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TRABAJO FIN DE GRADO

Sustainable Non-Isocyanate Polyurethane Hot-melt Adhesives

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ABSTRACT:

The formation of non-isocyanate polyurethanes (NIPUs) based on polyaddition of dicyclic carbonates and diamines represents one of the most promising alternatives for replacing conventional polyurethanes which are more toxic. However, the low reactivity of five membered cyclic carbonates, even in the presence of catalysts, restricts the use of this reaction for industrial applications. One way to improve the applicability of NIPU adhesives based on 5-membered cyclic carbonates is to synthesise hot melt NIPUs. In this study, a diamine and two dicyclic carbonates are combined to create sustainable hot melt NIPUs which have suitable properties to act as adhesives. The completion of the synthesis is followed by FTIR-ATR, and materials are characterised by ^{1}H-NMR. The behaviour of the polymers is addressed by rheology measurements and the adhesive properties are evaluated on stainless steel substrates by probe tack, lap-shear tests and Shear Adhesion Failure Temperature (SAFT) as well as Shear Resistance experiments. Finally, adhesion tests on different substrates (oak wood, PMMA and HDPE) are performed.

RESUMEN:

La formación de poliuretanos sin isocianatos basada en la poliadición entre diaminas y carbonatos dicíclicos, es una de las alternativas más prometedoras para remplazar los poliuretanos convencionales. Sin embargo, el uso de dicha reacción para aplicaciones industriales se ve limitada por la baja reactividad de los carbonatos cíclicos de cinco miembros, incluso en presencia de catalizadores. Una manera de mejorar la utilidad de los adhesivos de poliuretano sin isocianato basados en los carbonatos cíclicos de cinco miembros, es sintetizar ashesivos hotmelt. En este estudio, se combinan una diamina y dos carbonatos dicíclicos con el fin de formar hotmelts sostenibles que contengan propiedades adecuadas para actuar como adhesivos. La reacción se sigue por FTIR-ATR y la caracterización de los materiales se lleva a cabo a través de ^{1}H-RMN. El comportamiento de los polímeros es analizado mediante medidas reológicas. Las propiedades adhesivas son evaluadas en substratos de acero inoxidable a través de pruebas de pegajosidad (Tack), ensayos de cizallamiento (lap-shear), experimentos para medir la temperatura de falla de adherencia por cizallamiento (SAFT), y experimentos para analizar la resistencia al corte. Por último, pruebas de adhesión en diferentes substratos (madera de roble, PMMA y HDPE) son llevadas a cabo.

INTRODUCTION:

The production of conventional polyurethanes (PUs)grows every year as they are versatile polymers, which have several applications such as foams, elastomers, adhesives or coatings. Furthermore, polyurethane ranks 6th among all polymers based on the annual worldwide production.[1]Conventional polyurethanes are produced by a reaction between diisocyanates and polyols, where the nucleophilic center of the alcohol attacks the electrophilic carbon of the isocyanate group , forming the urethane bond (Figure 1a).[2]However, their synthesis is non-green due to the use of isocyanates, which are harmful for human health and also for the environment. In the context of REACH regulation, the European Chemicals Agency (ECHA) will restrict after February 2022 the use of isocyanates on their own, as a constituent in other substances or in mixtures for industrial and professional use when the concentration of diisocyanate compounds individually or in combination exceed 0.1 % by weight.[3] In addition, phosgene is employed in the synthesis of isocyanates, which is also highly toxic.
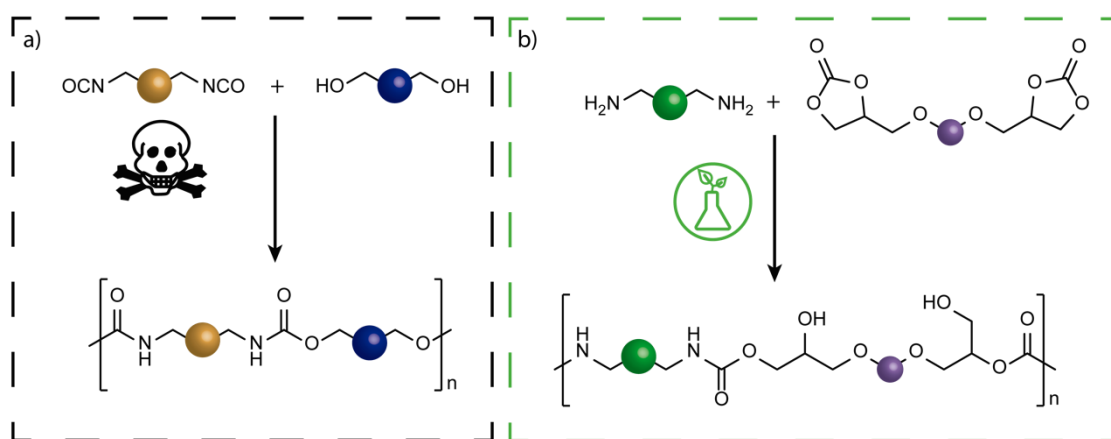

