

MONOCOMPONENT NON-ISOCYANATE POLYURETHANE ADHESIVES BASED ON A SOL–GEL PROCESS

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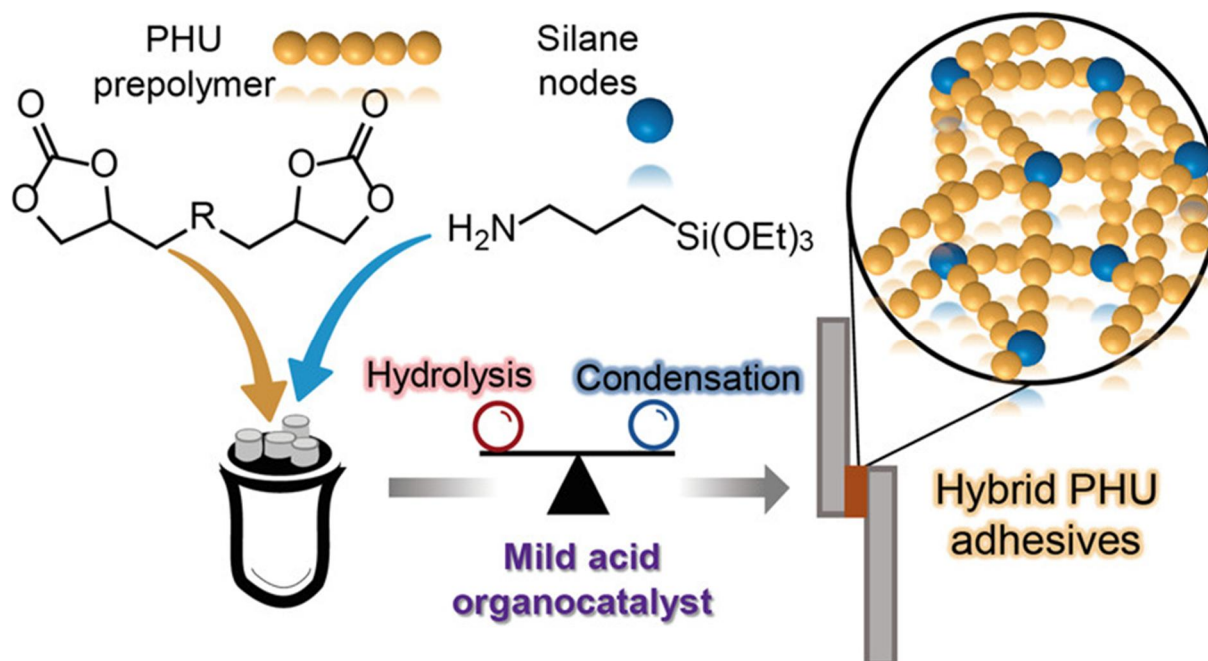
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KEYWORDS: adhesive properties, non-isocyanate polyurethanes (NIPUs), gel time, silane chemistry, hybrid materials, catalysts

ABSTRACT

Non-isocyanate polyurethanes (NIPUs) based on five-membered cyclic carbonates have emerged as the most promising alternative to replace more toxic, conventional polyurethanes. However, the low reactivity of five-membered cyclic carbonates has limited the preparation of one pot systems because of long curing times. This work focuses on the improvement and application of these materials as adhesives through the combination of NIPU chemistry and a sol–gel process that allows for curing by atmospheric humidity. The synthesis of NIPU prepolymers functionalized with (3-aminopropyl)triethoxysilane (APTES) is demonstrated, and their curing behavior and adhesion performance are investigated by means of rheological experiments and a lap-shear test, respectively. In spite of the ability of the alkoxysilane to cure under ambient conditions, our results show that the use of catalyst and elevated temperatures speeds up the curing process and leads to improved adhesion properties. Hence, it is demonstrated that the fastest curing and the best performance are achieved at 100 °C when acetic acid is employed as the catalyst. Finally, we demonstrate the importance of the soft (poly(propylene glycol)dicarbonate) to hard (resorcinol dicarbonate) ratio to achieve superior cohesion and adhesion properties in NIPU adhesives.



Introduction

Adhesives based on polyurethanes (PUs) are widely used due to the broad range of commercially available polyisocyanates and polyols, which make PUs highly versatile with respect to physical properties. Consequently, PUs have traditionally been employed in diverse adhesive applications such as bonding of footwear soles, wood (floor) to concrete (subflooring), and joining laminated wood beams in the construction industry. In addition, PUs are commonly used in rotor blades, in which large surfaces are required to be adhered, and in the automotive industry for fixing the windshield to the automotive frame. (1,2) To highlight the commercial importance of these materials, in 2015, adhesives and sealants represented the fourth highest product by market share in the global PU market, (3) and it is estimated that the market will be worth USD 9.38 billion by 2021. (4)

One of the major drawbacks in the use of PUs lies in the use of isocyanate-based starting materials, as this has several associated health risks. (5,6) First, common isocyanates are synthesized using phosgene, a highly reactive and lethal gas. (5) Second, the isocyanate compounds themselves are highly toxic compounds, which can be responsible for the development of different illnesses in manufacturers, users, and so forth such as occupational asthma or dermatitis. (6–8) In the context of the REACH regulation—implying the restriction of the use of substances containing free isocyanate—it is therefore important to find alternative and greener routes to PUs, involving nontoxic reagents. Thus, non-isocyanate PUs (NIPUs) have emerged in the last decade as an alternative to conventional PUs. Among the different approaches, the step-growth polyaddition of dicyclic carbonates and diamines (9,10) is certainly one of the most attractive alternatives for two main reasons. First, the starting monomers can be produced on a large scale by the

(organo)catalyzed coupling of CO₂ to epoxides (11) (that can be biosourced). Second, the polymerization reaction proceeds with 100% atom economy because no side-product is released during the polymerization. This is particularly attractive, as it allows for the preparation of NIPUs by high-throughput methods, such as reactive extrusion. (12)

Despite these promising characteristics, the low reactivity of five-membered cyclic carbonates typically leads to slow polymerizations as well as side-reactions that can limit the NIPU molar mass. Furthermore, materials with poor mechanical properties are often obtained. In this regard, different approaches have been applied to improve the properties of NIPUs based on five-membered cyclic carbonates such as the production of more reactive monomers, (13–16) the use of catalysts, (17,18) using trifunctional or polyfunctional carbonates, (19–22) the incorporation of inorganic compounds, (19,23) and the preparation of hybrid polymers in combination with acrylates, (22) methacrylates, (24) or partially carbonated epoxide monomers. (25) In spite of the significant improvements in terms of properties and polymerization kinetics, in all of the cases where the properties are optimal for industrial implementation (*e.g.*, using polyfunctional carbonates or epoxy comonomers) a cross-linked material is formed *in situ* at the initial stages of the polymerization, which limits practical use of the adhesive.

