Universidad del País Vasco Euskal Herriko Unibertsitatea

KIMIKA ZIENTZIEN FAKULTATEA

FACULTAD DE CIENCIAS QUÍMICAS

Universidad del País Vasco/Euskal Herriko Unibertsitatea

Facultad de Ciencias Químicas/Kimika Zientzien Fakultatea

Degree in chemistry

TRABAJO FIN DE GRADO

Synthesis of Water-Dispersible Isocyanate-Free Poly(hydroxyurethane)s from 5- and 8-Membered Cyclic Carbonates Using the Acetone Process

Author: Ion Olazabal Lorea

Supervisors: Agustin Etxebarria
Haritz Sardon

San Sebastián, July of 2017

GIPUZKOAKO CAMPUSA
CAMPUS DE GIPUZKOA
Pº. Manuel de Lardizabal, 3

ABSTRACT

Water-dispersible isocyanate-free poly(hidroxyurethane)s (PHU)s dispersions were made from amino-terminated poly(dimethylsiloxane), renewable diglycerol dicarbonate (DGC) and 8-membered cyclic carbonate ((bis) *N*-8-C) by means of phase inversion using the acetone process. First WDPHU polymers with different ratios of 5- to 8- membered cyclic carbonates were synthesized in bulk without the use of any catalyst. These polymers were characterized by FTIR, ^{1}H and ^{13}C NMR, TGA, DSC and SEC-GPC. Then dispersion experiments were carried out to find the optimal dispersion conditions. Changes in the ((bis) N-8-C) concentration, in the charge concentration and the initial PHU content in acetone were made to analyse the impact on the particle size and the particle size distribution of the dispersions. Stable dispersions with particle size around 200 nm were obtained using 70/30 5-8- membered cyclic carbonate ratio. Then films were made by ionic crosslinking mixing this dispersion with different carboxylic acid to compare the improve of mechanical properties and the influence of the amount of acid. The self-healing properties of the materials obtained were evaluated by parallel plate rheometry measurements and optical microscopy.

Resumen

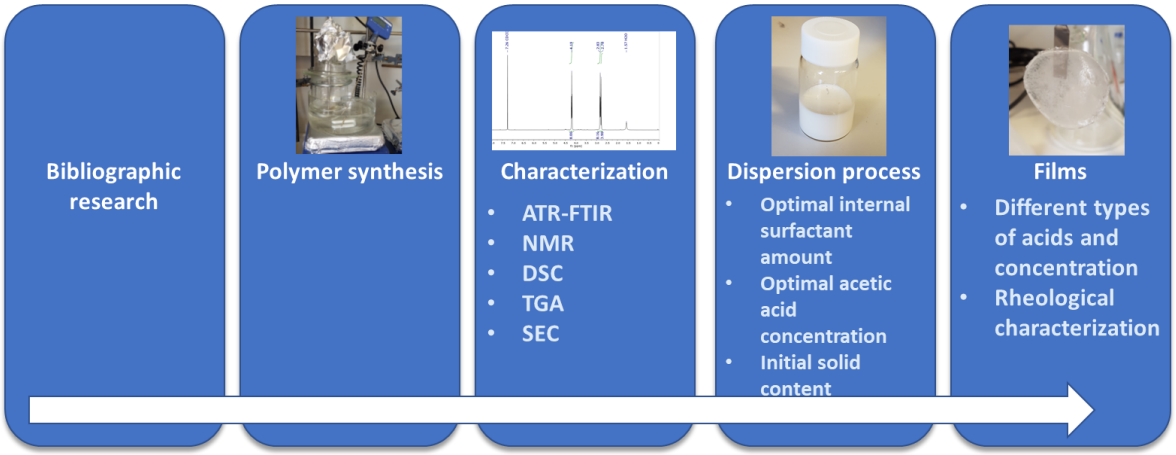
El objetivo de este trabajo es obtener dispersiones de poliuretanos dispersables en agua libres de isocianatos a partir de polidimetilsiloxano terminado en grupos amino, carbonato de diglicerol, el cual es un compuesto renovable, y un carbonato cíclico de 8 miembros ((bis)-N8C) mediante inversión de fase usando para ello el proceso de la acetona. Primero se sintetizaron en masa polímeros con diferentes relaciones de los carbonatos de 5 y 8 miembros sin usar ningún catalizador en el proceso. Estos polímeros se caracterizaron mediante FTIR, RMN ^{1}H y ^{13}C, TGA, DSC y SEC-GPC. Después se hicieron experimentos para determinar los parámetros óptimos para la realización de las dispersiones de los polímeros previamente sintetizados. Se hicieron experimentos usando diferentes concentraciones de ((bis)N-8-C), variando la concentración de carga, y la cantidad inicial de PHU en acetona con el objetivo de comprobar como afectaban estos factores al tamaño de partícula y su distribución obteniéndose dispersiones estables con un tamaño de partícula de alrededor de 200 nm usando una relación 70-30 de los carbonatos de 5 y 8 miembros respectivamente. Entonces se hicieron films a partir de las dispersiones mediante entrecruzamiento iónico mezclando las dispersiones estables con diferentes ácidos carboxílico para comparar la mejora de las propiedades mecánicas entre los diferentes ácidos y la cantidad usada de los mismos. Las propiedades autorreparables de los materiales obtenidos fueron evaluadas mediante reometría plato-plato y microscopia óptica.

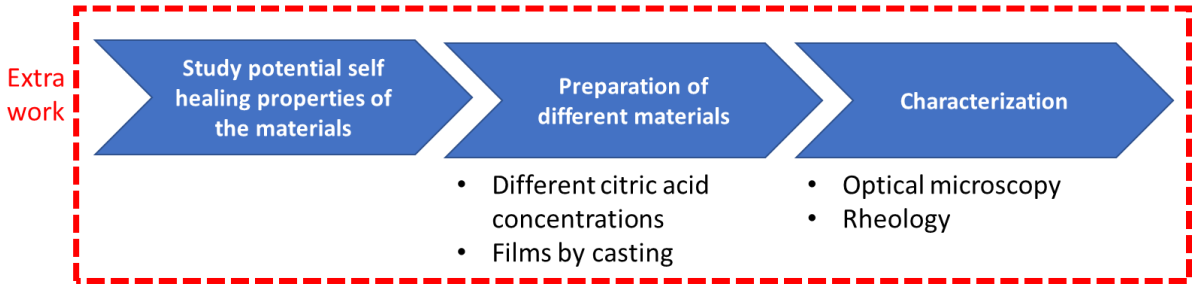
Index

1. OBJECTIVES

The aim of this project is to synthesise a new class of polymers named isocyanate free water-dispersible poly(hydroxyurethanes)s, to analyse its properties, learn how to improve them and to find potential applications. Polyurethanes are one of the most used class of polymers being the 5% of total polymer production in weight. They are used in wide a range of application from adhesives to coatings due to their high versatility. However, these materials have also some synthesis difficulties, being the main one the necessity of use isocyanates in the polymerization process which are highly toxic compounds. In addition, waterborne polyurethanes have gained a lot of attention in the last 20 years because of new regulations on volatile organic compounds (VOC)s and environmental global awareness of their effects. In this project a new way to synthesise polyurethanes is studied avoiding the use of isocyanates and getting water dispersible polyurethanes.

One of the most studied approach to synthesize NIPUs is the step-growth polyaddition of 5-membered cyclic carbonates with diamines which results in poly(hydroxyurethane)s (PHU)s. Among the different routes to prepare this polymer we selected the step polymerization of a 5-membered cyclic carbonate (DGC,) and an 8-membered cyclic carbonate and amine-terminated PDMS. To study the optimal conditions to achieve stable water dispersion we did different dispersions experiments changing the 5 to 8-membered cyclic carbonates ratios, acetic acid concentrations and initial solid content. We were especially interested in achieving stable dispersion, to know how the previous factors, affect to stability of the different dispersions, particle size and particle size distribution. Films were then made using the previously obtained stable dispersion and to improve the mechanical properties these dispersions were mixed with different acids to create supramolecular networks and evaluate how the functionality of the acid and the amount used can lead to a material with different characteristics. Finally, as an extra work we evaluated the formation of a supramolecular networks for preparing materials with self-healing properties.


Bibliographic research
Polymer synthesis
Characterization
• ATR-FTIR
• NMR
• DSC
• TGA
• SEC
Dispersion process
• Optimal internal surfactant amount
• Optimal acetic acid concentration
• Initial solid content
Films
• Different types of acids and concentration
• Rheological characterization


Extra work
Study potential self healing properties of the materials
Preparation of different materials
Characterization
• Different citric acid concentrations
• Films by casting
• Optical microscopy
• Rheology

2. INTRODUCTION

2.1. Waterborne polyurethanes (WPU)

Owing to stricter regulation on volatile organic compounds (VOC)s provided by the European Union and United States Environmental Protection Agency (EPA) and environmental care awareness, waterborne polyurethanes (WPU) have gained a lot of consideration in the last decades compared to solvent-borne polyurethanes. WPUs are versatile and environmentally friendly material that have been used successfully for years in many applications such as coatings or adhesives for numerous types of substrates like wood metal or plastic[1]. However, it is not possible to synthesize these polymers by conventional synthetic methods like emulsion or suspension polymerization because of the high reactivity of isocyanate with water leading to a non-desirable chemical reactions and products[2].

In the last decades many processes have been developed to achieve aqueous polyurethane dispersion such as the prepolymer mixing process and miniemulsion polymerization[3–5]. However, one of the most successful way to produce WPU is based on the acetone process which consists in a three-step procedure[6–8]. In the first step WPU hydrophilic and potentially charged groups are incorporated into the backbone of the polymer. These charged moeities are usually diols with ionic groups such as carboxylate, sulfonate or quaternary ammonium salt. Depending on the type of internal emulsifier obtained, we talk about cationic or anionic WPU. For example, one of the most common way to obtain WPU is by the addition of a diol containing acidic groups like 2;2-bis(hydroxymethyl) propionic acid (DMPA) that is deprotonated by a base such as triethylamine[9,10]. However, good results have been also reported in literature using cationic groups such as *N*-methyldiethanolamine. In the second step water is added to the PU/acetone mixture. In the last step the acetone is removed obtaining an aqueous polyurethane dispersion.

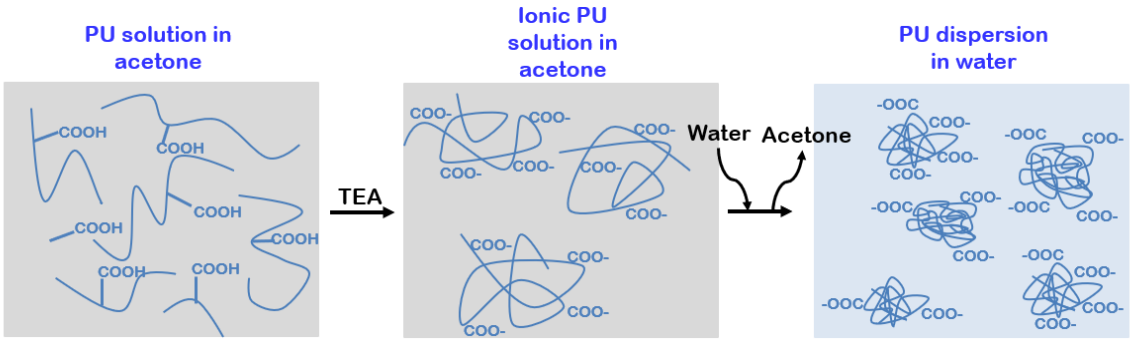


Figure 1. Scheme of acetone process for a system containing carboxylate groups in the main backbone.