Figure 1. a) Conventional synthesis of polyurethanes through step-growth polymerization of polyisocyanate and polyol; b) synthesis of non-isocyanate polyurethanes by polyaddition of bis(cyclic carbonate) and diamine.

Consequently, the research on non-isocyanate polyurethanes (NIPUs) has increased in the recent years. Among all the alternatives proposed for the synthesis of NIPUs, the most promising one is the polyaddition of dicyclic carbonates and diamines.[2,4] In this reaction, the nucleophilic nitrogen of the amine attacks the carbonyl group of the cyclic carbonate, opening the ring and forming the urethane bond (Figure 2b). The resulting materials are called poly(hydroxyurethane)s (PHUs). Indeed, the macromolecular chain contains one hydroxyl

group hanging off the chain for each generated urethane group. The main advantages of this polyaddition reaction are two. Firstly, cyclic carbonates can be produced by the coupling of CO_2 with epoxides, which represents a greener and safer alternative to the conventional synthesis of cyclic carbonates from diols and phosgene.[5] Secondly, side-products are not released during the polymerization, so it is a 100% atom economic reaction.[6]On the other hand, aminolysis of five membered cyclic carbonates have low reactivity, even in the presence of catalysts, and often requires elevated temperatures to speed up the reaction.[7–10]Moreover, low molar masses and materials with poor mechanical properties are often obtained. As a result, nowadays, this reaction is barely implementedindustrially.[11]

To design adhesives that compete with the performance of conventional PU materials, the formulation and processing of PHUs should conform to certain characteristics. This necessitates the identification of the key features of conventional PU materials and the understanding of how they affect the final application. To fabricate PU adhesives that display an optimal balance between adhesive and cohesive forces, most systems are chemically cross-linked. Aromatic isocyanates are also preferred, as they possess a uniform reactivity of the reactive groups, lower volatility resulting in easier workplace handling, and lower prices than aliphatic isocyanates. Polyether polyols are usually chosen as comonomers as they offer improved low-temperature flexibility, are in a liquid state with acceptable viscosity at room temperature and are much less sensitive to hydrolysis than polyesters.[12]

Recently, some authors have reported different ways to develop relevant solvent-free PHU formulations in the adhesive field. Solvent-free formulations are certainly the most attractive route to prepare adhesives as no toxic solvent is released upon evaporation and shrinkage phenomena are limited during the curing process. However, this requires a suitable combination of poly(cyclic carbonate)s and polyamines for the preparation of a viscous formulation that can be applied to the substrate. Thus, Cornille et al.[13] reported neat PHUs as adhesives for gluing beech wood, glass and aluminum (pre-covered by an epoxy paint). Greater values of lap-shear strength were obtained when wood and glass were bonded. Additionally, authors benchmarked the PHUs with two conventional PUs derived from isocyanates. Poly(hydroxyurethane)s presented greater results than those commercial PUs. Hot-melts adhesives represent another route for the preparation of solvent-free systems that are

employed by melting thermoplastic polymers on a heated substrate. When the temperature decreased below the T_g or T_m of the polymer, it solidifies reaching enough strength to keep together the substrates. Nair et al.[14] described the preparation of thermo-reversible hot-melt PHU adhesives based on a mixture of two dicarbonates and anaminotelechelic oligo(propylene glycol). Beside the good adhesion values up to 9 MPa on aluminum and 2 MPa on high density polyethylene, the authors showed that the substrates could be debonded manually after thermal treatment up to 100 ºC for 0.5 h and then rebonded with no noticeable loss of the lap-shear strength values.

