyamines, are known as greener and safer alternatives to conventional polyurethanes. Interestingly, the hydroxyurethane moieties present along the PHU's backbone offer unexplored opportunities in terms of enhanced adhesion and mechanical properties that could be a major breakthrough in many structural applications. Furthermore, PHUs have shown thermomechanical recyclability arising from the ability of hydroxyurethane moieties to participate in reversible exchange reactions. However, the relationship between the macromolecular structure, the processability, and the final properties of these materials have not been evaluated to a sufficient extent to establish a comprehensive overview of these emerging thermosets. In this sense, this work aims to address this research gap by investigating the rheological and thermomechanical performances of PHU thermosets and opening an unexplored door for future sustainable engineered structural applications. A special emphasis was put on PHU thermosets formulated using potentially biobased monomers. The rheological behavior during cross-linking of the PHU formulations was studied and highlighted the importance of the number of CC functionalities in the viscosity and gel time, ranging from 10 min to nearly 3 h. Moduli superior to 2 GPa and glass transition over 50 °C were obtained for short multifunctional CC. Finally, the dynamic network behavior of these PHUs was also demonstrated through stress−relaxation and reprocessing. High temperatures (over 150 °C) and pressure lead to a good recovery of the thermomechanical properties. Such materials appear to be an interesting platform for structural applications, particularly fiber-reinforced polymers, that can overcome many sustainability challenges.

KEYWORDS: Non-isocyanate Polyurethanes, Polyhydroxyurethanes, Renewable Materials, Dynamic Polymer Networks, Sustainability, Rheological Measurements, Stress Relaxation
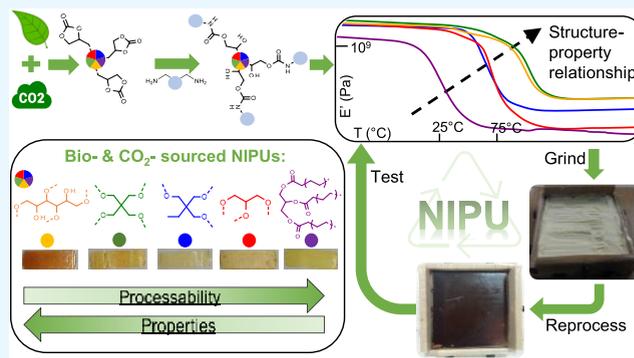
INTRODUCTION

Sustainability has become a key challenge in material science over the last 20 years.[1] Polymer-based structural materials can assess such challenges, in particular, fiber-reinforced ones. However, polymers adapted for such materials remain scarce and limited. Most of the biobased polymers suffer from unsatisfying properties to compete with conventional petroleum-based materials despite the important developments and perspective in the field.[2,3] In that sense, material sciences need to focus on new emerging polymers to meet both sustainability and high-performance goals to fulfill future industrial requirements. Polyhydroxyurethane (PHU) thermosets, among non-isocyanate polyurethanes (NIPU), could thus be a new alternative to both polyurethanes and epoxides thermosets, thanks to their bio- and CO_2-based cyclic carbonates monomers.[4]

The presence of hydroxyl groups within the PHU backbone was shown to bring PHU thermosets superior adhesive and mechanical properties over conventional polyurethanes (PU).[5] PHU thermosets have shown high versatility ranging from elastomeric to stiff behavior[5,6] depending on the macromolecular structures and the degree of functionality of the CCs.[7] Fleischer et al.[8] used pentaerythritol CC (PEC) and trimethylolpropane CC (TMC) with a reactive aliphatic amine (hexamethylenediamine HMDA) to obtain cross-linked PHUs. Their work was among the first to characterize PHU thermosets properties. The modulus of the synthesized PHUs ranged from a few MPa to 2.5 GPa, and elongation at break values superior to 3%. These properties could be suitable
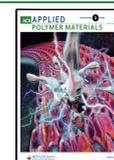
for high load-bearing applications. They also investigated the reactivity at several temperatures. It was found that temperatures higher than 70 °C were needed to obtain full curing. The need to reach a relatively high temperature for efficient curing was also reported in other studies[4,9] but was limited due to side reactions at temperatures over 100 °C.[4,10] Blattman et al.[7] also worked with TMC and HMDA. The obtained mechanical properties were significantly different than those from the previous study. Such differences can be explained mainly through the differences in the curing process. Thus, it highlights the appealing need to study the cross-linking behavior through rheological measurements before implementing such polymeric matrices in structural applications.

Another interesting aspect of PHUs is their ability to be reprocessed thanks to the transcarbamoylation mechanism already known in PU.[11] Over the past decade, Covalent Adaptive Networks (CAN) have appeared as an alternative to both thermoset and thermoplastic polymers. Such CANs combine high-performances and improved end-of-life compared to conventional polymers. Associative networks, so-called vitrimers, exhibit glass-like behavior at elevated temperatures with a constant cross-linking density during rearrangement of the network.[12] Dissociative networks possess reversible covalent bonds able to be broken in certain conditions.[13] Monie et al.[14] were able to reprocess self-blowing PHU foams. The same was observed for water-induced self-blown PHU foams.[15] Fortman et al.[16] studied the adaptative network properties of PHUs obtained from five and six-membered cyclic carbonates through stress−relaxation. They emphasized associative transcarbamoylation exchange reaction within the network. The thermal stability of six-membered CC-based PHUs allows better reprocessability while the degradation and reprocessing temperature for five-membered CC-based PHUs tend to overlap when a high degree of cross-linking was reached. Chen et al.[17] highlighted that PHUs exhibit both associative (transcarbamoylation) and dissociative (reverse cyclic carbonate aminolysis) mechanisms but stress−relaxation was not investigated. Hu et al.[18] reprocessed carbonated soybean oil (CSBO) and sorbitol ether carbonate (SEC) based PHUs. No stress−relaxation test was performed. Moreover, SEC reprocessability was rather poor due to the high degree of cross-linking and higher glass transition temperature. In vegetable oil-based PHUs, trans-esterification is also considered as a possible mechanism that facilitates the reprocessability of the cross-linked network.[19] If all hydroxyurethane functions possess the ability to rearrange through transcarbamoylation, PHUs reprocessability depends highly on the network structures and their physical properties. Therefore, in some cases, reprocessing parameters could be out of the operating window and the PHU polymer would degrade before the network rearrangement occurs. Although CANs are a major breakthrough for structural polymer applications,[20,21] the viability of PHUs for reprocessing and understanding of the mechanisms must be studied to a larger extent.

In general, an important scattering in properties and behavior was observed in the literature about PHU thermosets. Moreover, up-to-date, only few rheological studies on thermoset PHUs were conducted[6,22,23] and to the authors' best knowledge, never for potential load-bearing PHUs. In particular, fiber-reinforced polymers require such study to better assess the processability during the manufacturing process. Rheological measurements can thus give the viscosity over time and temperature, the pot life (time before the

mixture becomes unprocessable), and the gel time (time before the mixture act as a solid). These parameters are preponderant in many industrial processes when curing must be implemented.[24] While the low reactivity of the five-membered CC and the drastic increase in viscosity of the epoxy monomer after carbonation are well-admitted, they have not been fully addressed. Thus, the opportunities and properties of PHU thermosets have not been fully investigated while this pathway seems to be very promising for structural applications. More specifically, the relationship between the processability, the final properties, and the recyclability of PHU thermosets as a function of the macromolecular structure of the CCs, as much as their level of functionalization, must be assessed.

In this work, we, therefore, investigate the opportunities offered by several PHU formulations, their potential applications, and operating windows. Particularly, we propose to evaluate five potentially biobased five-membered CC of different degrees of functionality (trimethylolpropane, TMC; pentaerythritol, PEC; glycerol, GEC; sorbitol, SBC; and carbonated soybean oil, CSBO) cured with an aromatic amine (m-xylylene diamine, MXDA) to design suitable high-performance sustainable PHU thermosets. Sugar-derived polyols like pentaerythritol, glycerol, and trimethylolpropane can be obtained from starch by enzymes,[25] and epoxy monomers can then be synthesized through the reactions of the hydroxyl group from the polyols with biobased epichlorohydrin (ECH).[26] Epoxidized vegetable oils (cardanol, soybean, linseed, rapeseed, ...) are interesting as they do not require the use of ECH and can be obtained through the peroxidation of unsaturated bonds in their aliphatic chains. All epoxy can then be reacted with CO_2 to generate cyclic carbonates.[27,28] Biobased MXDA can be obtained from biomass-derived furfural.[29] The selected epoxy precursors in this study were chosen for their potential biobased origin, their ability to cross-link once carbonated, and their low initial viscosity. TMC has been used in several studies and was considered as the reference system. The fully biobased and highly functional PEC and SBC make them of particular interest to reach high-performances, but their high viscosity could be problematic. GEC is a liquid CC monomer and could allow a better flow of the curing thermoset, regarding the manufacturing process of structural materials. Fatty acid CSBO-based PHUs can increase ductility and decrease reactivity thanks to their long aliphatic chains.