The polymer particles are formed in the second step of the acetone process when the water is added and despite that the mechanism is not completely known, it is usually divided in three different stages. In the first stage a certain amount of water is absorbed homogeneously due to the hydrated ionic groups. The second step takes place when the system cannot absorb more water, at this moment the mixture becomes turbid as a result of the formation of particles by phase inversion[11]. During the phase inversion, the hydrophilic groups of the previously incorporated ionic groups occupy the polyurethane-water interphase as shown in the **Figure 1**. At this point further, water addition causes a restructure of the water polymer interface forming spherical polymer particles inside the water phase.

2.2. Non-isocyanate polyurethanes (NIPUS)

The most common chemical reaction for the synthesis of polyurethane is based on the polyaddition reaction between a diisocyanate and a diol. However, isocyanates are very toxic molecules which have been involved, among others, in the Bhopal disaster, the most tragic accident in chemical industry. With the global awareness about the toxicity of isocyanates, there is an emerging interest to find environmentally friendlier approaches towards non-isocyanate polyurethanes (NIPUs).

In the last decade advances in this field led to the development of a number of isocyanate-free processes. The four most studied pathways towards NIPUS as shown in **Figure 2.** They include: (1) step growth polyaddition of cyclic dicarbonates and diamines, (2) step-growth polycondensation of linear activated dicarbonates and diamines, (3) step growth polycondensation of linear activated carbamates and diols, and (4) ring opening polymerization (ROP) of cyclic carbamates[12,13].

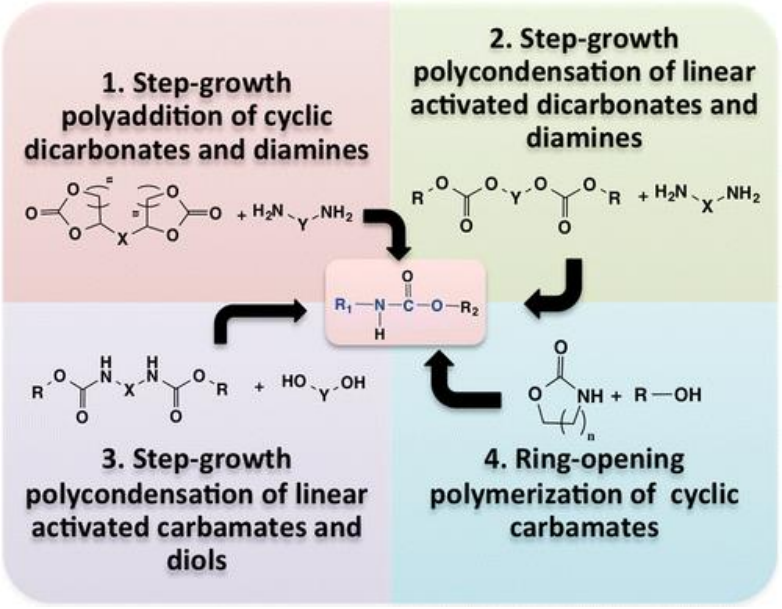
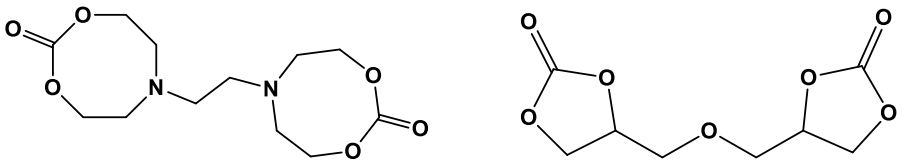


Figure 2. Most studied synthetic pathways to obtain NIPUs**.**

However, the first synthetic route represents the most promising and studied one. As such, we based this work on the synthesis of NIPUs using 5 and 8-membered cyclic dicarbonates. On one hand, 5-membered cyclic dicarbonates possess the advantage of being easily synthesized from the chemical insertion of CO_2 into naturally abundant epoxides but suffer from their low reactivity[14]. On the other hand, recently, it has been demonstrated that higher ring-sized cyclic dicarbonates are more reactive in comparison to the well-used 5-membered ones. In particular, 8-membered cyclic dicarbonate bearing nitrogen has shown to be readily active at room temperature for the synthesis of polyhydroxyurethane, with a catalytic activity 5 times greater than 5-membered ones[15]. Interestingly, the presence of nitrogen in its

backbone confers to it an interesting possibility to perform as an internal emulsifier for the preparation of water-borne polyhydroxyurethane (WDPHU).



(Bis) N-8-C **DGC**

Figure 3. Chemical structure of 5-membered cyclic carbonate, diglycerol dicarbonate (DGC), and 8-membered cyclic carbonate ((bis)N-8-C) used in this work.

2.3. Self-healing Polymers

One of the most interesting thing of natural tissues is their ability to repair on their own the damaged structures[16]. Nowadays researchers are trying to replicate this concept in different kind of materials like metals, ceramics or polymers[17]. Among these, the best result has been reported using polymers due to their physical properties and functionalization easiness[18]. In general terms self-repairing is defined as the ability of certain materials to repair the damage in their structures by itself without losing physical properties.

There are many strategies to achieve this property in polymeric materials and, in general, they are classified according to the necessity of external stimulus or the absences of them to initiate the reparation. A prerequisite of the healing process is the generation of a mobile phase which will allow the diffusion of active elements of the damaged surface in every case[19]. Supramolecular polymers are polymer networks based on reversible bonds and are well known for their self-healing properties due to highly directional and reversible non-covalent interactions. Different types of supramolecular interactions have been reported including ionomers and hydrogen bonding[20].

Ionomers are a class of polymer which contains a certain amount of acid groups in the salt form. Usually the ion content less than 15 mol% and repair process takes place by

electrostatic interactions between different polymer chains. Hydrogen bonding consist in non-covalent interaction between neutral organic molecules that contains atoms with different electronegativity attached to hydrogen. Despite of not being the strongest non-covalent interactions this type has been reported in the literature as responsible of many materials self-healing and self-assembly properties in low Tg polymers[21].

In this work we aimed:

1) To copolymerize the DGC, (bis) N-8-C, and amino terminated PDMS to obtain an isocyanate free WPHU. PDMS is used due to its unique properties such as hydrophobicity, low surface energy, biocompatibility, transparency, high thermal stability, non-flammability or great flexibility. Lots of researchers have used PDMS as a soft segment to combine the advantages of PDMS with those WPU to its properties for example Wu et al. incorporated PDMS to counter the weak water-resistance of WPU by increasing its hydrophobicity for coating applications. These polymers were used for the preparation of dispersions *via* the acetone process. The backbone of this polymers contains nitrogen atoms, coming from the 8-membered cyclic carbonate, that can be quaternized if an acid is added to the polymer solution in acetone.
2) To study the influence of different parameters on the dispersions stability.
3) To prepare films using carboxylic acids with different functionalities.
4) To assess the self-healing properties of the films.

3. EXPERIMENTAL PART

3.1 Materials

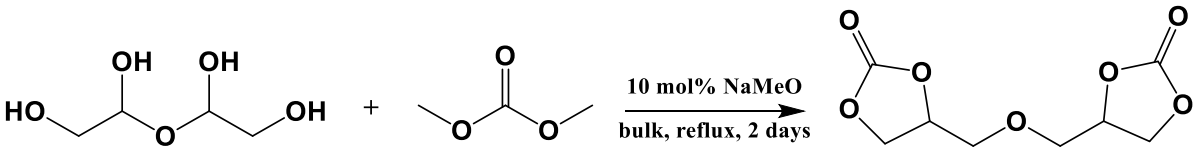
(bis) N-8-C and Diglycerol dicarbonate (DGC) were synthesized according to literature procedures[22,23]. Acetic acid (≥99%), citric acid (≥99.5%), butyric acid (≥99%), adipic acid (99%) and poly(dimethylsiloxane), bis(3-aminopropyl) terminated (amino-terminated PDMS) with a molecular weight around 2,500 g.mol^{-1} were purchased from Sigma Aldrich. Acetone

(technical grade) was purchased from Fisher. were purchased from Acros Organics. Deuterated solvents such as $CDCl_3$, DMSO-d_6 and $(CD_3)_2Cl$ were purchased from Euro-top. All materials were used without further purification.

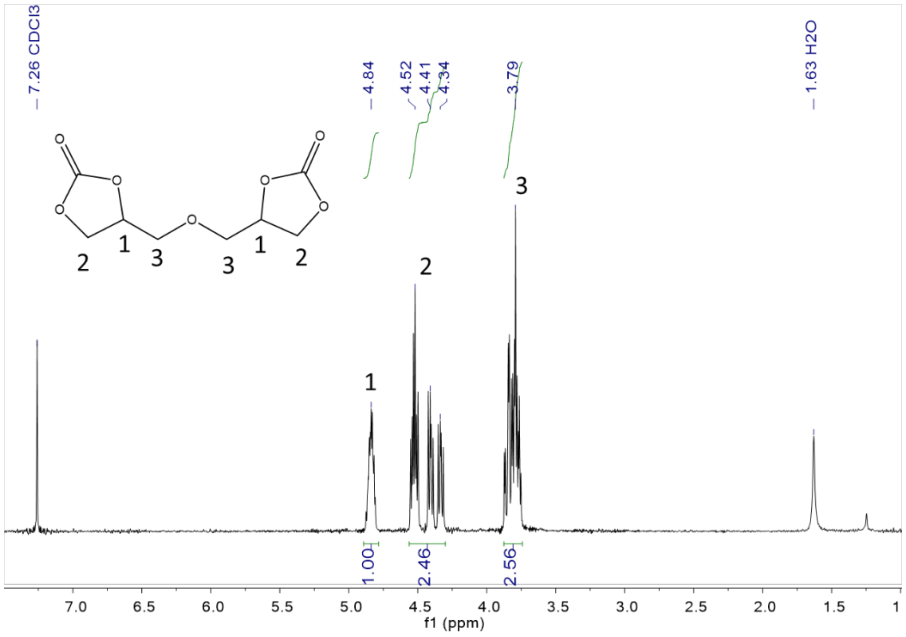
3.2 General procedure for the monomers and polymer synthesis

3.2.1. General procedure for the synthesis of diglycerol dicarbonate

In a typical procedure, 23.1759g diglycerol (0.2mol), 180.169g of dimethyl carbonate (2.0 mol) and 0.54g of sodium methoxide (0.01 mol) and acrylonitrile were introduced in a 1L flask. NaOme is a base which function is to catalyse the reaction and acrylonitrile is the solvent. The reaction was done in a N_2 atmosphere and the mixture was stirred for 48 hours under reflux at 100ºC. The dilution obtained was concentrated at low pressure using a rotavap. After this the liquid was divided in 4 flask and methanol was added to precipitate the product in a bath of acetone(-78ºC). Finally, the precipitate was filtered and dried. ^{1}H NMR was performed to characterize the product.



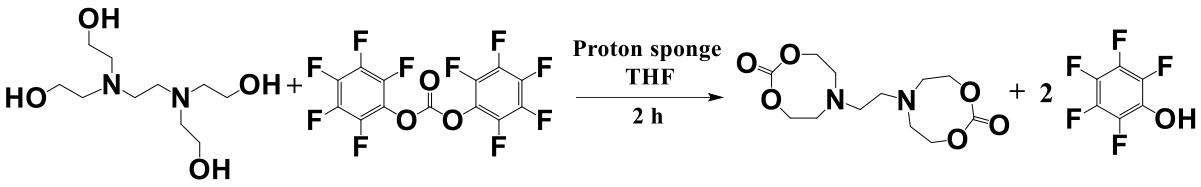
Reaction 1. Synthesis of DGC.



Spectrum 1. ^{1}H NMR of DGC in $CDCl_3$.