OBJECTIVE OF THE WORK

Hence, the purpose of this work is to synthesize sustainable PHUs from the polyaddition of dicyclic carbonates and diamines to be applied as hot-melt adhesives in an industrial scale. To achieve this, the previously explained polyaddition reaction was carried out to obtain thermoplastic materials with adhesive properties after a heating-cooling process. Different PHUs were synthesized using a diamine [m-xylylene diamine (MXDA), 1,12-diaminododecane (1,12-DAD), hexamethylenediamine (HMDA) or 1,3-cyclohexanebis(methylamine) (CBMA)] and a combination of two different dicyclic carbonate compounds [poly(propylene glycol dicyclic carbonate) (PPGdiCC) and resorcinol dicyclic carbonate (RdiCC) or PPGdiCC and 1,4-butanediol dicyclic carbonate (BdiCC)]. PPGdiCC was selected because PPG is one of the most commonly employed soft segments in polyurethane adhesives as it provides good adhesion to different substrates and also presents good hydrolysis resistance and hydrophobicity.[15] This segment was combined with other two dicyclic carbonates, to obtain a more malleable product, and to create hard/soft segment domains. In addition, the impact of the different diamines was studied to produce this phase separation and allow the formation of hot-melts.

To ensure that the reaction was completed, an FTIR-ATR and ^{1}H-NMR was employed. After that, rheological measurements were done to analyse the behaviour of each material at different temperatures, by measuring the storage modulus (G'), the loss modulus (G'') and the loss tangent (tanδ). Then, adhesive properties were studied by doing probe tack, lap-shear strength tests, shear adhesion failure temperature (SAFT) experiments and shear resistance experiments several times to demonstrate the recyclability of the adhesive. Moreover, lap-shear strength tests were performed in different substrates such as stainless steel, oak wood, poly(methyl methacrylate) (PMMA) and high density polyethylene (HDPE).

EXPERIMENTAL PART:

Reagents and materials:

Poly(propylene glycol) diglycidyl ether ($M_n \sim 640$ g mol^{-1}) (PPGDGE), resorcinol diglycidyl ether (RDGE), 1,4-butanediol diglycidyl ether(BDGE),tetrabutylammonium iodide (98%) (TBAI), hexamethylenediamine (HMDA), 1,12-diaminododecane (1,12-DAD), 1, 3-cyclohexanebis(methylamine) (CBMA)and deuterated dimethyl sulfoxide (DMSO-d$_6$) were purchased from Sigma Aldrich. m-Xylylene diamine (99%) (MXDA) was purchased from Acros Organics.1,3-bis(2-hydroxyhexafluoroisopropyl)benzene (97%) (1,3-bis HFIB) was purchased from Fluorochem. All reagents were used without further purification. Plexiglas XT 20070 [poly(methyl methacrylate) (PMMA), thickness of 3 mm], oak wood (thickness of 5 mm) and high density polyethylene (HDPE, thickness of 3 mm) substrates were purchased from Rocholl GmbH, Germany. Stainless steel AISI 316 (SS, thickness of 1.95 mm) and Polyamide (thickness of 2 mm) were kindly supplied by Oribay Group. The cyclic carbonates used in this study were synthesized by CO_2 coupling with the commercial precursors using a home-made catalyst in collaboration with the group of Christophe Detrembleur from the Center for Education and Research on Macromolecules (CERM) of the University of Liège.

Typical procedure for the synthesis of resorcinol dicarbonate (RdiCC):[16]