One potential method employed in PU chemistry in order to improve mechanical properties and applicability of PU adhesives is devoted to the reaction of PU prepolymers with alkoxy silane compounds in order to obtain a stable, yet curable material. Alkoxy silane groups can undergo cross-linking reactions to form a siloxane-linked network by a sol–gel process, which results in the improvement of the properties of the PU due to the incorporation of nanoscale inorganic domains. (26,27)

There are few examples of hybrid sol–gel NIPUs in the literature. (28,29) For instance, Caillol *et al.* (30) carried out the synthesis and characterization of different hybrid polyhydroxyurethane (PHU)–siloxane thermosets, cross-linked by a sol–gel process. They evaluated the effect of trifluoroacetic acid on the final properties of the materials. The insertion of alkoxy silane groups in the NIPUs allowed the polymer to be cured using atmospheric moisture at elevated temperatures.

Herein, in order to prepare an industrially relevant moisture curable PHU, we synthesize a range of hybrid NIPUs utilizing biobased Priamine 1074, different contents of dicyclic carbonates [poly(propylene glycol dicyclic carbonate) (PPGdiCC) and resorcinol dicyclic carbonate (RdiCC)], and an organosilane compound ((3-aminopropyl)triethoxy silane, APTES) as cross-linker. Films for physical characterization and adhesives were prepared through a sol–gel process by hydrolysis and condensation of the triethoxysilanes. As the curing process was not sufficiently fast at room temperature (RT) in the absence of catalyst, we explored the impact of temperature and different organocatalysts [methanesulfonic acid (MSA), acetic acid (HAc), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)] on the curing step. Moreover, the water uptake and gel content were measured, and lap-shear strength tests were performed to evaluate the adhesive performance of the products.

Experimental Part

REAGENTS

Poly(propylene glycol)diglycidyl ether ($M_n \approx 640 \text{ g mol}^{-1}$) (PPGDGE), resorcinol diglycidyl ether (RDGE), tetrabutylammonium iodide (98%) (TBAI), MSA (99.5%), and HAc (99%) were purchased from Sigma-Aldrich. APTES (99%) was obtained from Acros Organics. 1,3-Bis(2-hydroxyhexafluoroisopropyl)benzene (97%) (1,3-bis HFIB) was purchased from Fluorochem. Dimer fatty diamine (trade name: Priamine 1074) was received from CRODA. DBU ($\geq 98\%$) was purchased from Alfa Aesar. Deuterated chloroform (CDCl_3) and dimethylsulfoxide ($\text{DMSO}-d_6$) were purchased from Sigma-Aldrich. All reagents were used without further purification.

TYPICAL PROCEDURE FOR THE SYNTHESIS OF RDiCC

RDGE (20 g, 90 mmol), TBAI (1.66 g, 4.50 mmol), and 1,3-bis HFIB (1.84 g, 4.50 mmol) were charged to an 80 mL high-pressure autoclave. Subsequently, the cell was closed, the temperature was raised to 80 °C, the CO_2 pressure was adjusted to 100 bar, and the reaction was allowed to proceed overnight. RdiCC was obtained quantitatively after depressurization of the reactor, and no further purification was required. Nuclear magnetic resonance (NMR) spectra of the product are shown in Figure S2.

TITRATION OF THE CYCLIC CARBONATE BY ^1H NMR

A specified amount of cyclic carbonate (PPGdiCC or RdiCC) (around 50 mg) and standard solution of DMSO with toluene (around 30 mg of toluene dissolved in 5 mL of $\text{DMSO}-d_6$) were weighed into an NMR tube. Once the ^1H NMR acquisition was completed, characteristic peaks of carbonate a, b, and c (4.51, 4.29, and 4.92 ppm, respectively) and CH_3 (2.32 ppm) of toluene were integrated. The integration of CH_3 of toluene was fixed to 300. Carbonate equivalent weight (CEW) of PPGdiCC and RdiCC were calculated according to eq 1, where m_{CS} —mass of cyclic carbonate introduced into the NMR tube, $n_{\text{function of carbonate}}$ —molar amount of function carbonate in cyclic carbonate, I_a , I_b , I_c —integrations of characteristics peaks a, b, and c of carbonate, n_{toluene} —molar amount of toluene introduced in standard solution, I_{CH_3} —integration of peak CH_3 of toluene. The CEW values for each cyclic carbonate were obtained in triplicate determinations and are presented in Table S1 together with the amine hydrogen equivalent weight (AHEW) for amines.

$$\text{CEW} = \frac{m_{\text{CS}}}{n_{\text{function of carbonate}}} = \frac{m_{\text{CS}} \times I_{\text{CH}_3}}{(I_a + I_b + I_c) \times n_{\text{toluene}}} \quad (1)$$

TYPICAL PROCEDURE FOR NIPU PREPOLYMER PREPARATION

PPGdiCC (20.04 g, 0.06 equiv) and Priamine 1074 (13.23 g, 0.054 equiv) were added to a 100 mL jacketed glass reactor. The temperature was set at 80 °C for 24 h under continuous mechanical stirring at 200 rpm. The reaction was cooled down and the polymer stored. For the incorporation of

RdiCC, NIPU prepolymers were prepared as follows: PPGdiCC (6.58 g, 0.02 equiv), RdiCC (1.87 g, 0.014 equiv), and Priamine 1074 (7.26 g, 0.027 equiv) were weighed in a 100 mL jacketed glass reactor. The conditions and time were set up as for the preparation of the 100/0 PPGdiCC/RdiCC ratio. For the rest of the compositions, quantities of PPGdiCC and RdiCC were adjusted according to the percentages shown in Table 1, entries 9–11. In all cases, Priamine 1074 was kept at 0.9 equiv regarding to 1 equiv of carbonate.