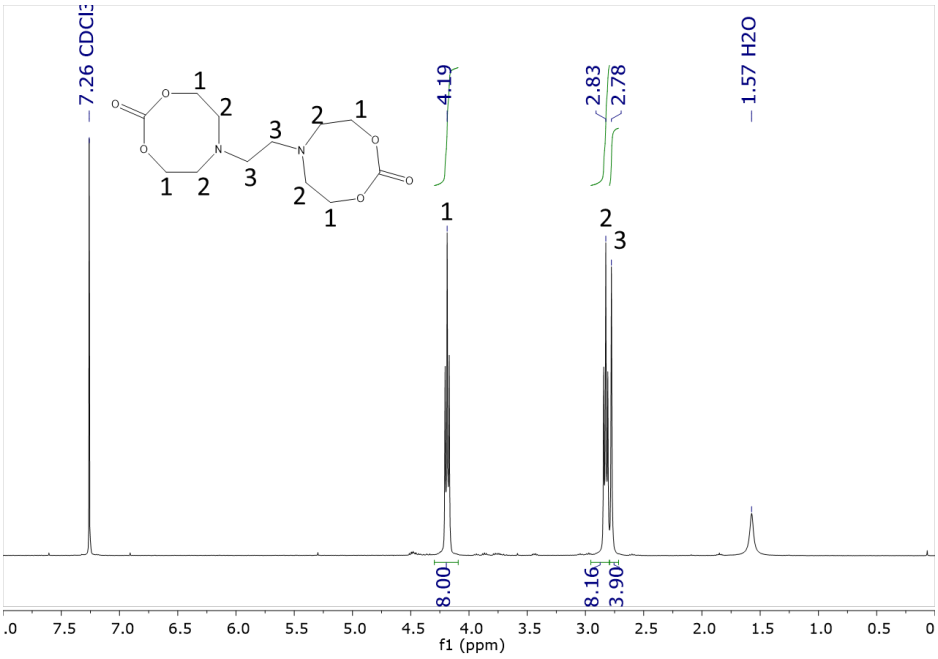
3.2.2. General procedure for the synthesis of (bis)N-8-C

In a typical procedure, a single neck round-bottom flask was charged with 5 g of N,N,N′,N′-tetrakis(2-hydroxylethyl)ethylenediamine (21.16 mmol), 2.247 g of 1,8-bis(dimethylamino)naphthalene (10.48 mmol), and 400 mL of anhydrous THF as solvent. An addition funnel was added to the round bottom flask and charged with 18,4g of bis(pentafluorophenyl)carbonate (46.69 mmol) and 50 mL of anhydrous THF. bis(pentafluorophenyl)carbonate and THF mixture were added dropwise in the round bottom and stirred for two hours. Then the reaction mixture was concentrated using a rotavap under reduced pressure at 30ºC and then is treated with excess ether (around 300mL). Finally, the mixture as placed in the fridge overnight and the precipitated powder was filtered in a Büchner under vacuum and dried.



Reaction 2. Synthesis of (bis)N-8-C.

^{1}H NMR was performed to characterize the product.



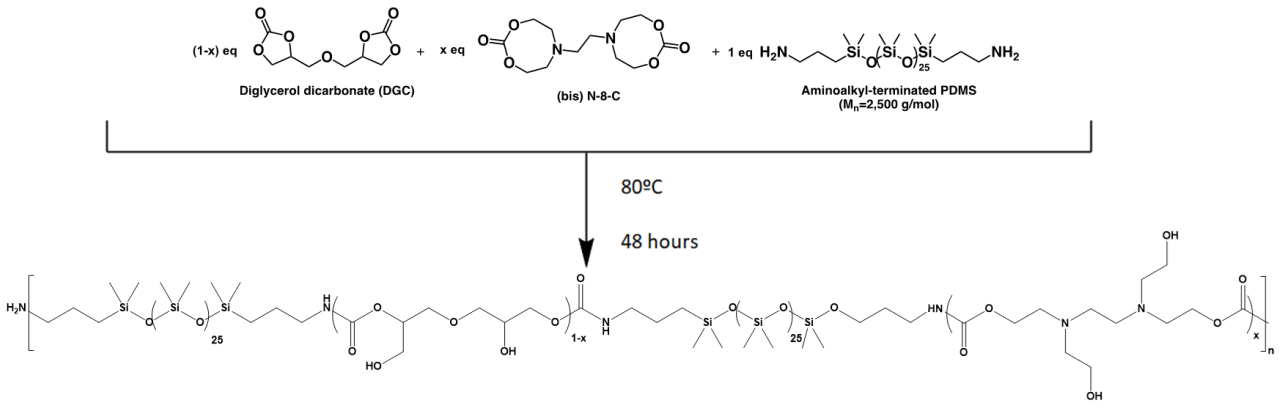
Spectrum 2. ^{1}H NMR of (bis)N-8-C in $CDCl_3$.

3.2.2. General procedure for the synthesis of poly(hydroxyurethane)s

In a typical procedure (**Table 1**), diglycerol dicarbonate ((1-x) equiv.), (bis) N-8-C (x equiv.) ($0 \leq x \leq 0.5$) and aminoalkyl-terminated PDMS (1 equiv., 0.015 mol, 37.5 g) were mixed together in a 250-mL flask equipped with a mechanical stirrer (200 rpm). The polymerization reaction was conducted at 80 °C for 48 hours.

Table 1. Reagent concentrations employed in the synthesis of polyhydroxyurethanes.

WDPHU	DGC (mol)	DGC (g)	PDMS (mol)	PDMS (g)	PDMS (mL)	(bis)N-8-C (mol)	(bis)N-8-C (g)
1	0,0140	3,054	0,0140	35,00	35,71	0,00000	0,000
2	0,0135	2,945	0,0150	37,50	38,27	0,00150	0,432
3	0,0120	2,625	0,0150	37,60	38,36	0,0030	0,867
4	0,0105	2,291	0,0150	37,50	38,27	0,00450	1,297
5	0,0090	1,963	0,0150	37,50	38,27	0,00600	1,730
6	0,0075	1,636	0,0150	37,50	38,27	0,00750	2,162



Reaction 3. Synthesis of poly(hydroxyurethane) from DGC, (bis)N-8-C and PDMS diamine.

3.3 Dispersion process

The dispersion process was carried out under different experimental conditions to study the effect of 3 different parameters (internal surfactant concentration, charge concentration and initial solid content). In a typical procedure a 250 mL jacketed glass reactor equipped with a mechanical stirrer was fed with 5 g of PHU and 5 g of acetone. After this a known amount of acetic acid was added to quaternize the nitrogen atoms in the polymer backbone and the stirrer was set at 250 rpm. Once the polymer was completely dissolved in acetone, water was added using a pump at 1 mL per minute. Then, the dispersion was let stirring a few minutes and is divided in two samples. While the acetone of one of the samples was removed under low

pressure by means of rotatory evaporator, acetone was let in the other sample for particle size and particle size distribution comparison.

To evaluate the effect of internal emulsifier, dispersions were made under the same conditions (5 g of polymer, 50% initial solid content, 7,5 mL of water) using copolymers with different DGC/(bis) N-8-C ratios. In all cases excess acetic acid was used to ensure complete quaternization of the nitrogen in (bis)N-8-C.

To analyze the effect of the charge concentration on the particle size we performed the dispersion using the 70/30 DGC/(bis)N-8-C mole ratio polymer because lower particle size and stable dispersions were achieved with this material. The general procedure was applied, the initial solid content was 50%, the volume and the acetic acid amount used is a range of 25-125 mol % acetic acid per quaternizable nitrogen.

The effect of the initial solid content was evaluated doing dispersion following the general procedure with 70-30DGC/(bis)N-8-C polymer with 125 mol% acetic acid with regard to the mole of quaternizable nitrogen. The solid content covered in this experiment range from 40 to 60 wt%.

3.4. Procedure for the film preparation

The films were prepared using the dispersion made of the poly(hydroxyurethane) composed of 70 mol% DGC and 30 mol% (bis)N-8-C, 50 wt% initial solid content and 75 mol% acetic acid with regard to the mole of quaternizable nitrogen. First a known amount of carboxylic acid was added to 4 g of dispersion. The solution was stirred for 40 minutes until compete dissolution of the acid and then transferred into a Teflon mold. Then the films were dried 48 hours at room temperature and 48 hours at 30ºC in the oven under vacuum.

3.5. Characterizations methods

^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR). NMR spectra were recorded at room temperature with Bruker Avance DPX 300 or Bruker Avance 400 spectrometers at 300.16 and 75.5 MHZ for the ^{1}H and ^{13}C spectra respectively using deuterated acetone, DMSO and chloroform as solvents. The NMR chemical shifts were reported as δ in parts per million (ppm) relative to the traces of non-deuterated solvent (e.g. δ = 2.50 ppm for d_6-DMSO or δ = 7.26 for $CDCl_3$). Data were reported as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (J) given in Hertz (Hz), and integration. Normal ^{1}H was used to characterise every monomer and reactant used. Quantitative ^{1}H NMR spectras were carried out to confirm the ratio of different monomers in the polymer and to ensure that the amount of acid in the films was the expected one and ^{13}C NMR was used to characterize the polymer structure.

Fourier transformation infrared spectra (FT-IR). FT-IR spectras were obtained by FT-IR spectrophotometer (Nicolet 6700 FT-IR, Thermo Scientific Inc., USA) using attenuated total reflectance (ATR) technique (Golden Gate, spectra Tech). Spectra were recorded between 4000-525 cm^{-1} with a spectrum resolution of 4 cm^{-1}. All spectra were averaged over 10 scans.

Size exclusion chromatography (SEC). SEC was performed in at 30º C as eluent using a Waters chromatograph equipped with four 5 mm Waters columns (300 mm "x" 7.7 mm) connected in series with increasing pore sizes. Toluene was used as a marker. Polystyrenes of different molecular weights, ranging from 2,100 g mol^{-1} to 1,920,000 g mol^{-1}, were used for the calibration.

Thermogravimetric analysis(TGA). A thermogravimetric analyzer (TGA-Q500 V20, 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°C to 950°C at a heating rate of 10°C/min under N2 atmosphere (50mL/min).

Differential Scanning Calorimetry (DSC). A differential scanning calorimeter (DSC-Q2000, TA Instrument Inc., USA) was used to analyze the thermal behavior of the samples A total of 6-8 mg of samples were first scanned from -160°C to 100°C at a heating rate of 10°C/min to eliminate interferences due to moisture. The samples were then cooled to -160°C to remove the thermal history of the samples and reheated to 100°C at 10°C/min. The glass transition and melting temperatures were calculated from the second heating run.

Dynamic Light Scattering (DLS). The particle diameter (Dp) and particle size distribution (polydispersity) of the PHU dispersions were measured by Dynamic Light Scattering (DLS) using a Zetasizer-Nano S from Malvern operating with a 4 mW He–Ne laser (633 nm wavelength) and a fixed detector angle of 173 (non-invasive backscattering geometry NIBSTM) and with the cell holder maintained at constant temperature by means of a Peltier element. The samples were diluted with deionized water before the measurements to avoid multiple light scattering. The final value was an average of three measurements.

Transmission Electron Microscopy (TEM). TEM was performed using a Philips Tecnai 20 microscope working at accelerating voltage of 200 kV. Diluted samples of the dispersions (0.005-0.01 wt %) were prepared.

Rheometry measurements. Small-amplitude oscillatory experiments were performed in a stress-controlled Anton Paar Physica MCR101 rheometer and the experiments were carried out using 25 mm parallel plate geometry. All the experiments were conducted in linear viscoelastic conditions for the studied temperature range (strain = 0.5 % and frequency 1 Hz).