Synthesis of dicarbonates was performedin collaboration with the laboratory of Christophe Detrembleur, University of Liège. Resorcinol diglycidyl ether (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. Resorcinol dicarbonate was obtained quantitatively after depressurization of the reactor and no further purification was required. All dicarbonates were synthesised using this procedure.NMR spectra of the products are shown in figures 2, 3 and 4.
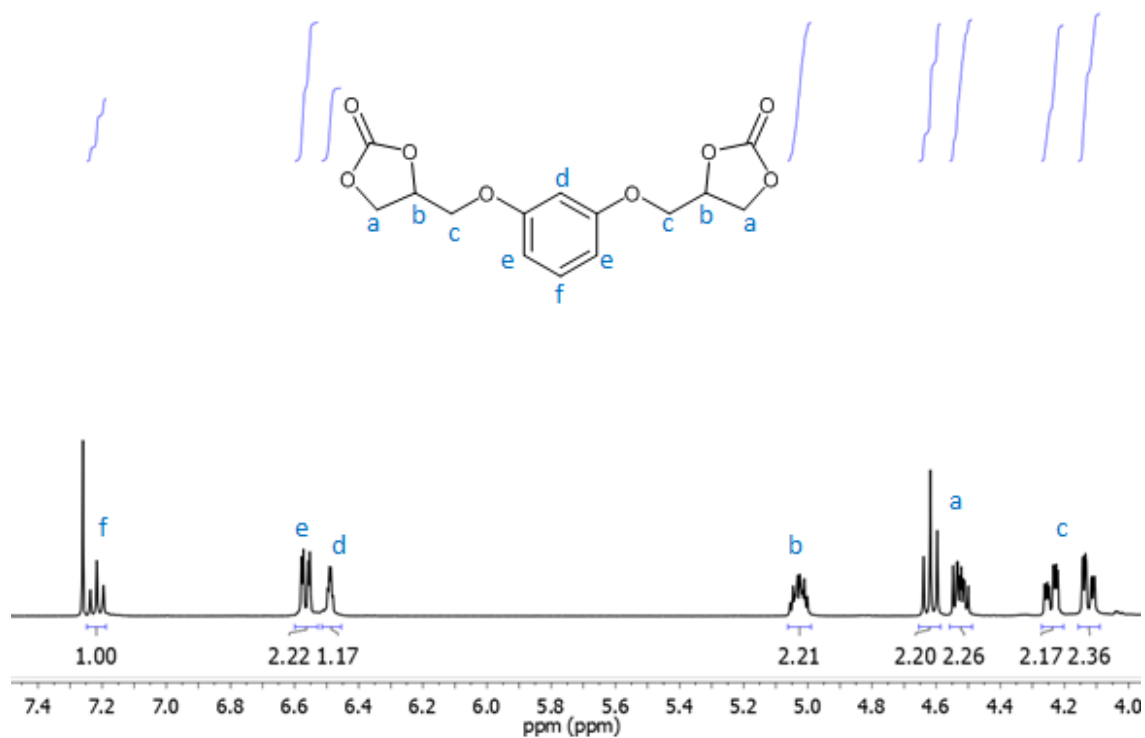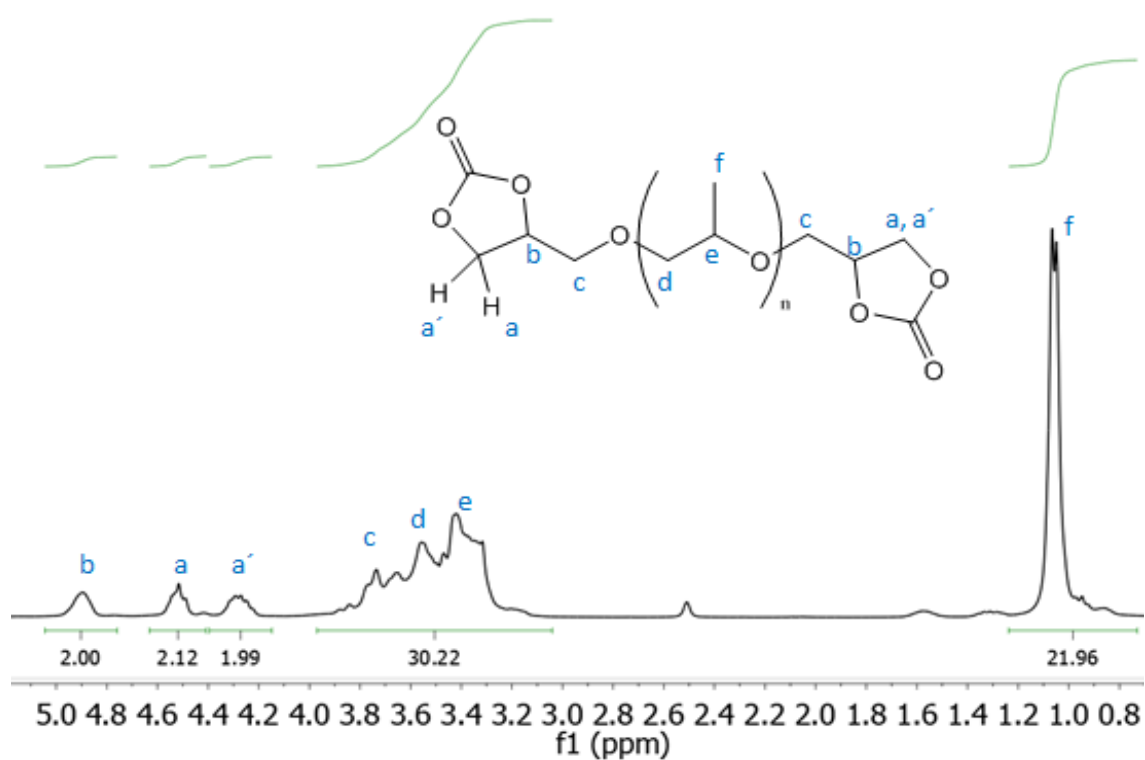
Figure 2. ^{1}H-NMR of RdiCC.