The synthesized cyclic carbonates were structurally characterized using mass spectrometry and ^{1}H NMR. The rheological behavior during the curing of PHU thermosets was investigated and compared with the viscosity of starting cyclic carbonates as a first approach. The final properties of fully cured neat matrices were then evaluated followed by their adaptive network properties and ability to be reprocessed in the case of the most interesting formulations.

■ EXPERIMENTAL SECTION

Sample Preparation. *Materials.* Trimethylol propane triglycidyl ether (TMPTGE, epoxy equivalent weight EEW = 145 g/equiv, $\eta_{25°C}$ = 0.15 Pa·s) and TetraButyl Ammonium Iodide (TBAI) were purchased from SigmaAldrich. Pentaerythritol polyglycidyl ether (PEPGE, IPOX CL16eco, EEW = 163 g/equiv, $\eta_{25°C}$ = 1 Pa·s) was kindly provided by IPOX Chemicals. Glycerol polyglycidyl ether (GPGE, Denacol EX314, EEW = 143 g/equiv, $\eta_{25°C}$ = 0.15 Pa·s) and sorbitol polyglycidyl ether (SPGE, Denacol EX-614B, EEW = 172 g/equiv, $\eta_{25°C}$ = 5 Pa·s) were kindly provided by Nagase Chemtex Corporation. Epoxidized soybean oil (ESBO, EEW = 240 g/equiv,
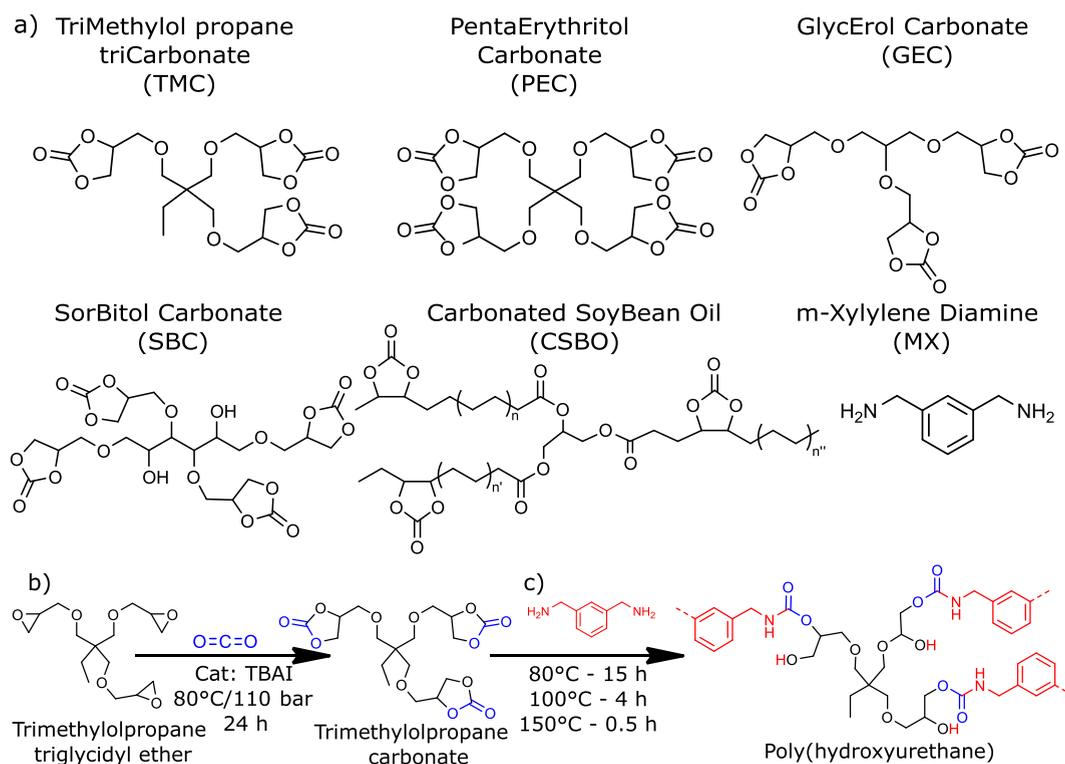
Figure 1. (a) Idealized (macro)molecular structures of the resins precursors and (b) model reaction from TMPTGE epoxy monomer to TMC cyclic carbonate to (c) p(TMC-MX) PHU thermoset.

$\eta_{25°C}$ = 0.5 Pa·s) was purchased from Vandeputte Oleochemicals. Carbon Dioxide was provided by Air Liquide. *m*-Xylylene diamine (MXDA, amine hydrogen equivalent weight AHEW = 68 g/equiv) was purchased from TCI. All reagents were used as received without any further purification.

Synthesis of Cyclic Carbonate Monomers. All cyclic carbonates, as represented in Figure 1a were synthesized using CO_2 under supercritical conditions ($scCO_2$) as already reported in previous works.[22,27] About 60 g of PEPGE, GPGE, SPGE, or ESBO epoxy precursors were converted to PEC, GEC, SBC, and CSBO respectively. TBAI catalyst (2.5 mol %) was mixed with the epoxy precursors and poured into a high-pressure 100 mL stainless steel reactor. The reactor was then filled with CO_2 and maintained under supercritical conditions at 80 °C and 110 bar for 24 h at 350 rpm, except for SPGE which was maintained at 100 °C to avoid the solidification of the product inside the reactor. For converting TMPTGE to TMC, the same protocol was performed in a 2 L stainless steel reactor with 1 kg of the epoxy precursor. In order to remove unreacted CO_2, the resulting yellowish viscous products were then degassed several times at 80 °C under vacuum until no bubbling occurred. The extent of the reaction was evaluated by means of ^{1}H NMR spectroscopy following the complete disappearance of the corresponding epoxy peaks and the appearance of the corresponding carbonate ones. The model reaction of the carbonation is shown in the first part of Figure 1b.

^{1}H NMR TMPTGE (CDCl₃, ppm): δ = 0.84 (t, 3H, methyl group), 2.6−2.72 (m, 6H, oxirane), 3.12 (m, 3H, oxirane). TMC (CDCl₃, ppm): δ = 0.84 (t, 3H, methyl group), 4.4−4.5 (m, 6H, cyclic carbonate), 4.83 (m, 3H, cyclic carbonate). PEPGE (CDCl₃, ppm): δ = 2.61−2.8 (m, 8H, oxirane), 3.14 (m, 4H, oxirane). PEC (CDCl₃, ppm): δ = 4.42−4.52 (m, 8H, cyclic carbonate), 4.85 (m, 4H, cyclic carbonate). GPGE (CDCl₃, ppm): δ = 2.64−2.83 (m, 6H, oxirane),3.19 (m, 3H, oxirane). GEC (CDCl₃, ppm): δ = 4.44−4.54 (m, 6H, cyclic carbonate), 4.86 (m, 3H, cyclic carbonate). SPGE (DMSO$_{d6}$, ppm): δ = 2.72 (m, 8H, oxirane), 3.10 (m, 4H, oxirane). SBC (DMSO$_{d6}$, ppm): δ = 4.27−4.53 (m, 8H, cyclic carbonate), 4.93

(m, 4H, cyclic carbonate). ESBO (CDCl₃, ppm): δ = 2.98 (m, 6H, oxirane). CSBO (CDCl₃, ppm): δ = 4.75 (m, 6H, cyclic carbonate).

Synthesis of Polyhydroxyurethane Thermosets. PHU thermosets were cross-linked using a CC/amine ratio of 1:1. The amount of amine was calculated using eq 1. The carbonate monomer was degassed under vacuum at 60 °C for 1 h in order to remove any potential trapped air bubbles prior to use. MXDA was then added and the mixture was thoroughly hand-mixed for 5 min at room temperature. The as-obtained mixture was then poured into 60 °C preheated PTFE mold and pressed in a Carver 4122CE manual thermopress at 80 °C and 3 bar for 15 h. The pressure was then released, and the curing was completed in an oven at 100 °C for 4 h. A postcuring step of 30 min at 150 °C was finally applied to ensure a fully cured system. Prior to any tests, samples were conditioned at 23 °C and 50% relative humidity for 2 days. The representative model reaction of the aminolysis of TMC cyclic carbonate is shown in Figure 1c. Once cured, the PHU formulation is referred as p("Carbonate"-MX), p indicating that the formulation is polymerized, "Carbonate" being the used CC (TMC for example) and MX the curing agent (*m*-xylylene diamine).

$$m_{MXDA} = m_{CC} \times \frac{AHEW}{CEW} \tag{1}$$

with m_{MXDA} and m_{CC} being the mass in grams of MXDA and CC respectively. AHEW and CEW are the amine hydrogen equivalent weight and carbonate equivalent weight in g/equiv, respectively.

Reprocessing of Polyhydroxyurethane Thermosets. The as-cured PHU thermosets were ground into a fine powder using a cryomill's cryogenic vibratory mill. The samples used for tensile testing were first cut into small pieces and then ground three times for 3 min in a cryogenic vibrating chamber with 3 steel balls. The powder was then poured into a Teflon-coated 70 × 70 mm² steel mold. The mold was preheated to 160 °C in a press for 15 min. After that, a 6 MPa pressure was slowly applied and maintained for 15 h. The mold was then removed from the press and cooled at room temperature. The as-obtained film was then removed from the mold and cut for DMA

and FTIR analyses. The samples were also immersed into THF in order to evidence the welding of the samples via the formation of covalent bonds at high pressure.