Table 1. Gel Time Values for All of the Different Studied Compositions and Conditions

entry	composition (PPGdiCC/RdiCC)	temperature (°C)	catalyst	t_{gel}^b (min)
1	100/0	120	no catalyst	23.5 ± 0.7
2		100		55.8 ± 2.5
3		80		153.5 ± 4.9
4		60		369.5 ± 12
5		25		^a
6	100/0	100	DBU (1 wt %)	42.8 ± 4.0
7			HAc (1 wt %)	9.8 ± 0.4
8			MSA (1 wt %)	39.7 ± 5.6
9	95/5	100	no catalyst	46.8 ± 4.0
10	90/10			32.1 ± 0.8
11	80/20			33.3 ± 1.7
12	60/40			18.6 ± 1.9

^a No crossover after 15 h of measurement. ^b Gel times values from the crossover between G'' and G' .

TYPICAL PROCEDURE FOR ALKOXY-SILANE PREPOLYMER PREPARATION

In a 250 mL three-neck round-bottom flask equipped with a half-moon Teflon helix stirrer, 2 g of the NIPU prepolymer was weighed. The flask was placed into an oil bath at 40 °C under a N_2 flow for 10 min. Then, APTES (2 molar equivalents with respect to the number of cyclic carbonates groups) was added, and the mixture was allowed to react for 45 min. For the measurements using acid or base catalysts, the catalyst was added at the end of the reaction and stirred for 30 s to obtain a homogeneous mixture.

CHARACTERIZATION AND METHODS

NUCLEAR MAGNETIC RESONANCE

^1H spectra were recorded on a Bruker Advance DPX 300 spectrometer at 25 °C. Deuterated chloroform, CDCl_3 , was used as solvent.

FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier transform infrared (FT-IR) spectra were obtained using an FT-IR spectrophotometer (Nicolet 6700 FT-IR, Thermo Scientific Inc., USA) equipped with Golden Gate MK II with a diamond crystal. Spectra were recorded between 4000 and 525 cm^{-1} with a spectrum resolution of 4 cm^{-1} . All spectra were averaged over 10 scans.

RHEOLOGY MEASUREMENTS

Time sweep experiments were performed in a stress-controlled Anton Paar Physica MCR101 rheometer at different temperatures, at a frequency of 1 Hz and a strain of 1% in order to determine the crossover between loss modulus (G'') and storage modulus (G') (gel time). The experiments were carried out using 25 mm parallel plate geometry.

GEL CONTENT

The gel content was measured by Soxhlet extractions in refluxing tetrahydrofuran (THF) for 24 h. Afterward, samples were dried in oven at 70 °C for 24 h. Values were calculated with

$$\text{GC (\%)} = \frac{m_f}{m_i} \times 100 \quad (2)$$

where m_f is the final weight of the dried sample and m_i is the initial weight of the sample.

EQUILIBRIUM WATER CONTENT

Three samples (~30 mg) of each formulation were immersed separately into 10 mL of deionized water for 96 h. The equilibrium water content was calculated by

$$\text{EWC} = \frac{m_s - m_i}{m_i} \times 100 \quad (3)$$

where m_s is the weight of the swollen sample and m_i is the initial weight of the sample.

DIFFERENTIAL SCANNING CALORIMETRY

A differential scanning calorimeter (DSC-Q2000, TA Instruments Inc., USA) was used to analyze the thermal behavior of the samples. A total of 6–8 mg of samples was scanned from –80 to 100 °C at a heating rate of 20 °C min^{-1} . The glass transition temperatures (T_g) were taken from the inflection point in the heat capacity curve.

THERMOGRAVIMETRIC ANALYSES

A thermogravimetric analyzer (TGA-Q50, TA Instrument Inc., USA) was used to investigate the thermal stability of the samples. A total of 5–10 mg of samples was heated from 30 to 800 °C at a heating rate of 10 °C/min under a N_2 atmosphere (50 mL/min). The temperature at which the samples lost 5% of their weight was reported as the onset of degradation of the sample.

SIZE EXCLUSION CHROMATOGRAPHY

Size exclusion chromatography (SEC) was performed in THF at 35 °C (flow rate of 1 mL/min) using a Waters chromatograph equipped with three in series (Styragel HR2, HR4, and HR6) with increasing pore sizes (from 100 to 10⁶ Å). Toluene was used as a marker. Polystyrenes of different molecular weights, ranging from 573 to 3,848,000 g/mol, were used for the calibration. The molar masses reported relate to polystyrene.

LAP-SHEAR TESTS

The adhesion properties of the NIPUs were evaluated at 298 K and 50% RH using an Instron 5569 and applying a parallel force to the adhesive bond with a displacement rate of 1 mm min⁻¹. Stainless steel AISI 316 substrates with dimensions of 100 mm × 25 mm × 1.95 mm were used for single lap-shear measurements, and the gripping length on both sides of test specimens was 25 mm, according to DIN EN 1465. The tests were performed on 5 samples for each formulation to determine the average lap-shear strength. The lap-shear strength was calculated by the equation

$$\tau = \frac{P}{A} \quad (4)$$

where τ is lap-shear strength (N mm⁻² or MPa), P is the maximum loading force to remove and break the adhesive (N), and A is the overlapped area of adhesive joint (312.5 mm²). The nature of adhesion failure was also recorded based on visual inspection of the sample following the test.