Optical microscopy. Scratch-healing measurements were carried out at different temperatures using an optical microscope. The scratches were created using a feather disposable scalpel no. 21 (stainless steel). The microscopy glass slides were positioned in a microscope hot stage (Linkam Scientific Instruments, Ltd.). The system was then placed under

the focus of a bright-field optical microscope (Zeiss Axio Scope A1 with 10X objective and tungsten-halogen bulb).

4 Results and discussion

4.1. Synthesis and characterization of the poly(hydroxyurethane)s

To evaluate the optimum polymer formulation for the dispersion experiments and the effect of degree of neutralization on the final polymer particle size, a series of isocyanate-free poly(hydroxyurethane)s were synthesized using different 5- to 8-membered cyclic carbonates ratios as described in the experimental methods. Polymerization reactions were performed in bulk without catalyst under mechanical stirring at 80°C for 48 hours. The polymer structure was characterized using FTIR, ^{1}H and ^{13}C NMR, TGA, DSC and SEC.

The reaction completion was first assessed by FTIR (**Figure 4**). This technique allows us to see the different groups in a molecule, so we expected the absence of the cyclic carbonates characteristic peaks and the presence of the polymer urethane groups. As observed, the cyclic carbonates band centered at 1795 (DGC) and 1725 cm^{-1} ((bis) N-8-C) disappeared and signals attributed to the newly formed urethane group could be observed at 1726-1702 (C=O stretching vibration) and 1532 cm^{-1} (N—H bending vibration) This changes in the recorded spectrums confirms the complete disappearance of confirms that the reaction was complete successfully. PDMS bands are also in the spectra which means that the PDMS has react as expected and is in the polymer backbone. Characteristic siloxane bands of PDMS diamine were observed at 2962 cm^{-1} (C—H stretching of CH_3) and in the fingerprint region at 1257 cm^{-1} (CH_3 symmetric deformation of Si—CH_3), 1074 and 1010 cm^{-1} (Si—O—Si stretching vibration) and 785 cm^{-1} (Si—C stretching vibration and CH_3 rocking of Si—CH_3).

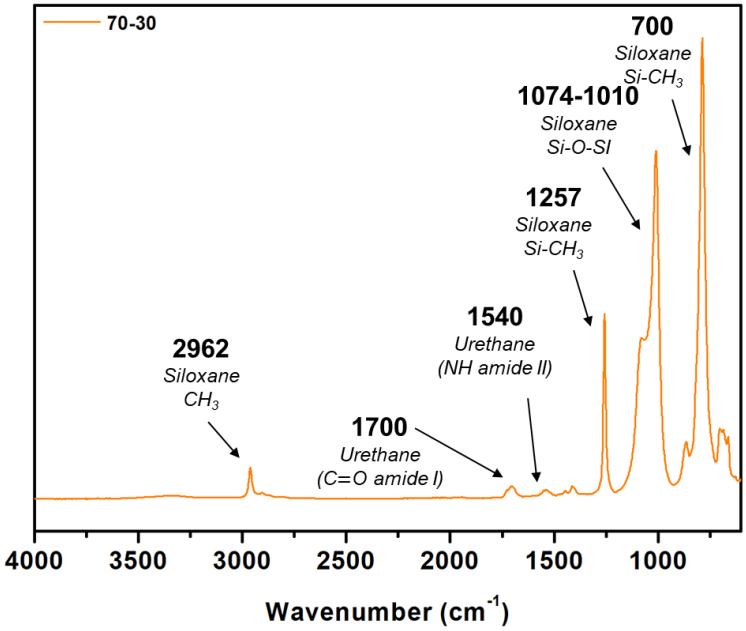
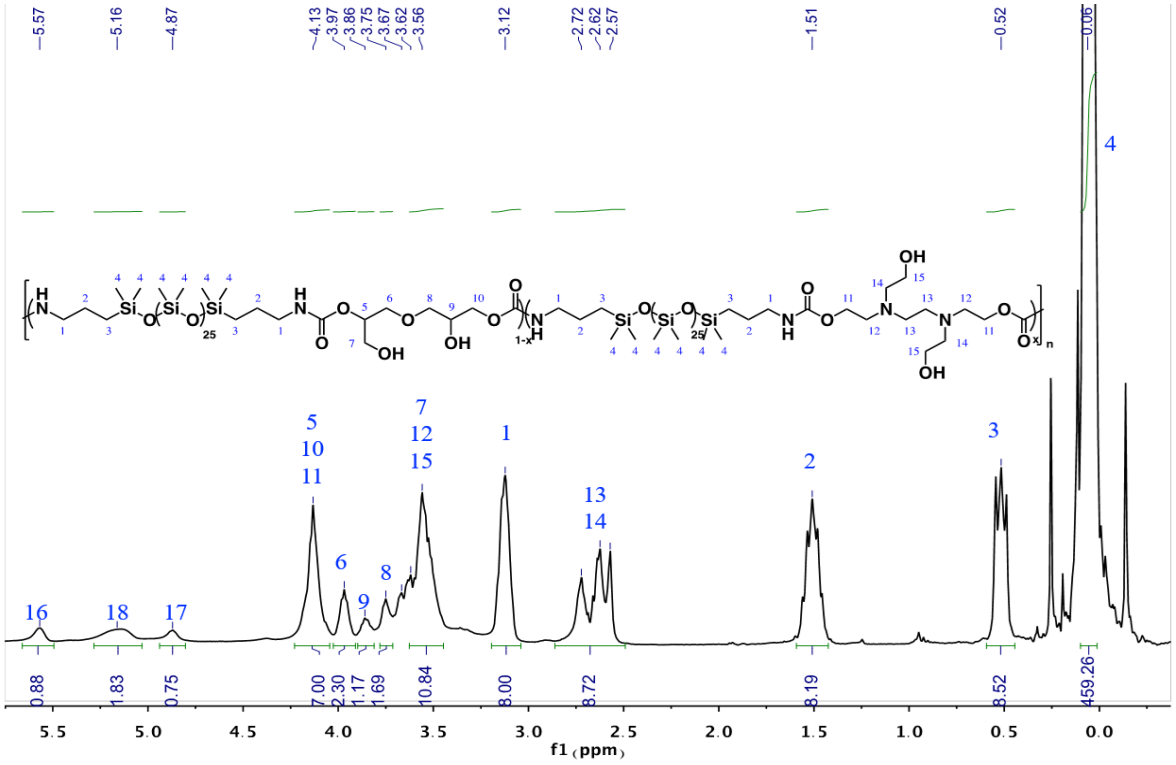


Figure 4. FTIR spectrum of the polyhydroxyrethane obtained from the polyaddition of DGC (0.7 equiv.), (bis)N-8-C (0.3 equiv.) and PDMS diamine (1 equiv.).

In addition, the formation of urethane was also confirmed by NMR spectroscopy (**Spectrum 3**). When the cyclic carbonates reacted with the amino-terminated PDMS. Moreover, the formation of urethane was also confirmed by means of NMR. The cyclic carbonates reacted with the terminal amino group of the PDMS and characteristic signals can be observed on ^{1}H-NMR spectra. More precisely the signals of the methylene protons in the DGC at 4.96-4.91, 4.52 and 4.27-4.20 ppm gradually disappeared while new signals related to the formation of urethane group appear at 4.13-3.97, 3.86, 3.75, 3.67-3.56, 3.12 and 2.72-2.57 ppm. In the carbonyl region we could observe in ^{13}C-NMR a peak at 156.91 ppm which corresponds to the (–NH–(C=O)–O–) urethane carbonyl group forming from DGC and (bis) N-8-C.



Spectrum 3. ^{1}H NMR of the polyhydroxyrethane obtained from the polyaddition of DGC (0.7 equiv.), (bis)N-8-C (0.3 equiv.) and PDMS diamine (1 equiv.).

The molecular weight of the different obtained polymers was measured by size-Exclusion chromatography (SEC) in THF (**Figure 5**). As observed the obtained molecular weight are in the range of 13.7 to 21 kDa and the dispersity index was close to 2 a very common value in step growth polymerization.

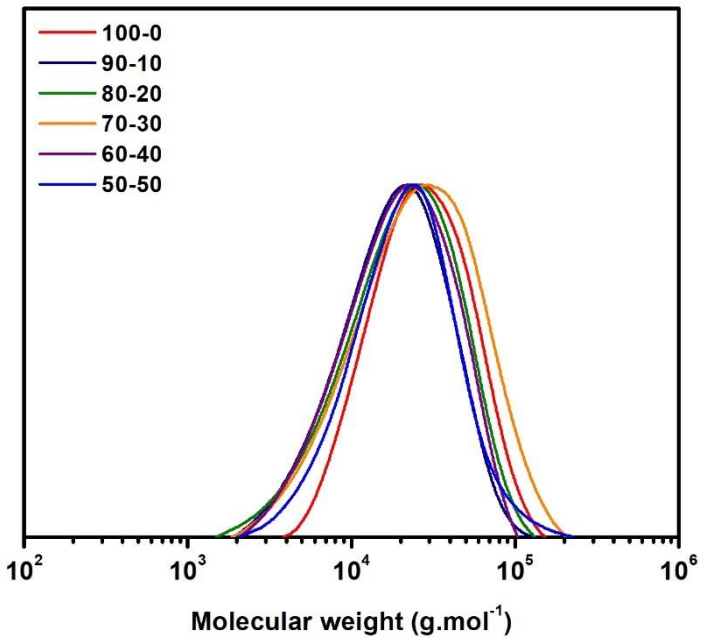


Figure 5. SEC chromatogram of the synthesized polyhydroxyurethanes.

Finally, the thermal properties of the polymer were measured by means of thermogravimetric analysis (TGA) as shown in **Figure 6** and differential scanning calorimetry (DSC) (**Figure 7**). As the obtained TGA curves showed, all polymers exhibit good thermal properties until 200 ºC.

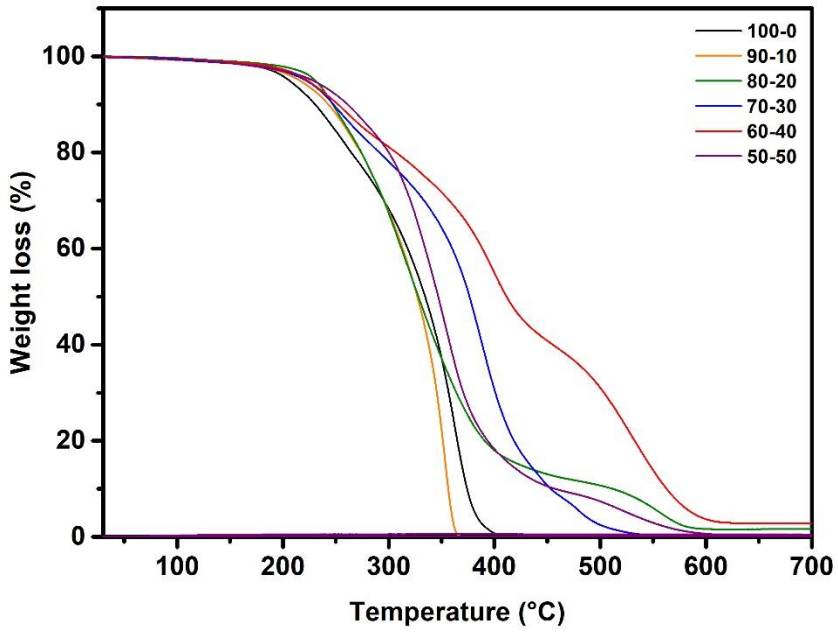


Figure 6 TGA thermogram of the synthesized poly(hydroxyurethanes).