Chemical Characterization. *Chemical Structure Characterization.* *^{1}H NMR Spectroscopy.* This was used to determine the (macro)molecular structures of the monomers using a Bruker AMX-500 instruments. Sixteen scans were performed at room temperature at a frequency of 500 MHz. The chemical shifts are given in ppm. Around 10 mg of each products was dissolved in 0.6 mL of deuterated chloroform except for SBC in which DMSO-d_6 was used as the deuterated solvent.

Carbonate Equivalent Weight. CEW was evaluated by means of ^{1}H NMR using an internal standard following Cornille et al.'s work.[5] A solution of approximately 15 mg of toluene, 25 mg of carbonate product, and DMSO-d_6 was prepared and poured into NMR tubes. The resulting weight of these mixtures was determined by gravimetry. The CEW was calculated using eq 2.

$$\text{CEW } (g/\text{equiv}) = \frac{M_n}{\text{functionnality}} = \frac{m_{c_5} \times I_{CH_3} \times M_{toluene}}{(I_a + I_b + I_c) \times m_{toluene}} \tag{2}$$

with m_{c_5} the mass of carbonate, I_{CH_3} the methylene integration values of toluene (2.92 ppm) fixed at 300, $M_{toluene} = 92.138$ g/mol the molar mass of toluene, I_a, I_b, and I_c, the integration of carbonate peaks at 4.29, 4.40, and 4.92 ppm, respectively, and $m_{toluene}$ the mass of toluene.

Mass Spectrometry. MS spectra of synthesized CCs were recorded on a matrix-assisted laser desorption/ionization mass spectrometer (MALDI-MS) using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG (third harmonic) operating at 355 nm with a maximum output of 65 μJ delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10000. All samples were analyzed using trans-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix,[30] which was prepared as a 40 mg·mL^{-1} solution in CHCl$_3$. This solution (1 μL) was applied to a stainless-steel target and air-dried. Therefore, 1 μL of this solution was applied to the target area already bearing the matrix crystals and air-dried. The molecular weight of the synthesized carbonates was estimated using eq 3.

$$M_n = \frac{\sum_{n=1}^n I_i \times M_i}{\sum_{n=1}^n I_i} \tag{3}$$

with I_i the intensity of the identified peak as an approximation of the molar composition and M_i its respective mass.

Infrared Fourier Transform. FTIR attenuated total reflectance (ATR) measurements were performed on a Bruker FTIR Tensor 27 spectrometer. Thirty-two scans per recording were performed over a range of 4000−600 $^{-1}$ with a 4 cm^{-1} resolution.

Swelling Index, Gel Content, and Water Uptake of PHU Thermosets. To determine both swelling index (SI) and gel content (GC) of the formulations, three samples of about 20 mg were weighted (m_0) and soaked in a polar (THF) and nonpolar (toluene) solvent for three weeks. Samples were then collected, excess solvent was removed using absorbent paper, and then weighted (m_1). SI was calculated using eq 4. The same samples were then dried at 80 °C under vacuum for 24 h and weighted (m_2). The GC was calculated using eq 5.

$$\text{SI} = \frac{m_1 - m_0}{m_0} \times 100 \tag{4}$$

$$\text{GC} = \frac{m_2}{m_0} \times 100 \tag{5}$$

Moisture uptake (MU) and water uptake (WU) of PHU thermosets were assessed. PHU samples of about 50 mg were weighed (m_{0a}) and dried for 24 h at 80 °C in a vacuum oven. Samples were then weighed again (m_{0b}) and dipped into demineralized water.

After 24 h, samples were taken back and excess water was removed using absorbent paper and weighed again (m_1). The water uptake was calculated using the same formula as the SI measurement using (m_{0a}) for MU and (m_{0b}) for WU.

Physical Characterization. *Rheological Measurements of CC and Uncured PHU Thermosets.* Rheological properties of the polyhydroxyurethane thermosets during curing were measured using an Anton Paar Modular Compact Rheometer MCR302. Two disposable parallel aluminum plates of 25 mm diameter, with a 1 mm air gap, were used. A 2% strain was applied at 1 Hz. About 1.5 g of the CC-MX mixture was poured into the bottom plate. Nonisothermal analyses were performed from 25 to 200 °C at a 10 °C/min heating rate. Isothermal rheological analyses for PHU thermoset curing were performed at 80 °C with the aforementioned parameters. The viscosity of synthesized CC as a function of temperature was measured from 25 to 150 °C following the same described protocol.

Thermogravimetric Analysis and Differential Scanning Calorimetry of CCs and PHU thermosets. *Thermogravimetric Analysis.* TGA was performed on a TA Instruments TGA Q500. For each sample, about 10 mg of product was used. The analysis were conducted from 25 to 800 °C following a 20 °C/min heating ramp under a N$_2$ flow of 60 mL.min^{-1}.

Differential Scanning Calorimetry. DSC was conducted on a TA Instruments DSC Q2000. About 10 mg of product was weighed in an aluminum pan. For each sample, two heating ramps from −80 to 200 °C at 10 °C/min heating rate were performed under N$_2$ atmosphere.

Dynamical Mechanical Analyses of PHU Thermosets. Dynamical Mechanical Analysis (DMA) was conducted on a TA Instruments DMA Q800 in tension mode. Rectangular samples of 20 × 8 × 0.8 mm^3 were used. The gauge length was fixed at 10 mm, and a 0.01 N preload was used. The DMA analyses were performed from −80 to 150 °C at a 3 °C/min heating rate, and a 0.1% strain was applied at 1 Hz. The DMA results were used to determine the cross-linking density ($\nu_{E'}$) of samples using rubber elasticity theory as described in eq 6.

$$\nu_{E'} = \frac{E'_{T_{\alpha+50}}}{3RT_{\alpha+50}} \tag{6}$$

with $T_{\alpha+50}$ being the temperature of the rubbery plateau set 50 K after the α transition taken at the maximum of the tan δ curve, $E'_{T_{\alpha+50}}$ the storage modulus in Pa at the specified temperature and R the perfect gas constant (8,314 J mol^{-1} K^{-1}).

Stress−Relaxation of PHU Thermosets. Isothermal stress−relaxation tests were conducted on the DMA Q800 in tension mode. Rectangular samples of 20 × 8 × 0.8 mm^3 were used. The gauge length was fixed at 10 mm. Once the specified temperature was reached, the sample was held for 1 min before a 1% strain was applied. The strain was kept constant for 600 min or when stress−relaxation was reached. Stress−relaxation of the dynamic cross-linked network is defined using a Maxwell model as described in eq 7. The dynamic covalent behavior was highlighted using the Arrhenius relationship by plotting τ^* as a function of $1/T$ as shown in eq 8. The hypothetical topology freezing temperature (T_v), where the material is theoretically switching from solid to liquid behavior due to the exchange mechanisms within the network, was estimated at the relaxation time $\tau^*_{T_v}$ using eq 9 and eq 10.[31,32]

$$\frac{G(t)}{G_0} = e^{-t/\tau^*} \tag{7}$$

$$\tau^* = \tau_0 e^{E_a/RT} \tag{8}$$

$$\tau^*_{T_v} = \frac{3\eta}{E'_{rubbery}} \tag{9}$$
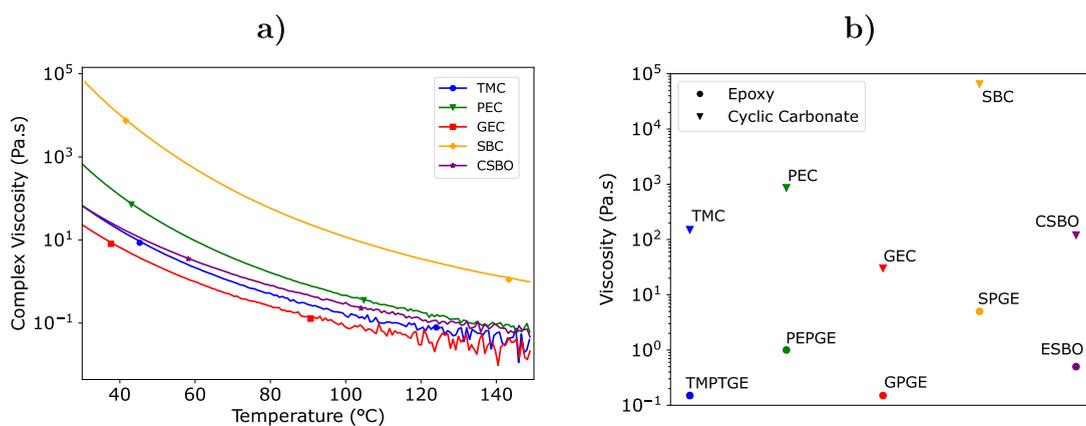
Figure 2. (a)Viscosity evolution of the cyclic carbonates over temperature and (b) comparison of the viscosity of epoxy and carbonate monomers at 25 °C.

$$T_v = \frac{1000 E_a}{(\ln \tau_{T_v}^* - \ln \tau_0)R} - 273.15 \tag{10}$$

with G being the relaxation modulus in MPa, τ the time constant in second, E_a the activation energy in kJ/mol, R the perfect gas constant (8.314 J·mol^{-1}.K^{-1}), T the temperature in Kelvin, and η the freezing viscosity (10^{12} Pa·s).