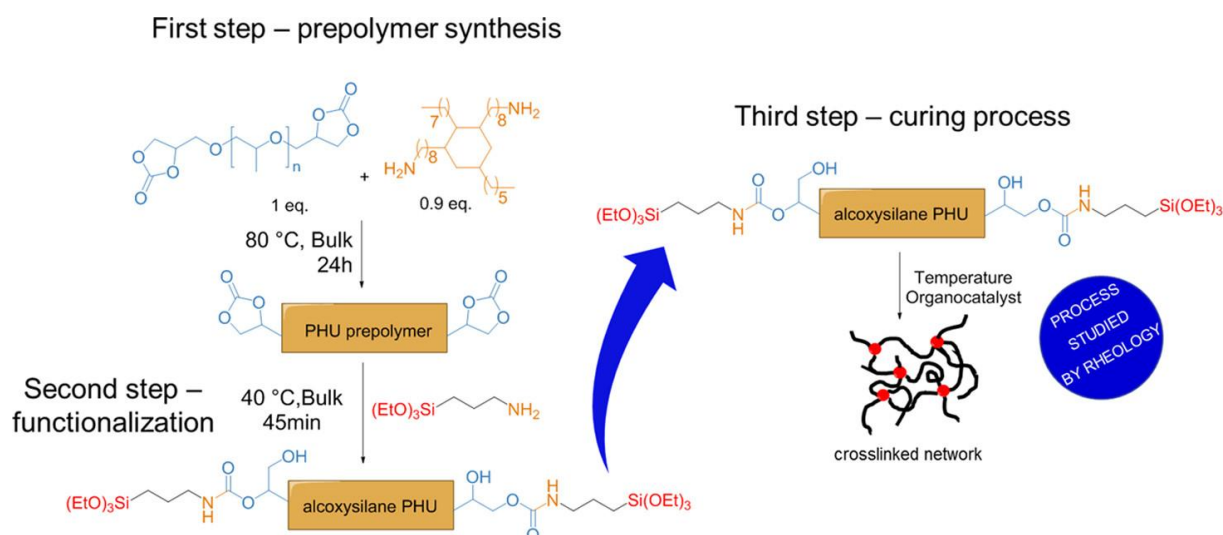
Lap-shear test specimens were prepared as follows. The surfaces of the substrates were cleaned following the procedure described elsewhere. (20) Adhesive formulations were prepared following the typical procedure for the rheological measurements. The adhesive joints were prepared by spreading the viscous material (~50 mg) onto the cleaned substrates, placing the second substrate into contact and applying light pressure manually. The overlapping area was in all cases 312.5 mm². The adhesive joints were allowed to cure in an oven at 100 °C for 24 h. Specimens were prepared five times for each composition to determine the average values. For the evaluation of the performance after water uptake, lap-shear test specimens were first prepared as described above and were then immersed in water for 96 h prior to measuring.

Results and Discussion

SYNTHESIS OF TELECHELIC TRIETHOXY-SILANE PHUS OLIGOMERS AND THEIR CURING

PPGdiCC was synthesized at the kilogram scale by the quantitative organocatalyzed coupling of CO₂ to PPGDGE for 24 h following a previously reported procedure. (31) The completion of the reaction was noted by ¹H NMR spectroscopy by the complete disappearance of epoxy group signals at 3.14, 2.78, and 2.61 ppm and the appearance of peaks related to the carbonate group at 4.78 and 4.66 ppm (Figures S1 and S2).

The preparation of PHU hybrids was then performed following an adapted procedure from previous work, (29) consisting of a three-step strategy as illustrated in Scheme 1: (a) synthesis of PHU prepolymer end-capped by cyclic carbonates (PHUdiCC), (b) functionalization of the prepolymer by aminolysis of the cyclic carbonates with APTES, and (c) curing by hydrolysis and condensation of the ethoxysilane functionalized PHUs.



Scheme 1. Synthesis and Preparation of PHU Monocomponent Adhesives

For the first step, the preparation of the PHU prepolymer (PHUdiCC) was carried out using an excess of PPGdiCC relative to the diamine, with a cyclic carbonate to amine molar ratio of 1/0.9 (Scheme 1; first step). PPGdiCC was selected because PPG is one of the most commonly employed soft-segments in PU adhesives, as it provides good adhesion to different substrates and also presents good hydrolysis resistance and hydrophobicity. (32) Priamine 1074 was used, as it is a commercially available biobased diamine, which also confers hydrophobicity to the materials. (33) The reaction was carried out for 24 h without a catalyst and solvent. The monomer conversion was monitored by FTIR–attenuated total reflection (ATR) by following the decrease of the relative intensity of the carbonyl stretching vibration band of the carbonate at 1798 cm^{-1} (Figure 1a). The intensity of the bands at $3035\text{--}2800\text{ cm}^{-1}$ (corresponding to C–H and $\text{CH}_2\text{--O}$ stretching band of alkanes and ether, respectively), whose intensities did not change with reaction time, were used to normalize the areas. After 24 h, a new band at 1700 cm^{-1} characteristic of the carbonyl of the urethane group was clearly observed, together with the carbonyl band of the cyclic carbonate (1798 cm^{-1}) at the PHU ends. ^1H NMR spectroscopy of the PHU prepolymer (Figure 1b) showed the characteristic resonance of the PPG repeating units at 3.3–3.8 and 1.12 ppm, as well as a signal at 3.13 ppm associated with the methylene group next to the reactive amine group of the Priamine and the characteristic resonance of the aliphatic chains of the diamine at 1.46, 1.24, and 0.86 ppm. Molecular weight values were characterized by SEC measurements (Table S2).

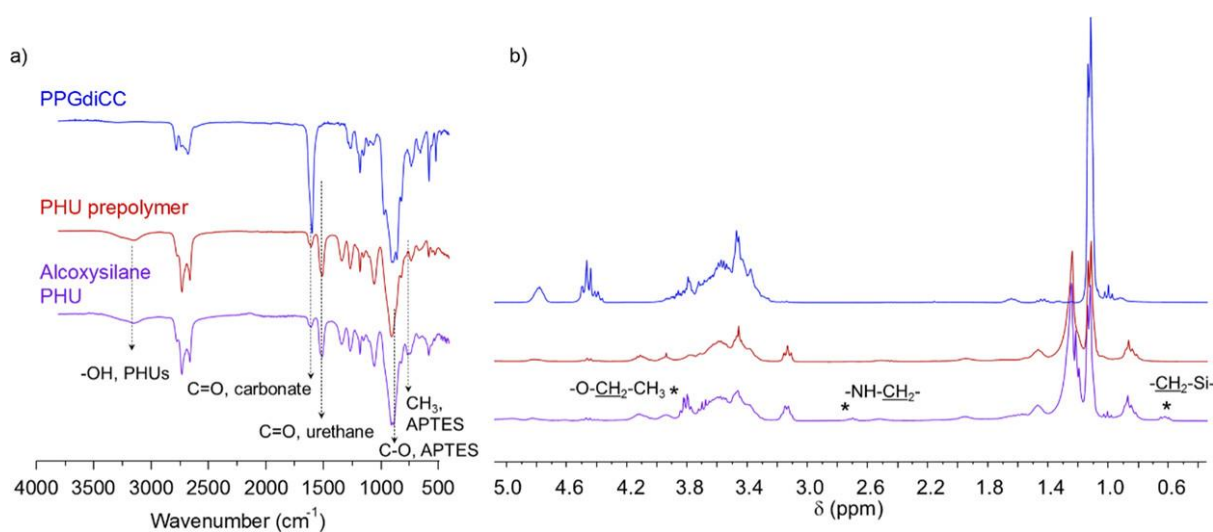


Figure 1. FTIR-ATR (a) and ¹H NMR (b) characterization of PPGdiCC, PHU prepolymer, and NIPUs before preparation of the film. New signals are marked with * confirming the reaction with APTES.