Observing DSC measurements of the PHUs (**Figure 7**) we observed two glass transition temperatures Tg at -120ºC and -63ºC. The first one is characteristic of the PDMS chain and the second one corresponds to the soft segment of the PHU which are in the range of -54ºC to -63ºC depending on the ratio of (bis)N-8-C. Interestingly, increasing the (bis) N-8-C amount led to a decrease of the Tg of the soft segment. This can be explained considering a higher phase separation between the PDMS diamine soft segment and the hard segment composed of DGC and (bis) N-8-C. The obtained properties of each copolymer are summarized in **Table 2**.

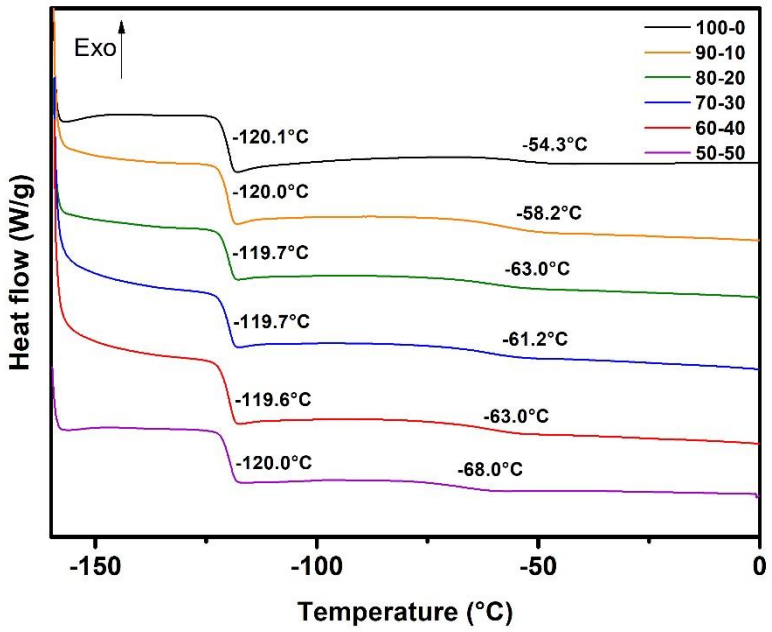


Figure 7. DSC thermogram of the synthesized poly(hydroxyurethanes).

Table 2. Summary of the water-dispersible poly(hydroxyurethane)s synthesized from DGC, (bis)N-8-C and PDMS diamine and their properties.

			DSC		SEC		DLS			
WDPHU	DGC (mol%) [a]	(bis) N-8-C (mol%) [a]	Tg_1 ºC [b]	Tg_2 ºC [b]	M_n (g/mol) [c]	Dispersity [c]	Dp (nm)[a]	PDI[d]	Dp(nm)[e]	PDI[d]
1	100	0	-120.1	-54.3	21,000	1.6	-[f]	-[f]	-[f]	-[f]
2	90	10	-120.0	-58.2	13,700	1.7	-[f]	-[f]	-[f]	-[f]
3	80	20	-119.7	-63.0	14,400	1.8	450.8	0.199	472.5	0.096
4	70	30	-119.7	-61.2	17,200	2.0	228.6	0.229	232.0	0.182
5	60	40	-119.6	-63.0	14,500	1.7	211.7	0.028	212.8	0.047
6	50	50	-1195	-63.0	16,000	1.7	-[f]	-[f]	-[f]	-[f]

[a] Calculated regarding the mole of PDMS diamine. [b] Data calculated from the second heating run of the DSC analysis. [c]Mn values were obtained by SEC in THF. [d] Particle sizes and particle size distributions were calculated using dynamic light scattering (DLS) in water/acetone mixture over 3 experiments. [e] Particle sizes and particle size distributions were calculated using dynamic light scattering (DLS) after acetone removal over 3 experiments. [f] Dispersions were unstable and resulted in precipitation.

4.2. Effect of various parameters on the properties of the dispersion

It is known that the particle size and particle size distribution of WPU are important parameters that are substantially affected by not only the amount of internal surfactant but also by the dispersion solid conditions such as solid content. Thus, in order to explain the effect of these parameters on the dispersion and test the effectiveness of the synthesized polymer to form stable water dispersions, the synthesized polymers were subjected to 3 dispersion experiments.

To determine the effect of the (bis) N-8-C molar ratio, which goes from 0 to 50 mol%, six dispersions were prepared under the same conditions. These dispersions were made dissolving 10 g of polymer in 10 g of acetone, adding excess acetic acid to ensure the full quaternization of nitrogen atoms per (bis) N-8-C nitrogen atom and adding 15 mL of water at 1 mL per minute. As can be observed the targeted solid content was 50 wt%. The phase inversion was carried out at 250 rpm and room temperature. After that, the obtaining dispersions were divided in two samples and for one of them, the acetone was removed by rotatory evaporation while the other was kept with acetone. Both samples were diluted with deionized water prior to particle sizes measurements by means of dynamic light scattering (DLS) to evaluate the effect of the acetone removal on the particle size. The final values given in the **Tables 3 and 4**.

Table 3. Particle sizes obtained before the removal of acetone at different monomers ratio.
[a]Precipitation occurred.

Effect of DCG/(bis) N-8-C ratio on particle diameter with acetone			
WDPHU	**DGC/(bis) N-8-C ratio**	**Particle size d(nm)**	**PDI**
6	50-50	-[a]	-[a]
5	60-40	266.53(±9.26)	0,028
4	70-30	202.13(±25,5)	0,229
3	80-20	461.65(±15,3)	0,199
2	90-10	-[a]	-[a]
1	100/0	-[a]	-[a]

Table 4. Particle size obtained after removal of acetone at different monomers ratio. [a]Precipitation occurred.

Effect of DCG/(bis) N-8-C ratio on particle diameter without acetone			
WDPHU	**DGC/(bis) N-8-C ratio**	**Particle size d(nm)**	**PDI**
6	50-50	-[a]	-[a]
5	60-40	257.6(±125)	0,047
4	70-30	204.2(±23.73)	0,182
3	80-20	472.5	0,096
2	90-10	-[a]	-[a]
1	100-0	-[a]	-[a]

As shown in the tables, no stable dispersion could be obtained using WDPHU1 and WDPHU2 because precipitation occurred, meaning that the internal emulsifier in the dispersion could not stabilize enough the particles and as every nitrogen are quaternized, this precipitation was not due to the charge effect. In the case of WDPHU1, as expected, without the presence of (bis) N-8-C, the internal surfactant, no stable dispersion could be obtained. An increase of (bis) N-8-C up to 20 mol %, yielded dispersion with a particle size of 462 nm, which provided stable dispersion in the presence of acetone. However, removal of acetone resulted in precipitation of the polymer. When the amount of internal emulsifier was incremented to 30 and 40 mol % (WDPHU4, WDPHU5), the particle size decreased and reached a plateau around 200 nm. In this range removing the acetone didn't lead to a high increment on the particle size. We expected similar result with WDPHU6, but, surprisingly this dispersion resulted in precipitation and the particle size exceeded the upper detection limit of the DLS machine. We can explain this phenomenon because of the presence of high charge concentration which led to repulsion and subsequently precipitation[24]. We could conclude that increasing the internal emulsifier decreased the particle size and enable to obtain more stable dispersion but at a certain concentration the effect was not beneficial. As a result, we determined that the optimal (bis) N-8-C amount was 30 mol% (WDPHU4) owing to the low particle size and the stability of the obtained dispersion.

Once we found the optimal dispersion composition, the effect of the acid concentration was studied. We made 6 different dispersion varying the amount of acid used in a range from

25-125 mol % of acetic acid in regard with the mole of nitrogen in the internal surfactant. The influence of the degree of the neutralization can be seen in **Table 5**.

Table 5. Particle size obtained using WDPHU4 treated with different acetic acid concentration.

Effect of the amount of acid used per quaternizable nitrogen on particle diameter					
Before removal of the acetone			After removal of the acetone		
Acetic acid (mol %)	Average particle size d(nm)	Average PDI	Acetic Acid (mol %)	Average particle size d(nm)	Average PDI
25	432.9 (±2.2)	0,773	25	489.5 (±17.5)	0.94
50	275.2 (±22.6)	0.289	50	266.4 (±22.0)	0.28
75	216.0 (±1.1)	0.134	75	212.2 (±0.9)	0.097
100	272.8 (±6.5)	0.256	100	247.8 (±0.7)	0.28
125	196.1 (±22.63)	0.148	125	188.8 (±15.8)	0.16

As observed, the particle size decreased as the acid concentration increased until the use of 100 mol% of acetic acid. Indeed, the addition of more acid does not quaternized more nitrogen.

It is known that the initial polymer content is a parameter that can have a great impact on the phase inversion process as a result in the final particle size. To study this variable, same types of experiments were carried out using WDPHU4 and 75 mol% of acetic acid to ensure the best dispersion conditions obtained until this point. The initial solid content was achieved dissolving 5 g of polymer before starting the inversion phase process in different amount of acetone (3.3 g, 5 g and 7.5 g acetone for 60 wt%, 50 wt% and 40 wt% initial solid content respectively). The obtained results are shown in **Tables 6 and 7.**

Table 6. Effect of the initial solid content on the particle size.

With acetone			
Solid content	Acetic Acid%	Average particle size d(nm)	PDI
40%	125%	267.3 (±30.97)	0.27
50%	125%	188.8 (±15.84)	0.15
60%	125%	193.2 (±5.37)	0.27

Table 7. Effect of initial solid on content on dispersions when the acetone is removed.

Without acetone			
Solid content	**Acetic Acid%**	**Average particle size d(nm)**	**PDI**
40%	125%	201.4 (±25.45)	0.31
50%	125%	196.1 (±22.62)	0.16
60%	125%	210.05 (±4.17)	0.14

On the range of initial solid content studied, no significant differences on the particle size once the acetone was removed can be observe. In addition, the morphology of 70-30 dispersion was assessed by TEM. As we can see in **Figure 8**, we obtained spherical particle with a diameter around 200 nm with similar sizes for each particle.

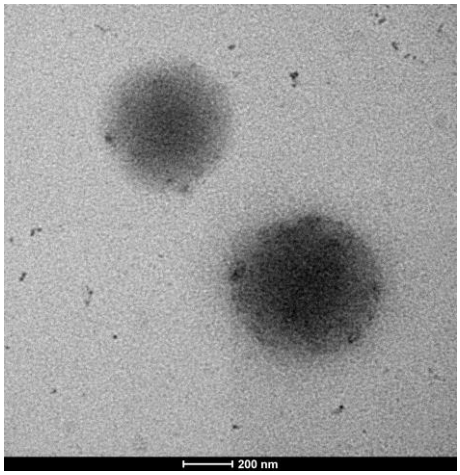


Figure 8. TEM picture of the dispersion obtained from WDPHU4.