Tensile Testing of PHU Thermosets. The mechanical properties of the virgin matrices were investigated through monotonic tensile testing on a ZwickRoell Z2.5 equipment up to failure with a 2.5 kN load cell at a 1 mm/min displacement rate according to ASTM D638 standard requirements.[33] For each formulation, five dog-bone type V samples were tested. The elastic modulus was computed between 0.1% and 1.0% strain by linear regression.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cyclic Carbonates for PHU Thermosets. All cyclic carbonates were fully characterized and the results are summarized in Supporting Information (Supporting Table 1). ^{1}H NMR, mass spectrometry, TGA, and DSC curves can be found in supplementary data. The full conversion was confirmed by ^{1}H NMR through the full disappearance of epoxy peaks between 2.9 and 3.2 ppm and the appearance of carbonate signals between 4.3 and 4.9 ppm as shown in the Supporting Figures 1−5). The complete conversion was further confirmed by mass spectrometry (Supporting Figures 6−10). Being consistent with the insertion of CO_2, the quantitative conversion of epoxy to cyclic carbonate derivatives was observed by the complete shift of the ionized entities as ascribed to starting materials to a higher 44 mass unit per epoxy function converted.[27] All mass spectra are characterized by a distribution of different ionized entities, highlighting the presence of different molecules in both starting and resulting materials. This distribution is related to the presence of halohydrin formed during the polyol epoxidation as observed by Camara et al.[34] For both ESBO and CSBO, the distribution of mass is related to the different aliphatic chain length of triglycerides in soybean oil as reported by Poussard et al.,[27] and to the number of unsaturated bonds epoxidized. Several studies have shown that the best molar ratio between CCs and primary amine functions for PHUs synthesis was 1:1.[35,36] For these reasons, the effective determination of carbonate content has to be performed accurately. More specifically, CEW was evaluated using an internal standard (toluene) to determine the average number of carbonate per gram of products.[5] Thanks to this method,

average functionality can be estimated from molar mass and CEW (Supporting Table 1). All CCs have a functionality superior to 2.5, making them suitable for thermoset matrices.

In most thermoset industrial applications, the viscosity and the thermal stability of products are important parameters. For these reasons, TGA and rheological measurements were applied to the synthesized carbonates. TGA analyses (Supporting Figure 11) evidence no major degradation before 200 °C. Figure 2a depicts the evolution of the viscosity with temperature, and Figure 2b allows the comparison of the viscosity of each CC with respect to the starting epoxy monomer. Carbonating epoxy monomers drastically increases the viscosity of the medium by a 200−1000 factor. However, no clear relationship can be observed, complicating the prediction of the final carbonate viscosity. For example, while TMPTGE and GPGE have similar initial viscosity, the resulting TMC shows higher viscosity than the GEC. SBC was found to be almost solid at room temperature. Still, it remains that the number of CC functions in the monomer is responsible for the viscosity of the mixture. While these low-viscosity epoxy precursors are commonly used as a reactive diluent for diglycidyl ether of bisphenol A,[37] in some cases (SBC and PEC mostly), they become too viscous to be processable within an industrial process such as liquid resin infusion or resin transfer molding. In these techniques, viscosities between 0.5 and 1 Pa·s are desirable.[24] However, the viscosity of the obtained CCs can be adapted through the use of low-viscosity difunctional CCs to meet industrial requirements.[8,38]

Study on the Relationship between CC Structure and the Rheological Curing Behavior of Polyhydroxyurethane Formulations. Rheology is an interesting tool to investigate the cross-linking behavior of thermosets, particularly pot life and gel time. Pot life can be directly related to the processability of a mixture, highlighting the time when the viscosity remains low enough to be processable. Gel time refers to the beginning of gelation, where the formation of the polymer network starts due to the cross-linking of the polyfunctional monomers. The curing kinetics of the PHU thermosets was evaluated through rheological measurements to determine the processing window of the formulations and the effect of the CC structure on the curing behavior. First, the effect of temperature was assessed through nonisothermal analyses. Complex viscosity and modulus are represented in Figure 3, parts a and b, respectively, and important values are
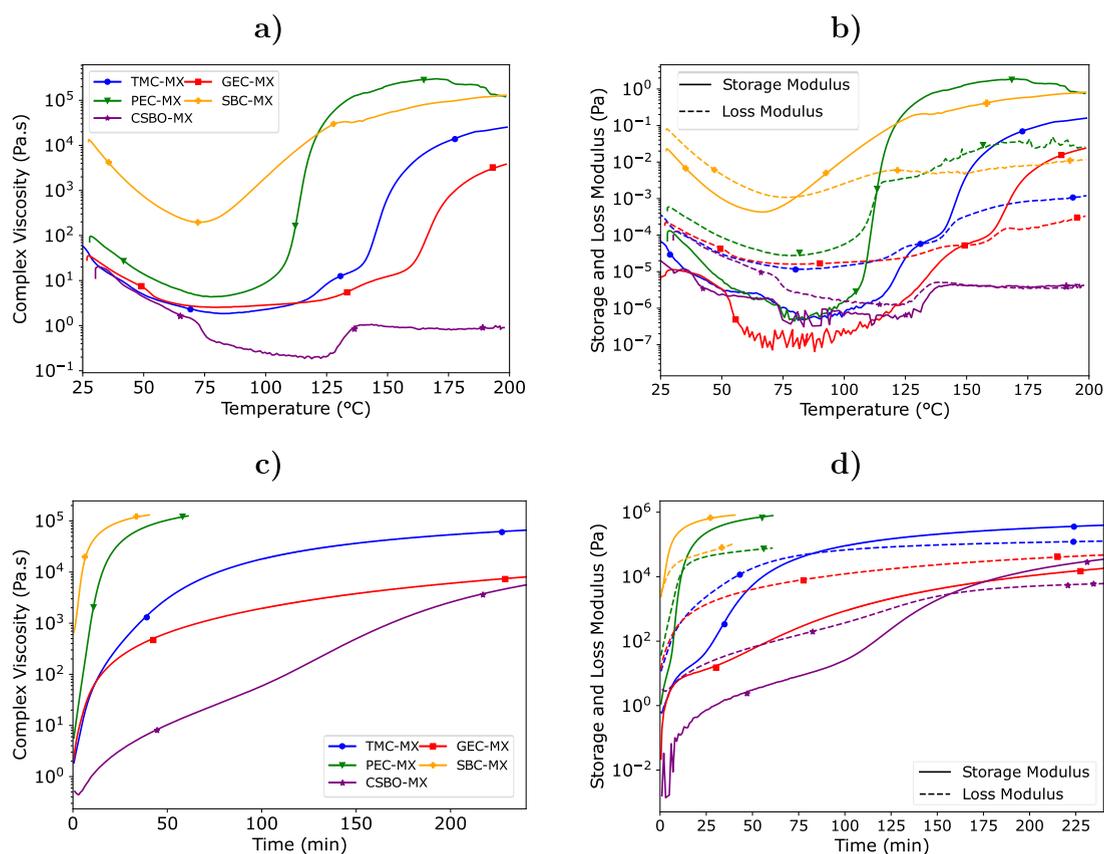
Figure 3. (a) Viscosity and (b) storage and loss modulus evolution of PHU formulations during nonisothermal curing rheological analyses. (c) Viscosity and (d) storage and loss modulus evolution of PHU formulations during isothermal curing.

Table 1. Rheological Results of the PHU Formulations

	Formulation	TMC-MX	PEC-MX	GEC-MX	SBC-MX	CSBO-MX
Non-isothermal	$\eta_{25°C}$ (Pa·s)	53	75	29	12209	15
	$\eta_{50°C}$ (Pa·s)	5	14	7	728	4
	T_{gel} (°C)	131	113	149	80	149
Isothermal at 80 °C	η_{init} (Pa·s)	2.8	10.6	4	1045	0.44
	pot life (min)	22.5	7	29.5	−	138
	gel time (min)	82.5	12	nd	1	157

reported in Table 1. Our first observations reveal an important variation in the initial viscosity from one formulation to another, being obviously highly influenced by the viscosity of the CC. However, while GEC monomer is less viscous than CSBO, it must be noted that the lowest viscosity at room temperature was achieved for the CSBO-MX mixture with 15 Pa·s compared to 29 Pa·s for GEC-MX. The CEW of CSBO being more important than for GEC, this cannot be attributed to the amount of curing amine in the mixture, being almost twice less in the CSBO mixture than with GEC. Therefore, the difference in viscosity could be attributed to the higher reactivity of the low molecular weight CCs obtained from glycidyl ether[39] compared to the carbonate in the fatty acid backbone.[27] That is, the reaction starts earlier in the case of GEC, implying higher initial viscosity. Complex viscosity follows a small decrease with increasing the temperature up to 80 °C for TMC-MX, PEC-MX, SBC-MX, and GEC-MX formulations and up to 130 °C for CSBO. For a sake of comparison, the melt-viscosity of the curing formulations was reported at 80 °C, whereby such temperature was considered during the curing methods, enabling a good compromise

between processability and curing time. At this temperature TMC-MX, GEC-MX, and CSBO-MX have comparable viscosities from 4 to 7 Pa·s and 14 Pa·s for PEC-MX. However, at this temperature, the melt-viscosity of SBC-MX remains too high to be considered easily processable. At temperatures higher than 90 °C, the viscosity increases drastically and a gel point is observed. Gel point was reached for all the formulations, highlighting effective cross-linking for all PHUs. Just after, storage and loss modulus curves reach a plateau and do not evolve significantly. However, the gelling temperatures are superior to the limit in which side reactions can occur.[40]