For the second step, the majority of the unreacted carbonate groups was reacted with APTES for 40 min at 40 °C, giving rise to an alcoxysilane-capped NIPU. The reaction temperature was reduced in order to avoid undesired condensation during the functionalization step. The effectiveness of the reaction was confirmed by the appearance of new bands at 959 and 1083 cm⁻¹ attributed to the CH₃ rocking and C–O symmetric stretching of APTES, respectively. (34) ¹H NMR spectroscopy also showed the appearance of new signals at 3.78, 2.68, and 0.60 ppm, corresponding, respectively, to the –O–CH₂–CH₃, –NH–CH₂–, and –CH₂–Si– of the reacted APTES (Figure 1b).

One of the greatest advantages of alcoxysilane-functionalized formulations is their ability to cure under ambient conditions by a sol–gel process. In order to investigate the curing ability of this telechelic PHU oligomer, the curing was followed by FTIR-ATR and rheological measurements. The rheological measurement was performed to determine the gel time ($G' = G''$ and/or $\tan \delta = 1$) at a single frequency and amplitude. The PHU alcoxysilane was first cured under ambient conditions for 15 h. Although FTIR-ATR spectra (Figure 2a) showed the disappearance of the characteristic bands of CH₃ rocking and C–O symmetric stretching of APTES centered at 959 and 1083 cm⁻¹, respectively, the loss modulus (G'') remained higher than the storage modulus (G'), confirming that PHU was not cross-linked (Figure 2b). No gel point (assigned when G' crosses G'') was observed, even after 15 h of reaction, suggesting the low capability of the telechelic PHU oligomers to cure under ambient conditions.

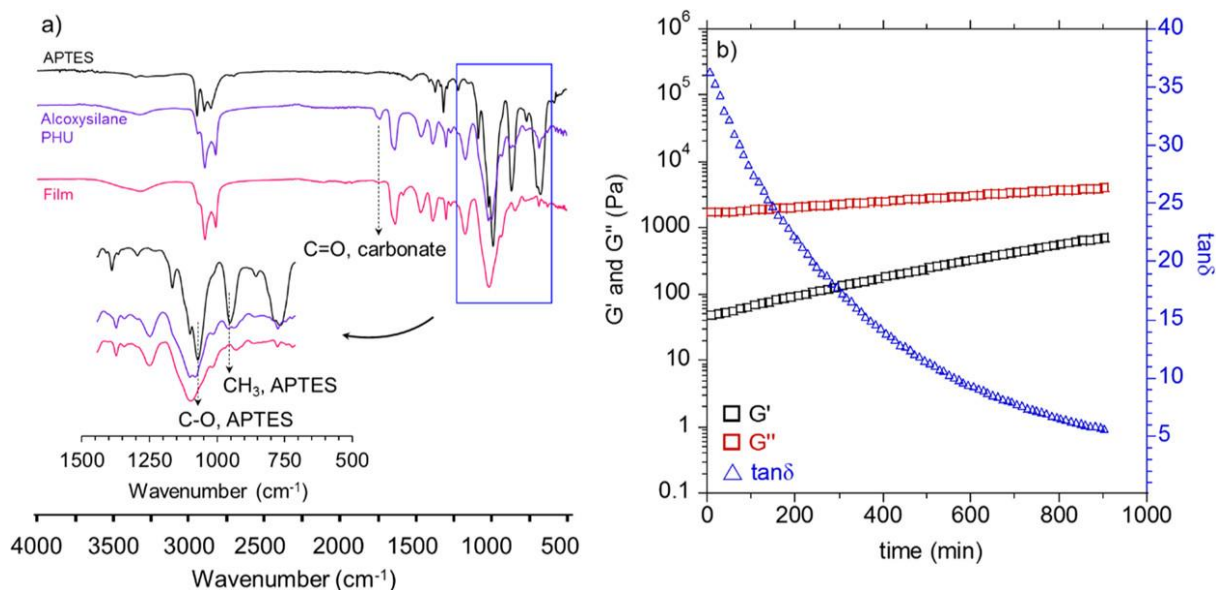


Figure 2. (a) FTIR-ATR spectra for the following of the curing process; (b) storage (G'), loss (G'') moduli and $\tan \delta$ values for the sample at 25 °C.

In order to favor PHU curing, we investigated the effect of temperature and the use of a catalyst. Figure 3a shows the values of G' and G'' at different temperatures. It is clear that the gelation process is highly temperature dependent. The gelation time (t_{gel}) was decreased considerably by raising the temperature, with a gel time of 20 min at 120 °C, while no cross-linking was noted at 25 °C after 15 h. The curing was then performed at different temperatures (100, 80, and 60 °C), and the temperature dependence of the gel time was calculated by the Arrhenius equation (35) and plotted in Figure 3b. This linear plot allowed for the calculation of the activation energy (E_a) of the process. As the sol-gel process implies two steps (hydrolysis and condensation of the ethoxysilanes), E_a was referred to the whole reaction. Without the catalyst, the activation energy value was 50 kJ/mol, which is in the range of the typical E_a for silica gels (~ 40 – 80 kJ/mol). (36–38)