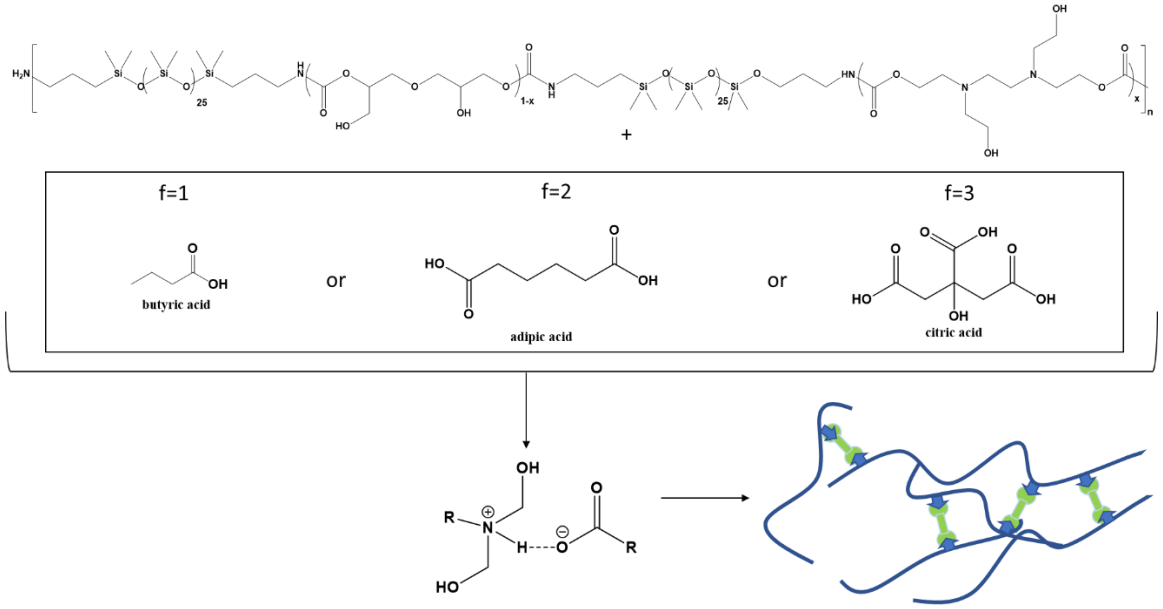
4.3. Preparation of WDPHU films

PDMS confers to our polymer an incredible low glass transition which leads to poor mechanical properties consequently hindering the rheological behavior of the films casted for the optimal dispersion. As expected the prepared material flowed as characterized by G" ≫ G' at temperatures as low as -10ºC in rheological parallel plate measurements.

Comin and coworkers have recently shown that supramolecular polymers can be easily prepared by blending PU bearing tertiary amine groups with multifunctional carboxylic acids[25]. The resulting ionic and hydrogen bonding interactions created using this method have shown to enhance the overall mechanical properties of the materials. Similarly, we mixed the dispersed polymer with different acids in order to see the effect of the number of carboxylic groups in the improvement of the mechanical properties. The multifunctional carboxylic molecules can attach to many nitrogen atoms of the polymer backbone leading to a supramolecular network that improves significantly the mechanical properties. In addition, we expected that the formation of hydrogen bonds could improve even further the mechanical properties. Moreover, the reversible character of these bonds can provide different properties to the material such as self-healing properties. On account of these facts we decided to investigate the post-synthetic ionic crosslinking of our materials to overcome the issue rendered by PDMS. We decided to investigate carboxylic acids which functionalities vary from 1 to 3, *i.e.* butyric acid (monofunctional), adipic acid (difunctional) and citric acid (trifunctional).

4.4. Supramolecular chemistry using carboxylic acids

To improve the material mechanical properties, we decided to create supramolecular networks as described in **Scheme 3** using different types of acids and amounts to see the effect of both parameters on the films. First equimolecular amount of the carboxylic acids respect to the mole of nitrogen were added to 4 g of the optimal dispersion at room temperature. The films were then casted in a Teflon mold before drying, first 48 hours at room temperature and secondly in the oven at 30ºC under vacuum.



Scheme 1. Formation of supramolecular ionic structure from polyhydroxyurethane.

The three films were completely transparent indicating homogeneous incorporation of the carboxylic acids. When immersed in water the films turned white and completely opaque confirming the successful incorporation of the carboxylic acid. This change came from the precipitation of the carboxylic acid which provoked disruption of the ionic interactions.

Figure 9. Picture of the film after immersion in water for 48 hr showing the precipitation of carboxylic acid.

The structure of the non-covalent networks was analyzed by FTIR and NMR spectroscopies. Comparing the FTIR of the polymer with the material obtained, we can observe the effect of the proton transfer reactions between the acid moieties and the nitrogen groups. This was described by Aboudzadeh et al[26], who studied the rheological behavior of supramolecular ionic networks based on multifunctional carboxylic acid and alkyl amine. Bands associated to hydrogen-bonded carbonyl groups and carboxylate anions were observed in the range of 1620 cm^{-1} and 1550 cm^{-1}. In our material, a broad band corresponding to the asymmetric COO^- carboxylate group overlapping with the N-H bending vibration can be observe at 1575 cm^{-1}, this signal was previously reported at 1532 cm^{-1}. The band of the symmetric carboxylate moiety appeared at 1404 cm^{-1} and we could observe the formation of a broad OH- stretching vibration ban at 3400 cm^{-1}. In the case of free acids this band is well defined and not so broad meaning that the acid is forming ionic bonds with the nitrogen atoms. Focusing in the urethane carbonyl stretching vibration band which is at 1726-1702 cm^{-1} a significant increment in the intensity can be observed when the acids are incorporated indicating the presence of hydrogen-bonded carbonyl groups.

In order to see the differences before and after the creation of supramolecular networks, the films were also characterized by ^1H NMR in deuterated acetone instead of $CDCl_3$ due to solubility issue. As we can see of the spectra, characteristic proton of citric acid appeared at 2.9 ppm and on account of the relation between the area of these peaks with the area of polymer peaks, we were able to confirm the amount of acid used in the citric acid amount experiments in **Figure 10.**

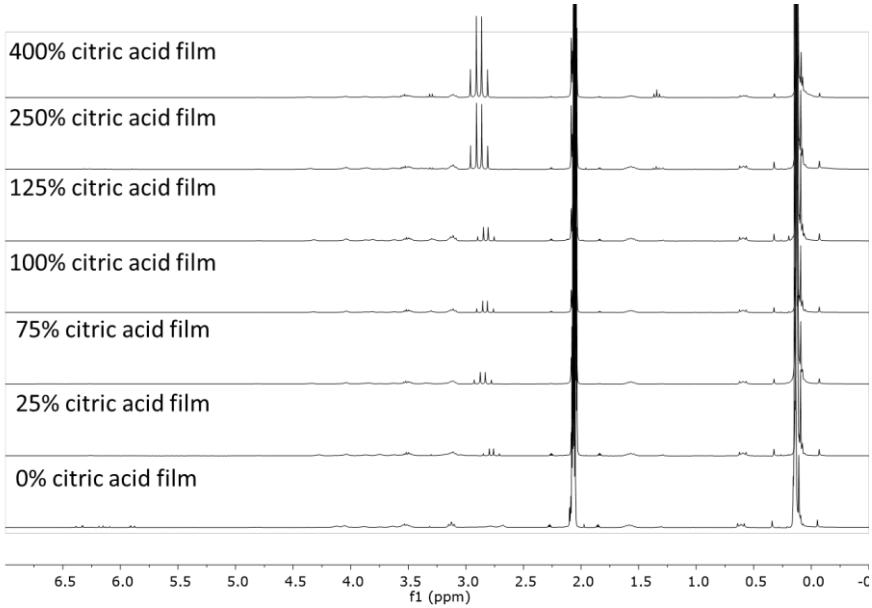


Figure 10. ^{1}H NMR of the films obtained with different citric acid concentration.

Exanimating these signals, we observed no trace of the acetic acid used in the dispersion process while we can see the peaks of the other acids, probably due to ionic exchange between acetic acid and excess carboxylic acid which allowed the acetic acid to evaporate during the drying process (**Figure 11**). Due to the formation of carboxylic ion, COO^-, as expected we could not see carboxylic protons but a small peak around 6.6 ppm due to the protonation of the tertiary amine. Also, we observed that the protons of the methylenes groups adjacent to the quaternary nitrogen atoms shift from 2.8 to 3.32 ppm.

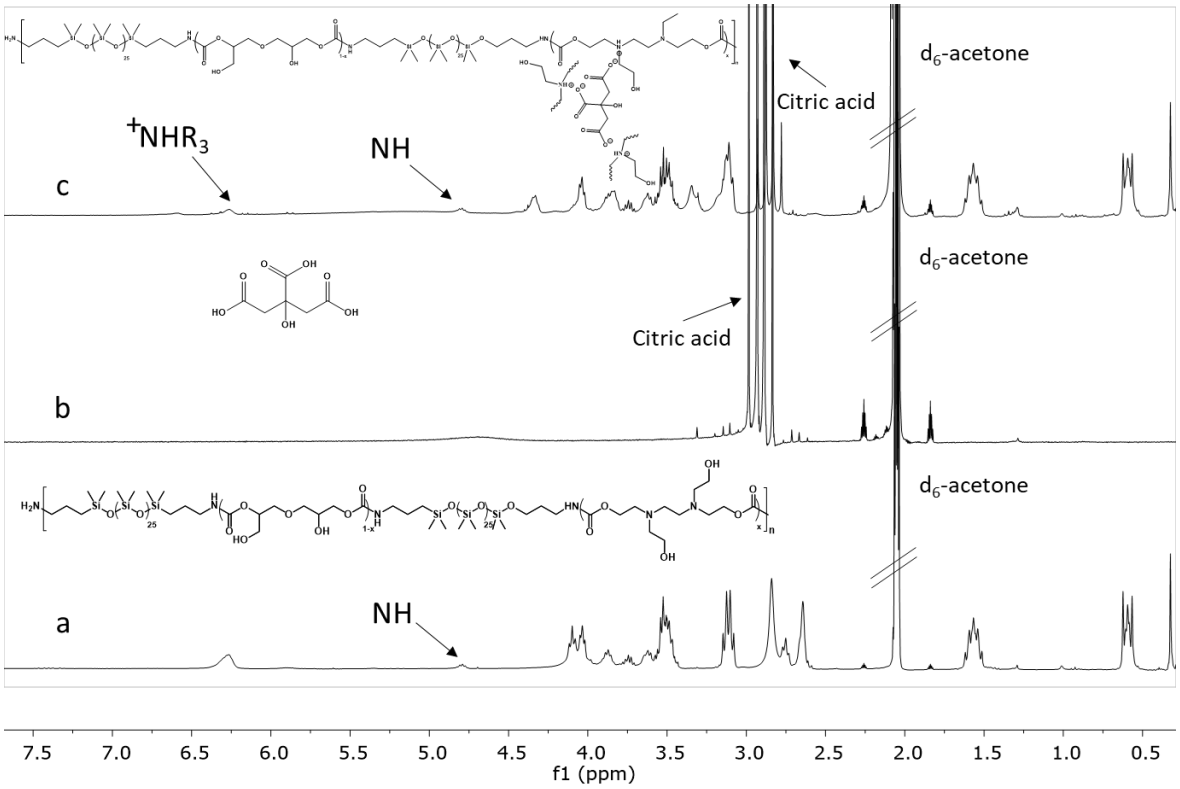


Figure 1. [1]H-NMR spectra of (a) WDPHU70-30 (b) citric acid and (c) WDPHU treated with 100% citric acid film in deuterated acetone.

Comparing the differences in both characterization techniques between the polymer and the supramolecular films we can conclude that we created a supramolecular network composed by ionic and hydrogen bonds. On one hand the ionic bonds were created by the reaction of carboxylic acid groups and nitrogen on the other hydrogen bonds are mainly due to the interactions of hydroxyl groups of the citric acid and polymer.

4.5. Supramolecular films mechanical properties

It is well known that the structural integrity of the systems bases on supramolecular interaction such as hydrogen bonds are highly dependent on temperature. The rheological properties of the films as a function of temperature were evaluated and compared with a blank film casted directly from the optimal dispersion. As can be seen **Figure 12** the incorporation into the dispersion of mono and difunctional carboxylic acids did no change the liquid behavior of the material in the temperature range tested, as G" > G'. However, the material treated with adipic acid had a higher modulus compared with the blank. In contrast the film made using citric acid exhibits a great change in the properties of the material, in this case we could observe an elastomeric region (G' > G") below 65ºC[27]. We assumed that the presence of this viscoelastic region was because of the presence of a supramolecular network composed by the ionic and hydrogen bonds previously described. At 65ºC crossover occurred between both modulus being the viscous modulus predominant. At 65ºC or higher temperatures the material behaved as a liquid, but this does not imply the complete loss of the supramolecular network, but only that it can flow because the hydrogen bond interactions are weaker. Additionally, reverse temperature sweep displayed similar values for both modulus, proving the reversible generation of strong ionic hydrogen bonds.