The differences in terms of behavior can be attributed to several factors. First, the number of CC functions plays a significant role in this behavior. Indeed, higher functionality was already observed to increase the viscosity of the monomer, herein, it also leads to faster gel point and a more cross-linked network.[41] Accordingly, if highly functional CCs can be used to obtain fast and dense cross-linking, they drastically affect the processability of the mixture. Second, for each formed hydroxyurethane function, the density of hydrogen bonds

increases leading to less mobility in the network and, as a consequence, an increase in the bulk steric hindrance lowering the reaction rate.[42] While a higher temperature tends to break hydrogen bonds, it also eases the ring-opening of the CC by the primary amine,[8,34] leading to a faster network formation. Hence, the system is facing opposite effects between the decrease of the viscosity and the increase of reactivity and cross-linking with temperature. Such observations were already highlighted in thermoplastic PHU where hydrogen bonds were shown to drastically affect the polymerization.[43] Finally, the optimal curing temperature of the PHU thermosets must be adapted to limit side reactions while ensuring full curing. For these reasons, we proposed here a three-step curing protocol for our formulations with an initial curing stage at 80 °C.

Isothermal rheological analyses were performed at 80 °C. The viscosity and moduli evolution for the five formulations is presented in Figure 3c,d, and numerical values are summarized in the second part of Table 1. As can be seen in Table 1, the initial viscosity of the PHU formulations differs drastically from each other, depending on CC functions and CC reactivity as observed previously. CSBO-MX stands as the less reactive monomer with a long pot life of 138 min and a low initial viscosity. Such results are in agreement with nonisothermal results and can be attributed to the less reactive CC in the aliphatic backbone.[39] TMC-MX and GEC-MX have similar behavior with an initial viscosity of around 3 Pa·s and a pot-life of 23 and 30 min, respectively, that can be considered sufficient for processing in many applications. The main drawback is the gelation time being superior to 1 h for TMC-MX and even 4 h in the case of GEC-MX. However, as it can be found in Supporting Figure 13, when the temperature increased up to 100 °C, the gelation was reached. This can be attributed to the CC in the middle of the GEC backbone being less accessible than the CC moieties, leading to higher energy required to fully react as highlighted by Cornille et al. in their model reaction.[42] As observed in nonisothermal analyses, the highly functional PEC leads to higher initial viscosity of 10 Pa·s as well as a too-short pot life (7 min) and gelation time (12 min). The same statements can be drawn from the highly functional SBC-MX where an initial viscosity superior to 1000 Pa·s, no pot-life, and a gel time of 1 min were observed highlighting the importance of the number of CCs in the curing properties of PHUs.

However, if the properties are affected by the number of CC functions and their structure the general behavior of all formulations appears to be similar. A continuous logarithmic increase of both viscosity and storage modulus happens from the beginning. Soon after the gel point is reached, a plateau is observed and no significant change can be noticed. The origin of the plateau can be explained by the completion of the reaction as well as by an elevated hydroxyl group density during the curing of PHU. These hydroxyl groups can participate to additional H-bonding within the mixtures, resulting in a higher viscosity while lowering the accessibility of remaining moieties (amine and/or CC) to cross-link. These observations are in accordance with Blain et al.[43] who highlighted that these additional hydrogen bonds can affect the progress of polymerization in the case of linear PHUs. This behavior is in accordance with the nonisothermal analyses previously reported in this work. In order to obtain a balance between an easy process, fast curing, and enhanced properties, the use of CC monomer mixtures could be considered.[44] For instance, GEC and CSBO being quite liquid and less reactive,

they could be of interest to tune the viscosity of our highly reactive and viscous PEC.

Thermomechanical Properties of the Polyhydroxyurethane Thermosets. As previously mentioned, all formulations were cured in a three-step protocol in order to determine their overall performances. The protocol was optimized to obtain the best properties while minimizing the need for long-time and high temperatures. The protocol was chosen on the basis of the rheological analyses. A long curing step (i.e., 15 h) at 80 °C was necessary to obtain a good extent of curing while avoiding side reactions related to the nucleophilic attack of the remaining amine groups onto the hydroxyurethane function.[40] Even though the cross-linking stage was first conducted at 80 °C, the network was not fully cured, requiring an additional curing step at 100 °C and a short 30 min postcuring at 150 °C in order to obtain the highest degree of cross-linking and better properties. The obtained PHU thermoset samples are depicted in Supporting Information (Supporting Figure 14).

FTIR spectra (Supporting Figures 15−19) confirmed the conversion of cyclic carbonates to hydroxyurethane linkage with the disappearance of the carbonyl group of carbonate at 1780 cm^{-1} and the appearance of a urethane signal at 1690 cm^{-1}. A small residual peak of CC was found in all formulations, revealing that some CCs were still unreacted. These observations are in accordance with DSC results in Supporting Figure 20a where a slight shift between 1 to 6 °C of the T_g of the thermoset was observed between the first and second ramps.

Swelling index and gel content were conducted in a polar and a nonpolar solvent (THF and toluene, respectively) in order to determine the cross-linking degree of the network. The results are summarized in Supporting Table 2. All PHUs swell more in THF than in toluene due to their polar character.[45] p(TMC-MX), p(PEC-MX), p(GEC-MX), and p(SBC-MX) present a high gel content (superior to 98%) and low swelling index (inferior to 5%), except for TMC reaching 56.6% when immersed in THF. CSBO presents a higher swelling index and a lower gel content in both THF and toluene. This higher SI can be explained by the low cross-linking density induced by the macromolecular structure of CSBO having a long and flexible aliphatic backbone. The higher SI can also be explained by a lack of reactivity of CCs in the middle of the aliphatic chains of CSBO compared to CCs obtained from glycidyl ether.[4] By contrast to p(CSBO-MX), p(PEC-MX) and p(SBC-MX) presenting the highest cross-linking density did not swell significantly, remaining below 1%. The poor reactivity of CSBO was further confirmed by the easiness to extract the remaining precursors after swelling in both solvents. Indeed, mass spectrometry revealed the presence of saturated triglycerides in CSBO (m/z 685.4) in the supernatant, which cannot be epoxidized nor carbonated. The SI and GC results are similar to those of other studies on similar formulations.[5,8]

The sensitivity of PHUs to water is a key point for structural applications. Indeed, the ability of materials to absorb water is usually considered as a major drawback for aging. In the case of PHU thermosets, the high hydrophilicity of the hydroxyurethane moiety has been reported in several studies.[8,22,46] This water absorption can lead to a decrease of the T_g.[14,15] This phenomenon is highly dependent on the chemical structures of both cyclic carbonates and curing amine, including their ratio.[47] Similar observations can be made from this study. p(CSBO-MX) presents a low (5%) water uptake (WU) due to

Table 2. Physical Properties of the Tested PHU Thermosets (Mean ± Standard Deviation)

		p(TMC-MX)	p(PEC-MX)	p(GEC-MX)	p(SBC-MX)	p(CSBO-MX)
DSC	T_g (°C)	60	80	54	60	20
TGA	$T_{d_{5\%}}$ (°C)	284	268	267	270	280
	$T_{d_{max}}$ (°C)	311	290	341	325	387
	char (%)	16.0	17.9	18.0	21.7	4.1
DMA	T_α (°C)	68	92	70	88	42
	E'_{glassy} (MPa)	3020	3650	2940	3690	1210
	$E'_{rubbery}$ (MPa)	5.33	13.10	1.60	15.30	1.40
	$\nu'_{E'}$ (mol/m^3)	559	1335	142	1580	139
tensile	E (MPa)	2472 ± 227	2999 ± 46	2780 ± 225	2658 ± 16	7 ± 2
test	σ_{max} (MPa)	88.8 ± 5.1	100.4 ± 2.0	50.6 ± 14.5	51.3 ± 9.6	3.3 ± 0.5
	ϵ_{max} (%)	4.20 ± 0.60	4.15 ± 0.32	1.87 ± 0.38	1.99 ± 0.40	200.26 ± 15.49
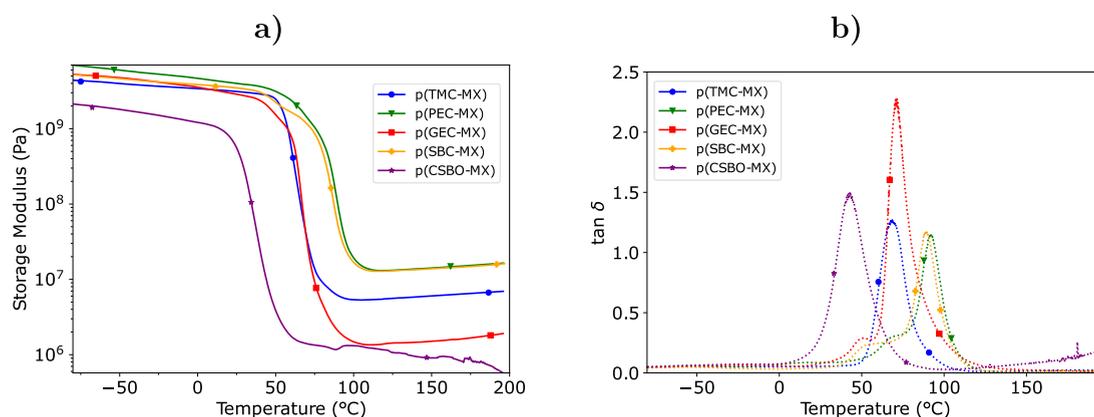
Figure 4. Dynamical mechanical analysis of the PHU thermosets. (a) Storage modulus evolution with temperature and (b) tan δ evolution.