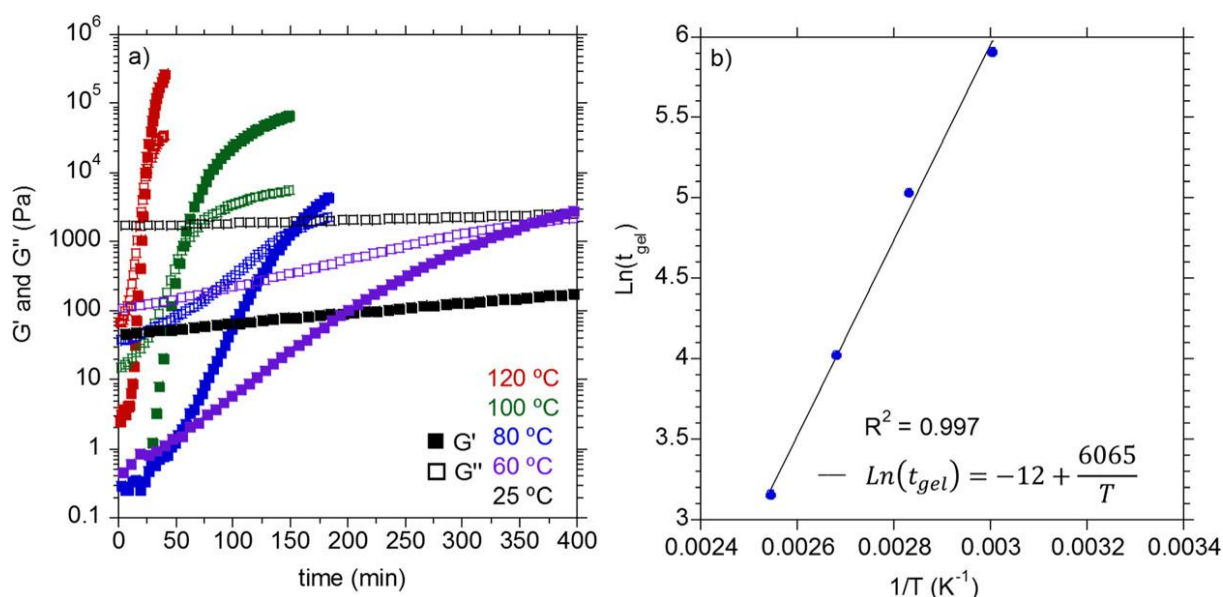


Figure 3. (a) G' and G'' values of the rheological measurements of the system depending on temperature, (b) plot representation of $\ln(t_{gel})$ vs $1/T$ for the measurements presented in (a).

The addition of a catalyst was then considered in order to accelerate the curing of the ethoxysilane moieties (Figure 4b). As both hydrolysis and condensation reactions of the ethoxysilane group can be promoted by acids and bases; (35) a strong base (DBU; $pK_a = 13.5$), (39) a strong acid (MSA; $pK_a = -1.9$), (40) and a mild weak acid (HAc; $pK_a = 4.75$) (41) (Figure 4a) were tested as catalysts added at 1 wt % for reactions performed at 100 °C. While the strong acid and strong base slightly enhanced the curing rate (t_{gel} of about 40 min vs 56 min, Table 1, comparison of entries 2, 6, and 8), the mild acid led to a much faster curing ($t_{gel} = 10$ min; Table 1, entry 7; Figure 4c). This faster curing with HAc agrees with results from Coltrain and Kelts (42) who found that a compromise is required in terms of hydrolysis and condensation to promote fast curing. When using a higher HAc concentration (5 wt %), a gel time of 20 min was obtained at a lower temperature (*i.e.*, 60 °C) (Figure S3).

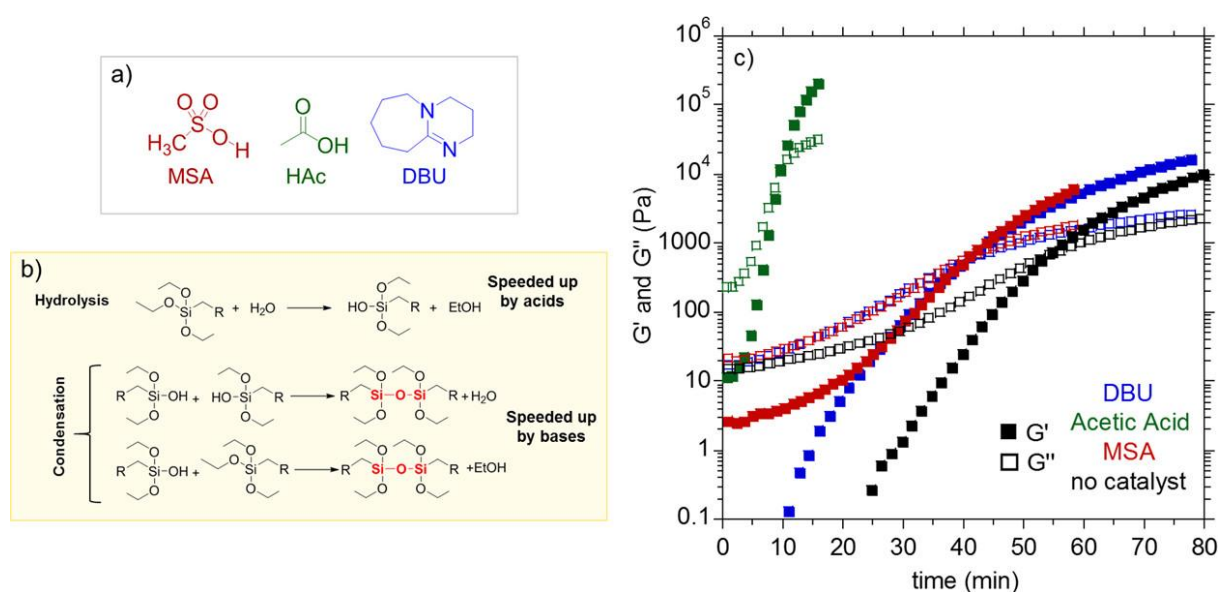


Figure 4. (a) Structures of acids (MSA, HAc) and base (DBU) employed for speeding up the curing process; (b)

hydrolysis and condensation scheme of alkoxy silane derivatives during the sol–gel process; (c) G' and G'' values for rheological measurements carried out at 100 °C in the presence of the different catalysts.

EVALUATION OF THE ADHESIVE PROPERTIES OF THE HYBRID PHU PRODUCTS

The adhesive properties of the hybrid PHU products (cured at 100 °C with 1 wt % HAc) on stainless steel were evaluated by lap-shear strength measurements. In order to ensure complete curing of the samples, materials were kept for 24 h at this temperature before measurement. In Figure 5a, the force–displacement curve of the sample based on telechelic triethoxysilane PPG (blue curve) is depicted. A low lap shear strength of 1.1 ± 0.2 MPa was measured by dividing the maximum load or force (expressed in N, issued from Figure 5a) by the adhesive surface area (expressed in mm²). The failure in this sample was cohesive, indicating that the internal forces of the adhesive were not strong enough. We envisioned that an increase in the rigidity of the adhesive might enhance these cohesive forces and, therefore, the lap-shear strength of the material.