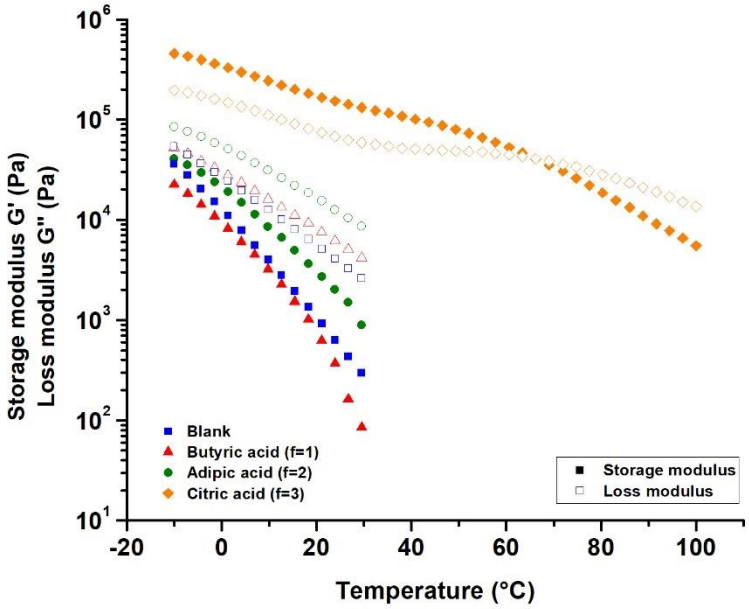


Figure 12. G´ and G´´ in function of the temperature for different acid crosslinked films (WDPHU4).

According to the results obtained, citric acid offers great mechanical properties improvement, so we decided to investigate the influence of the citric acid concentration on the rheological behavior. To study the influence of citric acid concentration, different amounts of citric acid were added to 4 mL of the optimal dispersion. These concentrations were in the range of 25 to 400 mol% per mole of nitrogen.

The obtained materials were transparent to slightly white at high acid content. **Figure 13** shows the evolution of the storage modulus G' and elastic modulus G" with increasing temperature from -10ºC to 100ºC at a constant frequency of 6,28 rad/s for the different films obtained. The point where the storage modulus and loss modulus cross in this graph indicates at which temperature the liquid behavior starts. Overall as more citric acid was incorporated the storage and loss modulus increased and the network liquid transition occurred in a wide range of temperatures depending on the acid concentration (from -10ºC using 25 mol% citric acid, up to >100ºC incorporating 400 mol% citric acid). Interestingly, as we would expect no

significant changes in the transition temperature from the network to the liquid state with excess citric acid (with respect to the mole of nitrogen), this transition kept evolving. We may hypothesize that the supramolecular network also involved: 1) hydrogen bond interaction between the acid and the numerous hydroxyl groups in polyhydroxyure-thane, and 2) hydrogen bond interaction within citric acid molecules via the pendant hydroxyl group, further favoring the formation of a tridimensional network.

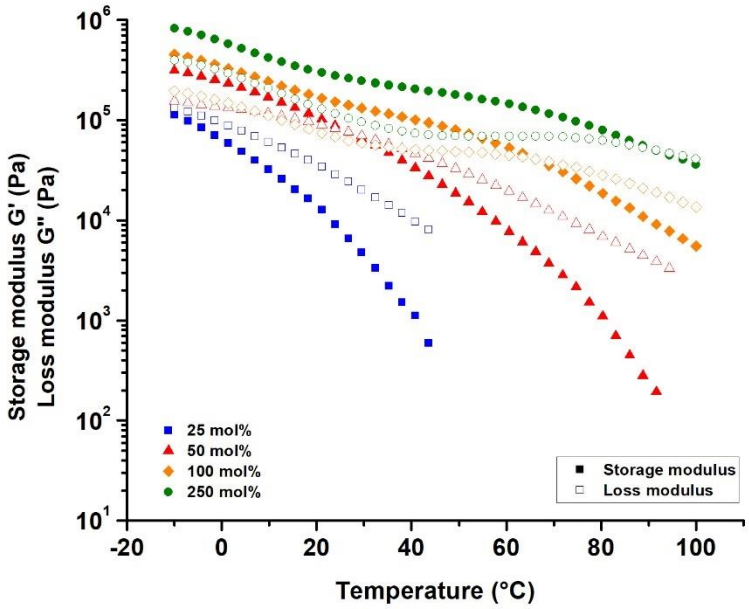


Figure 13. Evolution of the storage and loss modulus as a function of temperature for films prepared using different citric acid amounts.

4.6. Evaluation of the self-healing properties

Supramolecular polymers are polymer network based on reversible bonds and are well known for their self-healing properties. Because are materials presented similar features, such as well-defined temperature transitions between solid and liquid states, we decided to assess the self-healing properties of the films. Frequency sweep experiments in linear viscosity conditions were performed at different temperatures with the film obtained with 100% of citric

acid. The representation of G' and G" vs. frequency allowed us to clarify the nature of the interactions taking place in these structures[27]. The rheological behavior of films has a dependence with the time. At high frequencies it behaved as an elastic material (G'>G"), and on the contrary at low frequencies it behaved as a liquid. As it has been previously described, this behavior is characteristic of materials which possess bonds with temporary character such as reversible bonds. Indication of supramolecular interactions was also highlighted by the terminal region of the material. This zone which encompasses the lowest frequencies, is generally characterized for non-structured materials by -2 or -1 slopes for G' and G" respectively. In our case, alterations of this behavior revealed a structured polymer network, hindering the film from flowing[28]. However, even if the material presented a dominant elastic behavior, it did not prevent it from flowing with time. Regarding the influence of the temperature, an increase in temperature resulted in a decrease of both storage and loss moduli, similarly to the results obtained in temperature sweep experiments.

The promising rheological results made us to decide to investigate the self-healing properties of the material. The ability of the material to fill cracks and repair itself was studied by optical microscopy. The experiments were performed scratching the film with a disposable scalpel and the filling process was followed by optical microscopy at different temperatures (10, 25, 40, 60 and 80ºC). The damage refilling process could take places at temperatures as low as 10ºC. However, the film could not recover completely, and the scratch could be slightly seen by optical microscopy. Even at higher temperatures the scratch was still perceptible but as the temperature increased the filling process proceeded faster taking less than 1 minute to recover at 80ºC. Although the scratch provoked the rupture of the polymer chains, thus increasing the chain mobility around the impacted area, the supramolecular interactions hindered the surface rearrangement. A key factor to achieve the surface rearrangement is the increase of the temperature because this led to higher chain mobility promoting the material recovery in less time. That is the reason why at high temperatures the self-healing process is much faster.

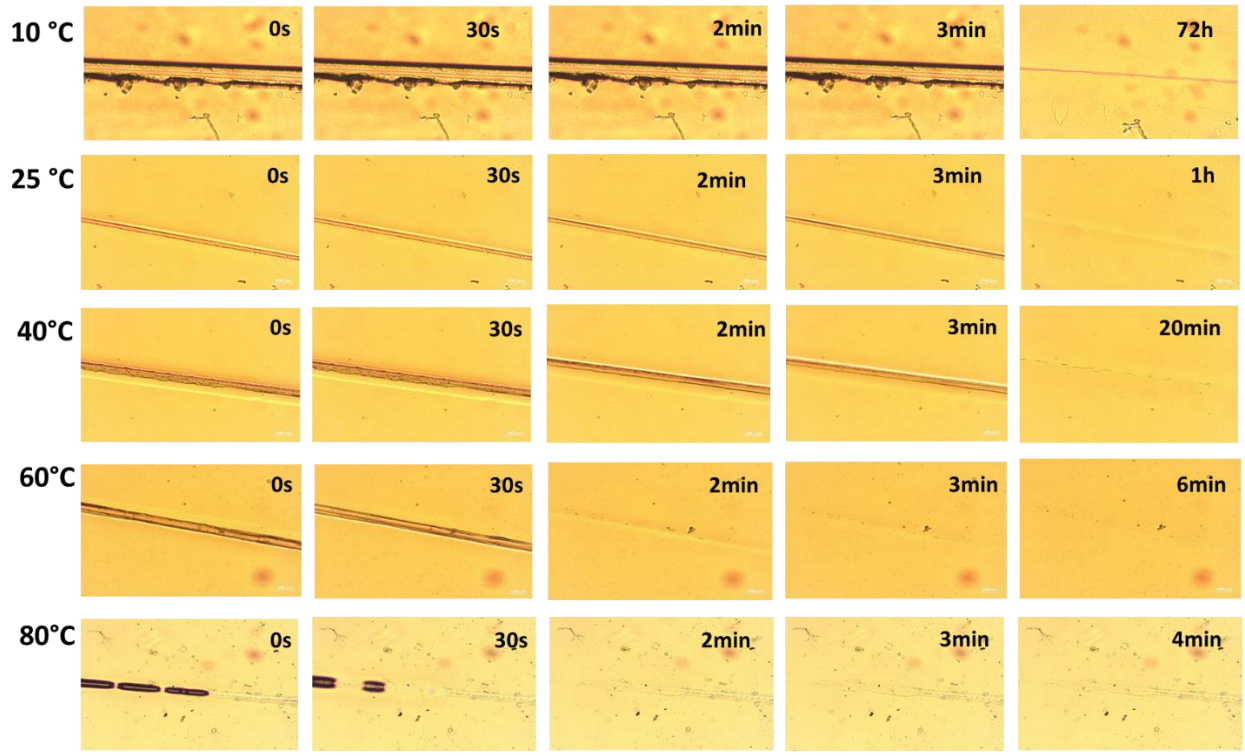


Figure 14. Crack refilling at different temperatures as observed by optical microscopy.

5. Conclusions

In this project, the preparation of waterborne non-isocyanate using 5- and 8 membered cyclic carbonates was studied for the first time. This involved the synthesis of the two monomers and the synthesis of different polymers and their characterization using ^{1}H NMR and ^{13}C NMR, FTIR, DSC, SEC and TGA. One of the most interesting thing of the synthesized polymer are the quaternizable nitrogen atoms coming from the (bis) N-8-C monomer. These atoms were used as internal emulsifiers in the dispersion process allowing to form stable dispersion of WDPHU in water. However, the most important property that these quaternizable nitrogen atoms provided to our material is versatility, enabling the post-functionalization of the polymer without more complicated synthetic reaction. It enables to obtain materials with a wide range of properties and applications in an easy way using the same starting material. For example, at the end of this project we evaluate the possibility of making materials that can be used in 3D printing. The process consisted in adding acrylic acid instead of citric acid to the dispersion along with a photoinitator. The acrylate moiety could be used to crosslink the material by UV light thanks to the photoinitiator making this material adequate to use in 3D printers. Preliminary test showed promising results in this area, but further experiments must be performed.