the hydrophobicity of the carbonate backbone and the low hydroxyurethane content (that can be expressed through the higher CEW compared to other monomers), while p(GEC-MX) and p(PEC-MX) present significant WU of respectively 47 and 25%. The p(TMC-MX) formulation is slightly lower (13%) due to the presence of methyl groups in the backbone. The WU must be considered for further applications as it could be detrimental in structural applications but of interest for specific applications such as hygromorph materials.[48]

When considering thermoset polymers, a sufficient level of curing must be reached to ensure optimal properties and stability for the manufactured parts. DSC is a powerful tool as it gives the T_g of the system as manufactured in a first heating ramp. A potential lack of curing can then be identified through a second scan by a shift of the T_g. The DSC thermograms are presented in Supporting Figure 20a. DSC curves highlight the broad range of results from one formulation to another on both levels of curing and T_g. The highest T_g was obtained for p(PEC-MX) polymer with 80 °C while for p(TMC-MX), p(SBC-MX), and p(GEC-MX) glass transition temperatures ranged between 55 and 60 °C. p(CSBO-MX) formulation has the lowest T_g, at 20 °C. The glass transition temperature is a function of the cross-linking density of the network, i.e., the number of CC functions in the carbonated precursors, and of the macromolecular structure of the precursors, a long aliphatic chain giving more flexibility, thus lowering the T_g.[5] In this case, the high T_g of p(PEC-MX) is explained by the high degree of functionality leading to a highly cross-linked thermoset. On the opposite, p(GEC-MX) and p(TMC-MX) bearing three carbonates exhibit a slightly lower T_g. Neither formulation presented any residual exothermic peak, and only a limited

shift of T_g is observed for p(TMC-MX) and p(GEC-MX). Such results emphasize, in addition to both GC and FTIR observations, the efficient curing protocol and the completion of the cross-linking to a sufficient extent. An exception can be raised with p(SBC-MX) that possesses a lower initial T_g than could be expected considering its high functional nature. An important shift in T_g from 60 to 75 °C is also observed. This results from the numerous hydroxyl functions in the backbone of SBC, increasing the steric bulk hindrance and lowering both reactivity and diffusion of the amines in the curing network.[43] It can be noted that a good level of curing and interesting glass transition temperatures were obtained for all studied PHU thermosets making them suitable for structural applications.[49]

The thermal stability of the cured PHUs was evaluated through TGA analyses under inert gas (N₂). Curves are presented in Supporting Figure 20b and values of interest are summarized in Table 2. p(TMC-MX), p(PEC-MX), p(GEC-MX), and p(SBC-MX) formulations present comparable thermal stability and good performances. Indeed, in all cases, the $T_{d_{5\%}}$ is superior to 260 °C. The maximum degradation peak is observed at temperatures superior to 290 °C. Residual char was found between 12 and 20% for the four previously cited PHU thermosets. Although it has comparable $T_{d_{5\%}}$ and T_{max} than the four previously cited PHUs, p(CSBO-MX) exhibit a very low residual char by contrast. Taking into account the macromolecular structure of CSBO, GC, DSC results, and mass spectrum, this can be attributed to the lower cross-linking density, the long aliphatic structure, and the presence of unreacted fatty acid and triglycerides. As a general observation, it must be noted that a higher degree of cross-linking favors the

thermal stability and the charring of the thermosets. Both degradation temperature and residual char are in the range or slightly higher than those of epoxy resins,[50] highlighting reasonable resistance to thermal degradation and sufficient stability to be used in thermoset applications.

Thermomechanical properties of synthesized PHUs were assessed through DMA analyses. Storage modulus and tan δ are represented as a function of temperature in Figure 4a-b respectively and values can be found in Table 2. The transition between the vitreous to the rubbery domain is defined at the maximum of the tan δ curve when chains are activated in large motions and named T_α.[51] This α transition appears within the same range as the glass transition determined by DSC. From the decrease of storage modulus between the glassy and rubbery domain, the cross-linking density can be evaluated and used to compare the different networks.[51] p(TMC-MX), p(PEC-MX), p(GEC-MX), and p(SBC-MX) present similar behavior with a high storage modulus superior to 3 GPa in the glassy domain and a rubbery plateau superior to 1 MPa. CSBO having a softer backbone and lower glass transition temperature presents the lowest storage modulus and T_α with 1210 MPa and 42 °C respectively. Moreover, it can be noted that the rubbery storage modulus drops with the temperature, highlighting a lower level of cross-linking and stability as already highlighted through gel content and TGA analyses. p(PEC-MX) and p(SBC-MX) formulations have the highest cross-linking density, as expected due to the high content of CC moieties. TMC presents a slightly lower cross-linking density than PEC and SBC but remains quite high when compared to literature.[5] Surprisingly, while p(GEC-MX) could be expected to have similar behavior and cross-linking density to p(TMC-MX) with comparable glass transition temperature and glassy modulus, it was found to present a lower cross-linking density, comparable to that of p(CSBO-MX). This can be explained by the lower mobility of the CC in the middle of the GEC backbone, being less accessible to react with the amine as already considered during rheological analyses. In other terms, the p(GEC-MX) network is less built than the other formulations. The shape of the peak in tan δ curves is known to be representative of the homogeneity for the polymer.[51] p(CSBO-MX) and p(TMC-MX) have a narrow and symmetric peak highlighting a good homogeneity of the network. p(PEC-MX), p(SBC-MX), and p(GEC-MX) do also have a narrow peak but a small shoulder can be found at the onset of the α transition. This emphasizes a relatively good homogeneity of the network in general but some phase separation could have been achieved within the network.[5,52]

Considering future structural applications, the mechanical properties of the PHUs were characterized by monotonic tensile tests. Strain−stress curves are presented in Supporting Figure 21. Young's modulus, maximum strength, and strain at break are summarized in Table 2. All p(TMC-MX), p(PEC-MX), p(GEC-MX), and p(SBC-MX) present equivalent mechanical behavior with a high Young's modulus between 2.4 and 3.0 GPa. p(TMC-MX) and p(PEC-MX) thermosets appear to be the more mechanically interesting with a strain at break superior to 4% and tensile strength of 89 and 100 MPa respectively, making them among the strongest PHU thermosets available in literature.[5,7,8,36] It must be noted that p(CSBO-MX) possesses an elastomeric behavior with a low modulus and tensile strength (7 and 3 MPa respectively) and high ductility (200%). Thus, p(CSBO-MX) could be of interest to toughen other PHU formulations. As a general

observation, the properties and the behavior of the formulated PHU thermosets appear to be suitable to compete with epoxy systems[53] as a greener alternative.

Covalent Adaptive Network Properties of Polyhydroxyurethanes. *Study of the Stress−Relaxation of Polyhydroxyurethanes.* Even whether they are derived from natural resources, the end-of-life of thermosets remains a major drawback when considering the environmental footprint of such materials. As an alternative, CAN polymers appear as a greener pathway to afford the recycling of so-often discarded materials.[20] PHUs are deemed promising candidates to efficiently replace nonreprocessable epoxy thermosets because they possess such dynamic network behavior. Previous works[11,16,18,54] highlighted two main mechanisms in the exchange reaction of PHU networks: the associative transcarbamoylation, represented in Figure 5a have been reported
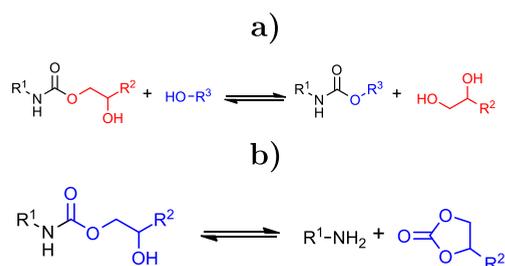

Figure 5. Polyhydroxyurethane potential rearrangement mechanisms. (a) Transcarbamoylation (associative). (b) Reverse cyclic carbonate aminolysis (dissociative).

to be the main mechanism but dissociative reverse cyclic carbonate aminolysis, represented in Figure 5b, was also reported. Associative mechanisms induced a constant cross-linking density during rearrangement while the dissociative mechanism is related to the breaking of reversible bonds, enabling the polymer to flow.