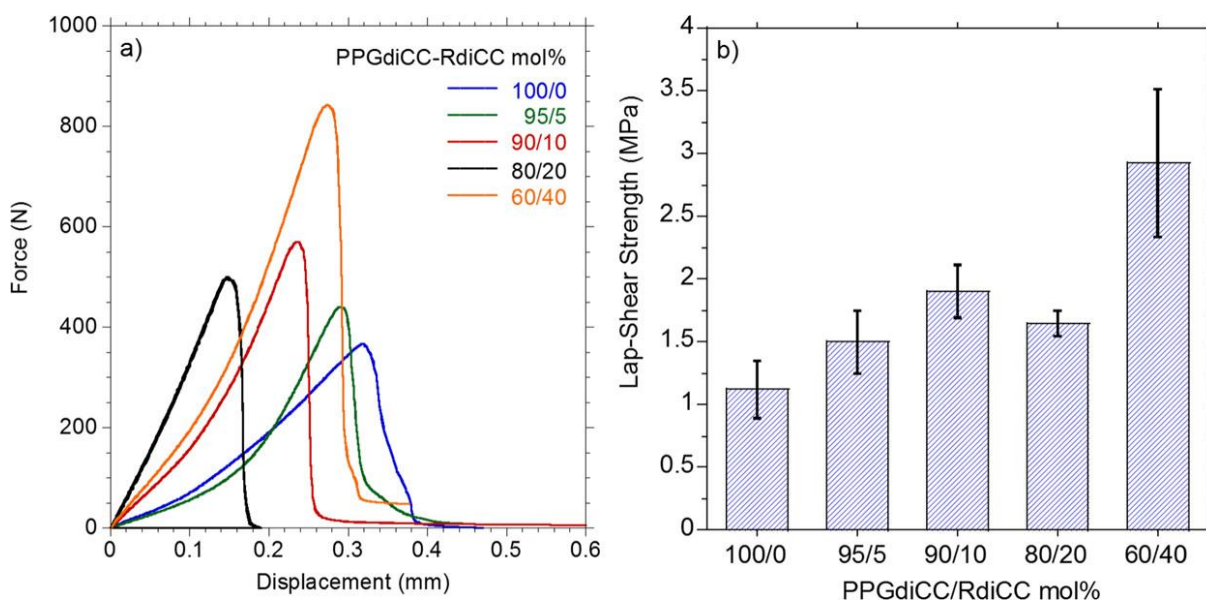
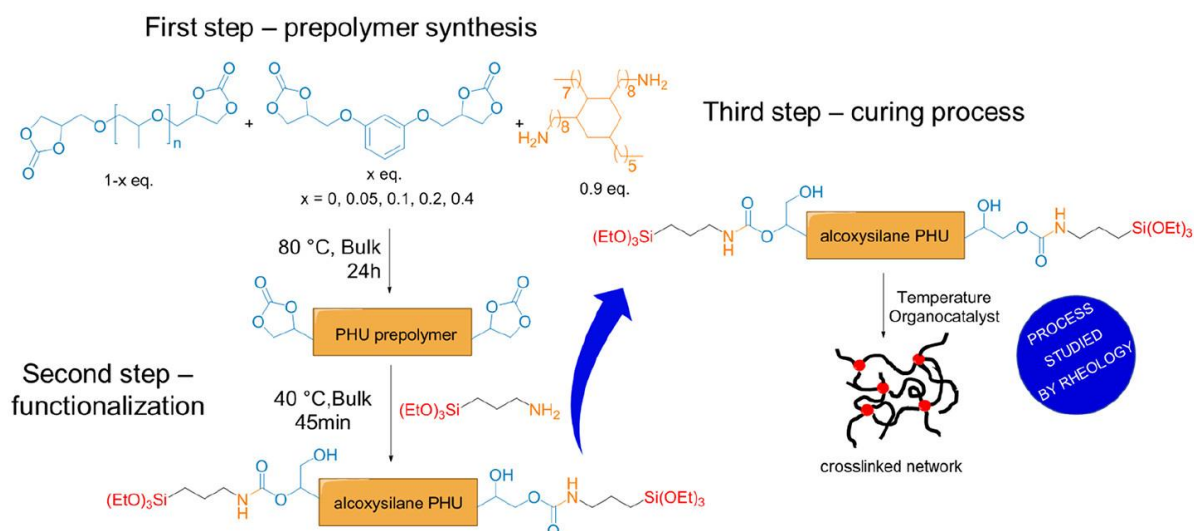


Figure 5. (a) Representing curves of the lap-shear strength for each composition; (b) values with error bars, representing standard deviation for each sample set.

Thus, in order to increase the cohesive strength, telechelic PHU oligomers were prepared by substituting part of PPGdiCC by a more rigid RdiCC (Scheme 2). Although resorcinol production is mainly petrol based, it can also be prepared from bioresources, for example, from catechins by fermentation or from glucose. (43) The curing process of the corresponding telechelic PHU oligomers was also investigated by rheology for four different PHU compositions at 100 °C without a catalyst (Table 1, entries 9–12). Importantly, the gel time decreased progressively and significantly by increasing the RdiCC content in the telechelic PHU, from 56 min for the RdiCC-free PHU to 19 min for the RdiCC-rich one.



Scheme 2. Synthesis of Adhesives Based on a Mixture of Soft (PPGdiCC) and Hard (RdiCC) Dicarbonates

While similar lap-shear adhesion strengths were obtained for cured hybrid PHUs prepared with up to 20 mol % RdiCC (Table S3), better performance (2.9 ± 0.6 MPa) was obtained with 40% of the comonomer. A possible explanation for this could be that the cohesive forces were enhanced via noncovalent interactions of the resorcinol moiety as observed by Detrembleur *et al.* (20) No further addition of RdiCC into the formulation was performed due to the high viscosity of the samples, which led to practical difficulties in efficient mixing of the components.