Finding the optimal dispersion conditions, we found that increasing the bis N8C ratio the particle size of the dispersions decreases until 50/50, At this composition there is too much charge that destabilize the system leading to a high particles sizes and polymer precipitation. According to the experimental results the best DGC/Bis-N8C ratio was 70/30 which allow us to obtain stable dispersion with a particle size around 200 nm. In addition, Using the previous 70/30 dispersion (WDPHU4) the tests about the effect of the acetic acid amount in the particle size show that as the acetic acid concentration is increased the particle becomes smaller due to generation of hydrophilic groups that interact like internal emulsifiers. Also, this experiment revealed that the particle size decreases until the amount the acid is equal to the quaternizable nitrogen. Therefore, we considered that the optimal amount of acetic acid was 100% per

nitrogen mol. Finally, the last dispersion experiment showed no correlation between the particle size and initial solid content in the range of 40%-60 initial solid content. Overall, we were able to carry out dispersion with good particle size and understand the effect on the particle size of the different parameters.

To improve the poor mechanical properties of the polymer due to the PDMS low Tg, we create supramolecular network by means of ionic and hydrogen bonds. The investigation about this topic revealed that the number of carboxylic group is critical to create supramolecular networks that a can improve the material mechanical properties. The rheological measurement concludes that the improvement with monofunctional and difunctional acids is very low. However, it was found that trifunctional acids like citric acid offers much better properties and we were able to obtain self-standing films with an elastic behavior at room temperature confirmed by rheological measurements. In addition, the results show that as the amount of citric acid is increased the mechanical properties increase, G' and G" crossover occur at higher temperatures and frequency sweep rheological measurements showed that despite the elastic behavior of the material it can flow with time. Unexpectedly if the citric acid carboxylic group mol exceeds 100% of nitrogen mol the improvement of the mechanical properties continues. This behavior can be explained by the formation of hydrogen bonds between the numerous hydroxyl groups of the polymer and the citric acid in excess.

Additional Work:

The evaluation of self-healing properties by optical microscope revealed faster repairing as the temperature is increased. The obtained material flows at temperatures as low as 10 ºC, taking the reparation process, if the temperature is increased to 80 ºC the film was repaired in less than 1 minute. This increasing in the speed is due to the higher mobility of the chains, this mobility is necessary to join the two broken parts and start the healing process. This supramolecular networks-based material has shown the potential to be used to prepare self-healing material.

5. Conclusiones

En este Proyecto se estudió por primera vez la síntesis de poliuretanos dispersables en agua libres de isocianatos a partir de carbonato cíclicos de 5 y 8 miembros. Para esto primero se sintetizaron dos de los tres monómeros y se sintetizaron copolímeros con diferentes relaciones de ambos monómeros. Tanto el polímero como el monómero se caracterizaron mediante RMN de ^{1}H, RMN de ^{13}C, ATR-FTIR, DSC, SEC y TGA. Una de las cosas más interesantes de los polímeros sintetizados son los átomos de nitrógeno cuaternizables provenientes del monómero bis-N8C. Estos átomos al cuaternizarse con ácido acético actúan como emulsificantes internos permitiendo la dispersión del polímero en agua y fueron imprescindibles para crear la red supramolecular. Sin embargo, la propiedad más importante de estos átomos cuaternizables es la versatilidad que le confieren al polímero haciendo posible además de los procesos previamente explicados la post-funcionalización del polímero de una manera sencilla sin necesidad de realizar más pasos sintéticos pudiéndose obtener materiales con un amplio rango de propiedades y aplicaciones de manera sencilla partiendo del mismo polímero. Por ejemplo, al final de este proyecto se consideró la posibilidad de hacer materiales que pudieran ser usados en impresión 3D. El proceso se realizaría de forma idéntica salvo que en vez de añadir ácido cítrico a la dispersión se añadiría acido acrílico y un fotoiniciador. El polímero podría ser curado gracias a los dobles enlaces de ácido acrílico mediante luz ultravioleta. Los ensayos preliminares arrojaron resultados prometedores, pero se necesitan realizar más experimentos para comprobar su total viabilidad.

Pudimos comprobar como al aumentar en contenido de Bis-N8C el tamaño de partícula disminuye hasta alcanzar una relación de composición de DGC/bis-N8C de 50-50 en mol. En esta composición hay demasiada carga que desestabiliza el sistema dando lugar a grandes tamaños de partícula y la consiguiente precipitación del polímero. De acuerdo con los datos experimentales obtenidos, los mejores resultados se obtienen con una relación 70-30 DGC/bis-N8C(WDPHU4) ya que se obtienen dispersiones estables con un tamaño de partícula de aproximadamente 200 nm. Usando la anterior dispersión se realizaron experimentos se

comprobó que a medida que se aumenta la cantidad de ácido acético el tamaño de partícula disminuye debido que cada vez tenemos más surfactante interno por la cuaternizacion de los nitrógenos. Adema este experimento mostro que el tamaño de partícula decrece hasta que se llega a la misma cantidad de ácido acético que moles de nitrógeno cuaternizables y, por lo tanto, se consideró que esta era la cantidad optima de ácido acético. El ultimo experimento que se realizó con las dispersiones fue el contenido inicial en sólidos en el cual se mostró que no había ninguna relación entre la concentración inicial de sólidos y el tamaño de partícula en el rango de 40-60% de contenido en sólido. En general se obtuvieron dispersiones con tamaños de partícula adecuados de alrededor de 200nm haciendo posible la obtención de dispersiones estables ya, se comprendió el efecto de los distintos parámetros en el tamaño de partícula.

Para mejorar las bajas propiedades mecánicas del polímero obtenido debido principalmente a la baja transición vítrea del PDMS creamos redes supramoleculares mediante enlaces iónicos y puentes de hidrogeno. La investigación acerca de este tema revelo que el número de grupos carboxílicos del ácido usado fundamental para la mejora de las propiedades mecánicas. Las pruebas reológicas realizadas concluyeron que la mejora al tratar las dispersiones con ácidos monofuncionales y difuncionales es muy baja. Sin embargo, usando ácido cítrico los resultados mostraron propiedades mecánicas mucho mejores obteniéndose films sólidos. Las pruebas reológicas a films con diferentes con diferente contenido de ácido cítrico mostraron como a medida que se aumentaba la concentración de ácido cítrico las propiedades mecánicas mejoraban, el cruce entre G’ y G” ocurre at temperaturas más alta contra mayor es la concentración de ácido cítrico y los ensayos reológicos en función de la frecuencia mostraban como a pesar del carácter elástico del material era capaz de fluir con el tiempo Además, sorprendentemente se comprobó que cuando el número de grupos carboxílicos del ácido cítrico es superior al de todos los átomos de nitrógeno las propiedades mecánicas continúan mejorando. Esto puede ser debido a la formación de puentes de hidrogeno entre las moléculas de ácido cítrico y los numerosos grupos hidroxilo que contiene el polímero.

Trabajo adicional:

Se estudiaron las propiedades autorreparables del polímero mediante microscopia óptica comprobándose como la velocidad de reparación del material aumentaba a medida que se incrementaba la temperatura. El material obtenido fluía a temperaturas tan bajas como 10 grados Celsius produciéndose la reparación del material en estas condiciones en una hora. Sin embargo, si se aumenta la temperatura se produce un gran incremento de la velocidad de reparación debido a la mayor movilidad de las cadenas. El material final obtenido mediante redes supramoleculares a demostró tener el potencial para ser utilizado en la preparación de materiales autorreparables.

6. References

1 H.-W. Engels, H.-G. Pirkl, R. Albers, R. W. Albach, J. Krause, A. Hoffmann, H. Casselmann and J. Dormish, *Angewandte Chemie International Edition*, **52**, 9422–9441.

2 H. Sardon, L. Irusta, M. J. Fernández-Berridi, J. Luna, M. Lansalot and E. Bourgeat-Lami, *Journal of Applied Polymer Science*, **120**, 2054–2062.

3 E. Rix, G. Céglia, J. Bajt, G. Chollet, V. Héroguez, E. Grau and H. Cramail, *Polym. Chem.*, 2014, **6**, 213–217.

4 D. Chattopadhyay and R. V. Kothapalli, *Progress in Polymer Science*, 2007, **32**, 352–418.

5 M. Barrère and K. Landfester, *Macromolecules*, 2003, **36**, 5119–5125.

6 H. Sardon, L. Irusta, M. J. Fernández-Berridi, M. Lansalot and E. Bourgeat-Lami, *Polymer*, 2010, **51**, 5051–5057.

7 D. Dieterich, *Progress in Organic Coatings*, 1981, **9**, 281–340.

8 A. K. Nanda and D. A. Wicks, *Polymer*, 2006, **47**, 1805–1811.

9 M. E. V. Hormaiztegui, M. I. Aranguren and V. L. Mucci, *European Polymer Journal*, 2018, **102**, 151–160.

10 N. Arshad, K. M. Zia, F. Jabeen, M. N. Anjum, N. Akram and M. Zuber, *International Journal of Biological Macromolecules*, 2018, **111**, 485–492.

11 C. Chinwanitcharoen, S. Kanoh, T. Yamada, S. Hayashi and S. Sugano, *Journal of Applied Polymer Science*,2003, **91**, 3455–3461.

12 L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau and H. Cramail, *Chemical Reviews*, 2015, **115**, 12407–12439.

13 H. Sardon, A. Pascual, D. Mecerreyes, D. Taton, H. Cramail and J. L. Hedrick, *Macromolecules*, 2015, **48**, 3153–3165.

14 Polymate Ltd. – International Nanotechnology Research Center,Migdal HaEmek, Israel, O. Figovsky, L. Shapovalov, Polymate Ltd. – International Nanotechnology Research Center, Migdal HaEmek, Israel, A. Leykin and Polymate Ltd. – International Nanotechnology Research Center, Migdal HaEmek, Israel, *Chemistry & Chemical Technology*, 2016, **10**, 553–559.

15 H. Tomita, F. Sanda and T. Endo, *Journal of Polymer Science Part A: Polymer Chemistry*, 2001, **39**, 4091–4100.

16 T. C. Mauldin and M. R. Kessler, *International Materials Reviews*, 2010, **55**, 317–346.

17 M. D. Hager, P. Greil, C. Leyens, S. van der Zwaag and U. S. Schubert, *Adv. Mater. Weinheim*, 2010, **22**, 5424–5430.

18 R. P. Wool and K. M. O'Connor, *Journal of Applied Physics*, 1981, **52**, 5953–5963.

19 S. Y. An, S. M. Noh, J. H. Nam and J. K. Oh, *Macromol Rapid Commun*, 2015, **36**, 1255–1260.

20 L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071–4098.

21 Y. Yang and M. W. Urban, *Chem Soc Rev*, 2013, **42**, 7446–7467.

22 A. Yuen, A. Bossion, E. Gómez-Bengoa, F. Ruipérez, M. Isik, J. L. Hedrick, D. Mecerreyes, Y. Y. Yang and H. Sardon, *Polymer Chemistry*, 2016, **7**, 2105–2111.

23 J. L. J. van Velthoven, L. Gootjes, D. S. van Es, B. A. J. Noordover and J. Meuldijk, *European Polymer Journal*, 2015, **70**, 125–135.

24 L. K. Saw, B. W. Brooks, K. J. Carpenter and D. V. Keight, *J Colloid Interface Sci*, 2003, **257**, 163–172.

25 M. Comí, M. Fernández, A. Santamaría, G. Lligadas, J. C. Ronda, M. Galià and V. Cádiz, *Macromolecular Chemistry and Physics*, **218**, 1700379.

26 M. A. Aboudzadeh, M. E. Muñoz, A. Santamaría, M. J. Fernández-Berridi, L. Irusta and D. Mecerreyes, *Macromolecules*, 2012, **45**, 7599–7606.

27 N. Oya, T. Ikezaki and N. Yoshie, *Polymer Journal*, 2013, **45**, 955–961.

28 T. V. Chirila, H. H. Lee, M. Oddon, M. M. L. Nieuwenhuizen, I. Blakey and T. M. Nicholson, *Journal of Applied Polymer Science*, , DOI:10.1002/app.39932.