The stress−relaxation has been investigated for all PHU thermosets on a DMA in tensile mode to assess the reversible nature. All PHU thermosets show stress−relaxation ability as can be seen in Figure 6a−e and through Arrhenius law in Figure 6f, highlighting the ability of the hydroxyurethane moieties to rearrange. The activation energy (E_a), the square residual (r^2) of Arrhenius fitting, and the freezing temperature (T_v) are summarized in Table 3.

The stress−relaxation analyses highlight that p(CSBO-MX) formulation differs in behavior when compared to p(TMC-MX), p(PEC-MX), p(GEC-MX), and p(SBC-MX) systems due to the important difference in the network structure. p(CSBO-MX) presents the lowest activation energy (65 kJ/mol) with stress−relaxation starting at low temperature (110 °C). The same observations were made by Hu et al.[18] highlighting that lower temperature and processing time were required for CSBO-based PHUs due to transcarbamoylation, reverse aminolysis, and transesterification mechanisms when compared to a denser network. p(TMC-MX), p(PEC-MX), p(GEC-MX), and p(SBC-MX) appear to be less sensitive to stress−relaxation with longer time and higher temperature required. A relaxation effect was already observed in p(TMC-MX) at 150 °C but requires time superior to 1000 min making it not suitable nor competitive with other CAN polymers. Temperatures higher than 180 °C were required to relax in a reasonable amount of time even though the relaxation started
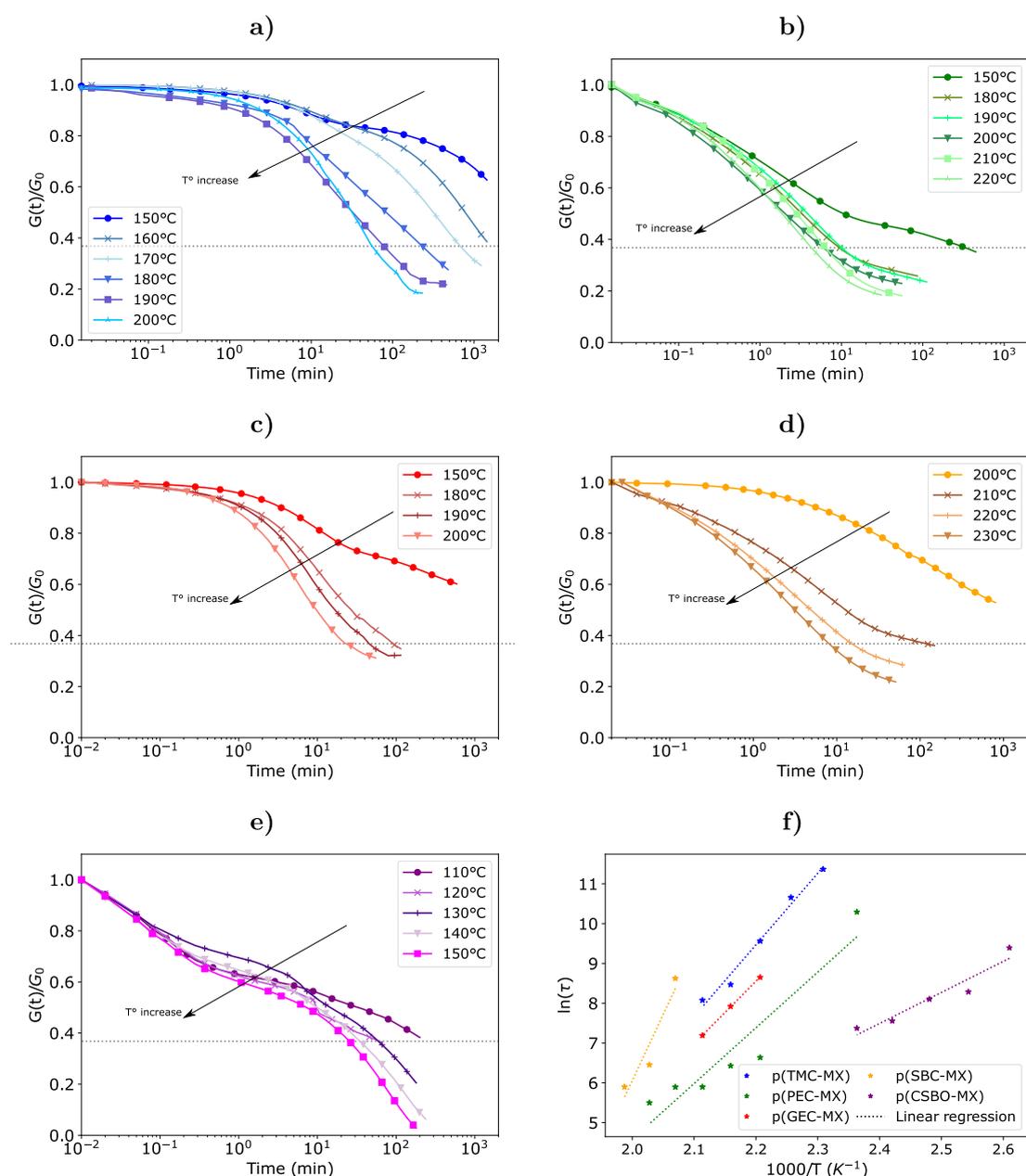
Figure 6. Stress−relaxation of (a) p(TMC-MX), (b) p(PEC-MX), (c) p(GEC-MX), (d) p(SBC-MX), (e) p(CSBO-MX), and (f) Arrhenius plot of the PHUs.

Table 3. Activation Energy of PHUs through Arrhenius Law Fitting

formulation	E_a (kJ/mol)	r^2	T_v (°C)
p(TMC-MX)	149.6	0.992	142
p(PEC-MX)	116.4	0.944	118
p(GEC-MX)	130.3	0.998	115
p(SBC-MX)	276.6	0.950	185
p(CSBO-MX)	64.8	0.957	29

at a lower temperature. At 180 °C, stress−relaxation was reached after 4 h for p(TMC-MX), 1 h 30 for p(GEC-MX), and 12 min for p(PEC-MX). It must be noted that no catalyst was used to promote transcarbamoylation and reverse aminolysis.

Noticeable differences can also be found in activation energy among the formulations. p(SBC-MX) did stress relax but requires high energy, with the risk to get overlapped with thermal degradation events. p(TMC-MX), p(PEC-MX), p(GEC-MX), and p(SBC-MX) possess closer properties with activation energy between 123 and 150 kJ/mol, remaining comparable to other studies on PHUs.[16,55,56] Indeed, Fortman et al.[16] observed activation energy between 110 and 140 kJ/ mol for six-membered CC-based PHUs with T_g around 50 °C. Chen et al.[55] synthesized five-membered CC-based PHUs with T_g around 20 °C, and they also observed high activation energy between 135 and 155 kJ/mol. However, the rearrangement in the PHU networks remains of high complexity when compared to more known dynamic functions such as disulfide bonds[56,57] and must be studied to a larger extent. As highlighted by Bakkali et al.,[11] different mechanisms can take place and be
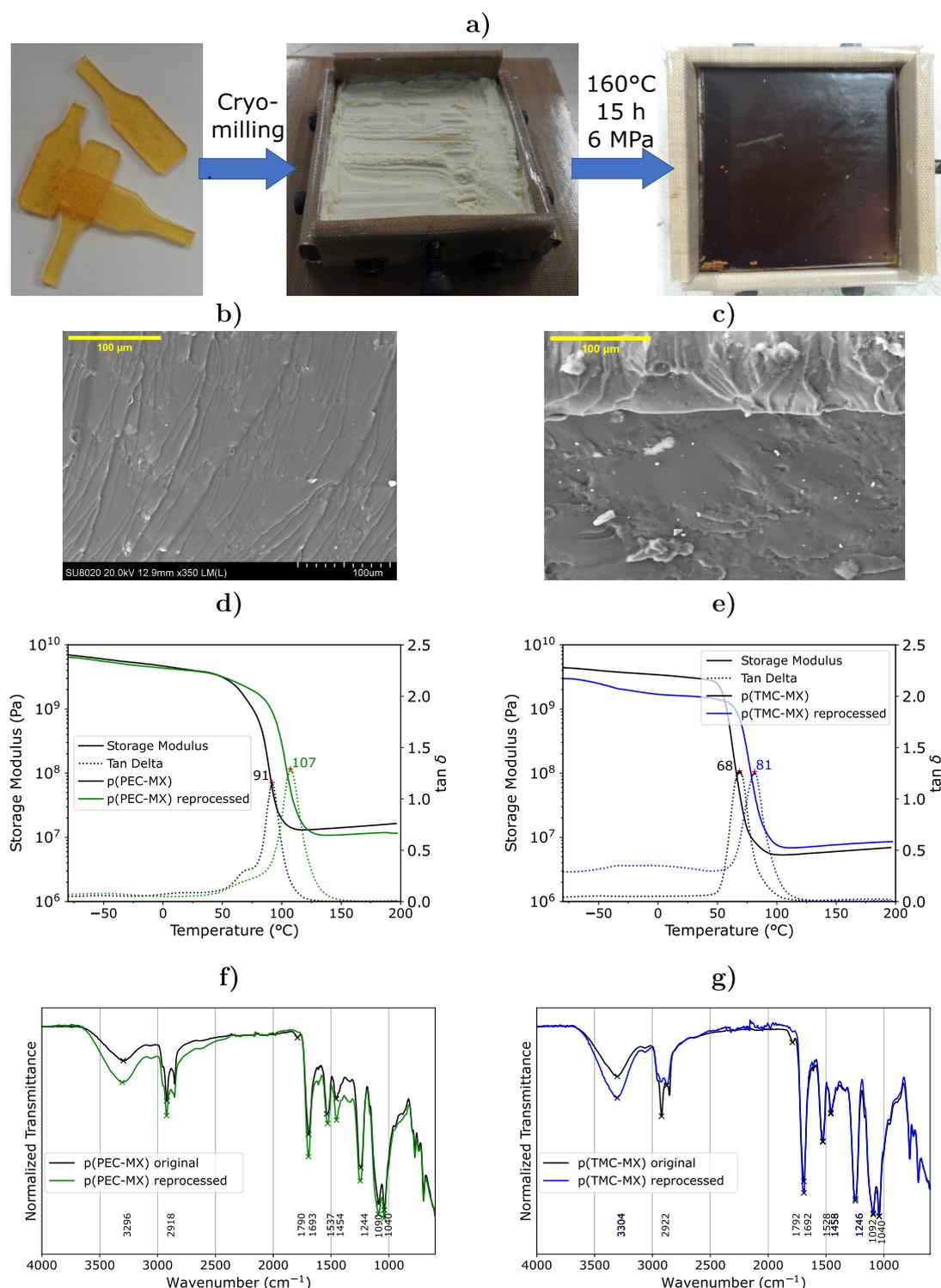
Figure 7. Reprocessing of PHUs. (a) General protocol and reprocessed p(PEC-MX), (b, c) SEM picture of freeze-fractured p(PEC-MX) and p(TMC-MX), (d, e) DMA of p(PEC-MX)and p(TMC-MX), and (f, g) FTIR of p(PEC-MX)and p(TMC-MX).