Gel content measurements for all samples containing different soft to hard ratios were carried out in order to understand the impact of the cross-linking degree on the adhesion properties. The gel content for all compositions remained at around 70% (Figure S7a), except for the adhesive prepared from the PHU oligomer synthesized with 40 mol % RdiCC. In this latter case, the gel content was around 80%. Therefore, both the covalent (gel content) and noncovalent interactions (π - π interactions of the aromatic rings) of the sample (20) are assumed to be responsible to some extent for the increase in the lap-shear strength of the specimens.

Aside from the shear strength, there are other properties that are important to study in order to evaluate the potential of an adhesive, including the water uptake and the thermal properties (the glass transition temperature, T_g , and the degradation temperature, T_d). Most adhesives should have a low water uptake in order not to swell during use and to avoid the delamination from the substrate. (19) Because of the presence of primary and secondary alcohols in their structure, PHUs and PHU adhesives are typically considered to be high water uptake materials. (44,45) In agreement with these works, the adhesives based on PPGdiCC only or PPGdiCC and RdiCC (with up to 20 mol % RdiCC) had a water uptake of around 11% (Table 2, entries 1–4). Increasing the resorcinol content in the PHU to 40 mol % decreased this water uptake, owing to the introduction of hydrophobic aromatic groups within the polymer chain (Table 2, entry 5). It may be noted that the water uptake values for all compositions are much lower compared to other PHUs employed as adhesives in the literature (20,45) and are comparable to NIPUs in which hydrophobic cyclocarbonated soybean oil was employed as part of the formulation. (19) Furthermore, lap-shear strength measurements were carried out after immersing the specimens 96 h in water to evaluate the performance of the most

hydrophobic adhesive. Interestingly, even after 4 days in water, the lap-shear strength of the adhesive was unaffected (Table S3, entry 6).

Table 2. Summary of Results for the Different Formulations Prepared^a

entry	composition (PPGdiCC/RdiCC)	catalyst	EWC ^b (%)	GC ^c (%)	T _g ^d (°C)	T _d 5% ^e (°C)
1	100/0	HAc (1 wt %)	11.3 ± 0.5	68.7 ± 0.7	-32	273
2	95/5		10.1 ± 1.3	65.8 ± 3.5	-33	270
3	90/10		12.0 ± 1.6	64.8 ± 2.5	-32	265
4	80/20		12.2 ± 0.6	70.7 ± 3.5	-32	272
5	60/40		6.0 ± 0.4	79.6 ± 0.5	-23	265

^a Curing conditions were set as 24 h at 100 °C. ^b Equilibrium water content measured after 96 h immersed in water. ^c Gel content after Soxhlet extraction in THF for 24 h. ^d Glass transition temperature. ^e Temperature at which sample lost 5 wt %.

On the other hand, the glass transition temperature defines at which temperature the adhesive is in its glassy state and becomes stiff and brittle. (2) The T_g for the adhesives was in the range of -32 to -23 °C (Table 2) allowing a low service temperature for all compositions. In addition, the thermal stability of the PHUs was investigated by thermogravimetric analysis (TGA) and no significant difference between the formulations was observed, with a degradation temperature at 5% (T_d5%) above 265 °C (Table 2) in all cases, in accordance with previous results using PUs based on APTES. (26)

EVALUATION OF THE ADHESIVE PROPERTIES OF THE HYBRID PHU AT RT

One of the greatest assets of alkoxy silane groups is their potential to undergo cross-linking reactions at ambient conditions in the presence of an appropriate catalyst. (46) Therefore, the optimal composition containing 60/40 PPGdiCC/RdiCC was cured at 25 °C employing 2.5, 5, and 7.5 wt % of HAc catalysis, and the adhesive properties were investigated. Rheological measurements proved that even at the lowest catalysts concentrations, cross-linking occurred (Figure S4). Nevertheless, the adhesion values in all cases were 3 times lower (Table 3) than in the case of curing the material at 100 °C which is related to the low values obtained of gel content for these compositions (Table S4).

Table 3. Lap-Shear Strength Values for the Composition 60/40 PPGdiCC/RdiCC Cured at 25 °C for 24 h with Different Loads of HAc

HAc (wt %)	lap-shear strength (MPa)
2.5	1.1 ± 0.3
5.0	1.1 ± 0.4

7.5	0.8 ± 0.01
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Although the T_g values of the compositions cured at 25 °C (Table S4) remained similar to the previous ones allowing a low service temperature, the equilibrium water content of these films increased significantly (up to 30%, Table S4), decreasing the resistance against delamination.

Conclusions

Monocomponent NIPU adhesives were synthesized by adding (3-aminopropyl)triethoxysilane to a previously prepared PHU prepolymer based on five-membered cyclic carbonates and Priamine 1074, allowing the curing process to proceed under ambient conditions through a sol–gel process. The activation energy of the sol–gel process was determined to be 50 kJ/mol by rheological measurements conducted at different curing temperatures. In order to speed up the curing, the addition of catalyst and the increase of the reaction temperature were considered. By using 1 wt % of HAc at 100 °C, the curing time was decreased fivefold. Furthermore, the use of 2.5 wt % of HAc allowed for curing to occur under ambient conditions, although the adhesive properties were slightly compromised. Finally, we found that the incorporation of 40 mol % of RdiCC hard comonomer increased the lap-shear strength more than 2.5 times, thus demonstrating the importance of the hard to soft ratio to obtain adhesives with good cohesion and adhesion properties.

Associated content

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.0c00062>.

- NMR spectra, AHEW and CEW values, molecular weights of PHU prepolymers, rheology measurements, physical and thermal characterization, and lap-shear strength values and nature of adhesive failure of adhesive joints (PDF)

Acknowledgments

The authors would like to acknowledge the technical and human support provided by SGIker (UPV/EHU and ERDF, EU). A.G.-L. acknowledges the University of the Basque Country for the predoctoral fellowship received to carry out this work. The authors would also like to thank the technical support provided by Dr. Alba Gonzalez Vives for the TGA analysis and Dr. Amaia Agirre for the GPC analysis. The authors from Liege thank le Fonds européen de développement régional (FEDER) et la Wallonie dans le cadre du programme opérationnel (Wallonie-2020.EU) in the frame of

the BIODEC project. C.D. is Research Director by F.R.S-FNRS and thanks FNRS for financial support. ORIBAY company also wants to acknowledge HAZITEK project for the project n° ZL-2019/00193.

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