activated at different temperatures. Moreover, the hydroxyl functions within the PHU backbone can be either primary or secondary functions with a competition between reactivity and steric hindrance.[45]

The topology freezing temperature (T_v) was also estimated. This temperature estimates the minimum temperature required for exchange reaction to occur.[58] The obtained values are consistent with the observed relaxation behavior and

identified E_a of the formulated PHUs. In particular, T_v is ranging between 115 °C for p(GEC-MX) and p(TMC-MX) to 185 °C for p(SBC-MX), explaining the quicker relaxation obtained for p(GEC-MX) and p(PEC-MX) at a lower temperature than for p(TMC-MX) and p(SBC-MX). On the contrary and in addition to the low E_a, p(CSBO-MX), possesses a T_v of 29 °C, only slightly superior to its T_g, in accordance with values found in the literature for trans-

esterification mechanisms[59] and underestimating that trans-esterification is the main mechanism in p(CSBO-MX) network.

Nonetheless, it remains that PHUs show a catalyst-free ability to behave as CAN, even if they cannot be compared to other CAN such as siloxane, Schiff base,[60] or disulfide bond.[56,57] In order to increase the transcarbamoylation rate, and as a consequence the potential of PHUs in recycling, a catalyst should be considered. A more intensive investigation should be conducted to better understand and improve this high-potential behavior.

Reprocessing of Polyhydroxyurethane Thermosets. As a proof of concept, p(TMC-MX) and p(PEC-MX) were reprocessed and characterized by DMA in tensile mode. Isothermal TGA in the air was performed at 160 °C for 15 h in order to ensure that no significant degradation was occurring during the reprocessing. Less than 5% of weight loss was observed during the TGA analysis as shown in Supporting Figure 22. Figure 7a represents the protocol used, and parts b and c of Figure 7 illustrate the obtained freeze-fractured reprocessed p(PEC-MX) and p(TMC-MX) by SEM images.

Both films obtained were homogeneous and translucid with only one hazy area due to the welding close to the edge of the mold. This first observation tends to prove the efficient network rearrangement of these thermosets through chemical rearrangement. In order to fully assess the chemical and not physical bonding, samples were immersed into THF for 3 weeks as reported in Supporting Figure 24. After 3 weeks, no segmentation of the polymer was observed, indicating that the rearrangement happened through exchanges of reversible bonds.[61] DMA storage modulus and tan δ as a function of temperature are presented in Figure 7d,e and numerical values are reported in Supporting Table 3. IR spectra of virgin and reprocessed PHU polymers are shown in Figure 7f,g. IR results highlight no change in spectra that could be related to side reactions, degradation, or any changes in the chemical structure. This indicates that the network remains of PHU nature. The DMA curves highlight a thermoset behavior with a high storage modulus at a temperature below the glass transition and a loss of 2 orders of magnitude after, the tan δ peak is unique and sharp. This confirms the homogeneity of the reprocessed sample. Storage modulus at 25 °C was almost fully recovered for the reprocessed p(PEC-MX) and of about 50% for p(TMC-MX) formulation. This result is in agreement with stress−relaxation analyses where p(PEC-MX) was found to relax faster than p(TMC-MX). T_v of p(TMC-MX), being 142 °C, a higher temperature is necessary to obtain comparable properties restoration as p(PEC-MX), having a T_v of 118 °C. Surprisingly the α transition was higher for both reprocessed formulations while comparable cross-linking densities are observed (slightly higher for p(TMX-MX), slightly lower for p(PEC-MX)). This increase in the α transition can be partly attributed to a postcuring effect, in particular for p(TMC-MX) due to the combined effect of pressure and temperature[61,62] even if DSC shown fully cured matrices for p(PEC-MX) and only a small increase of T_g for p(TMC-MX). No rigid urea linkage seems to have been formed during the reprocessing since no peak at 1650 cm^{-1} was observed even if it cannot be completely excluded and could further explain such phenomenon.[63] In both cases, the reprocessing appears to be feasible, with good mechanical properties recovered, even if the reprocessing operating window seems to be narrow for not inducing any thermal degradation.

■ CONCLUSIONS

Sustainable structural materials, in particular polymer-based, emerge as an essential platform to achieve environmental goals. Yet, despite the efforts made and the promising properties obtained from the final material, there is still a substantial lack of reliable solutions. Gathering green chemical processes, biobased building blocks, enhanced properties of the polymer, and improved end-of-life of the final structure is still a major lock-in in sustainability challenges. Among the numerous sustainable polymers developed over the past decades, polyhydroxyurethanes (PHU), from bio-CO$_2$-based precursors, are arising as versatile, safer, and greener alternatives to conventional polyurethanes in many applications. In particular, the high hydrogen-bonding ability of PHU thermosets can pave the way to enhanced properties. Up-to-date, no study on the relationship between the degree of functionality, the carbonate macromolecular structure, and the properties (processability, thermomechanical, reprocessability) has been conducted on PHU thermosets. As a consequence, a gap of knowledge was found, altering the vast implementation of PHUs to engineered applications. This paper investigates this relationship, from the cyclic carbonate synthesis to the end-of-life of the cross-linked network, considering the CC's structure and degree of functionality. Five potentially biobased cyclic carbonates were synthesized from their epoxy precursors with CO$_2$ in solvent-free conditions and cured with an aromatic diamine. The processability was investigated through rheology. The rheological curing behavior of PHU thermosets appears to be highly dependent on the functionality level, being quickly increased to a nonprocessable rank due to H-bonding. The properties of the cured networks were evaluated to emphasize the interest in high-performance matrices. High modulus, stress, and strain were highlighted with good thermal stability. The obtained thermomechanical properties are in the range to compete with polyurethanes as much as epoxies in structural applications. Moreover, the vitrimeric behavior of the formulated PHUs was investigated. All formulations exhibit the ability to stress relax in catalyst-free conditions. However, they require high temperature, high pressure, and a long time to reprocess, rendering this ability hardly suitable in such conditions. From the overall obtained results, trimethylolpropane- and pentaerythritol-based formulations appear as good contenders to epoxy matrices with reasonable viscosity (below 15 Pa·s at 80 °C), high mechanical, and thermal properties. Reprocessed PHUs show similar thermomechanical behavior as the original ones. Depending on both process and final applications, it must be noted that hybridizing PHUs with other chemistry (epoxy, methacrylate, thiol−ene, ...) could be reliable to extend their use. The composite manufacturing and characterization using PHU thermosets will be addressed in future works by our team.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.3c00879.

> Additional experimental details, materials, and methods, including monomer mass and ^{1}H NMR spectra, FTIR

results, representative tensile stress−strain curves, and photographs of the reprocessed samples (PDF)

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Notes

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