Figure 3. ^{1}H-NMR of PPGdiCC.

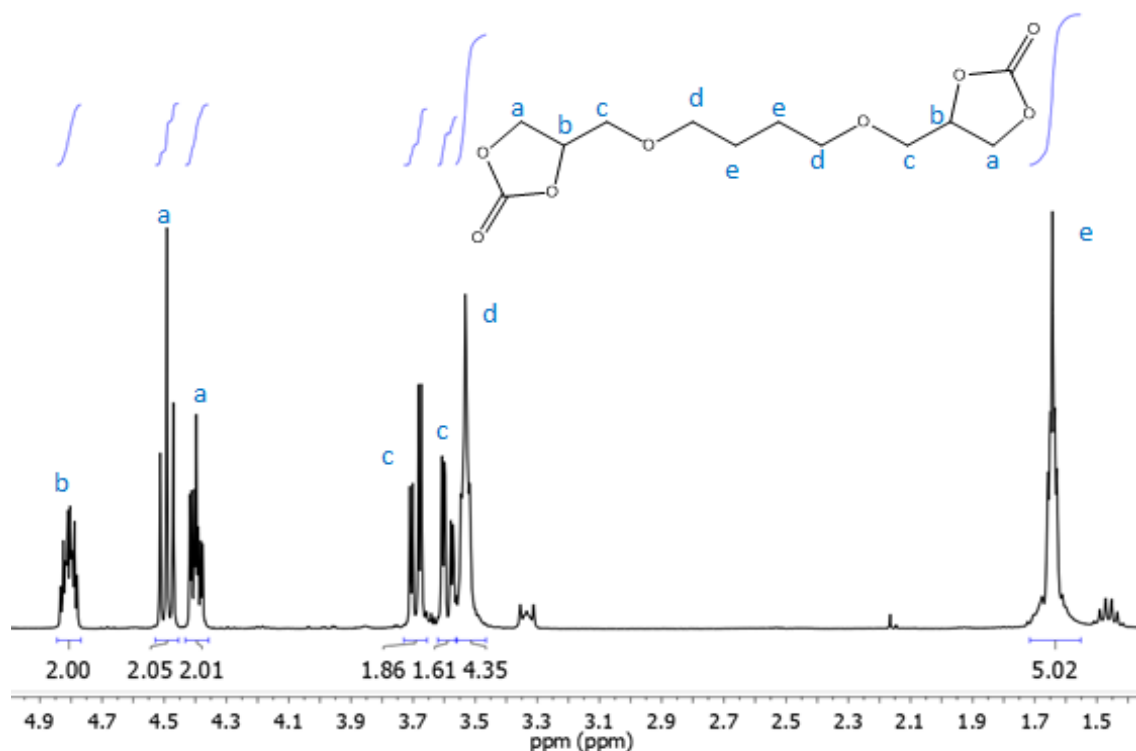Figure 4. ^{1}H-NMR of BdiCC.

Titration of the cyclic carbonate by ^{1}H NMR:[13]

This procedure is useful for determining the real carbonate equivalent weight of each molecule. At first, a specified amount of cyclic carbonate (PPGdiCC, RdiCC or BdiCC) (around 50 mg) and a standard solution of DMSO-d_6 with toluene (around 30 mg of toluene dissolved in 5 mL of DMSO-d_6) were weighed into an NMR tube. Once the ^{1}H 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, RdiCC and BdiCC were calculated according to 1.equation, where m_{C5} – mass of cyclic carbonate introduced into the NMR tube, $n_{function of carbonate}$ – 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_{CH3} – integration of peak CH_3 of toluene. The CEW values for each cyclic carbonate were obtained in triplicate determinations and are presented in Table 1.

$$CEW = \frac{m_{C5}}{n_{function of carbonate}} = \frac{m_{C5} x I_{CH3}}{(I_a + I_b + I_c) x n_{toluene}}$$

Equation 1. Cyclic Carbonate Equivalent Weight.

Table 1. Calculated CEW values.

Dicyclic carbonate	CEW (g/eq.)
RdiCC	190±5
PPGdiCC	333±4
BdiCC	167±4

Typical procedure for NIPU adhesive preparation:

RdiCC (4.25 g, 0.02 equiv), PPGdiCC (11.15 g and 0.03 equiv) and MXDA (4600µL, 0.07 equiv) were added to a 100 mL jacketed glass reactor. The temperature was set at 80 °C for 24 hours with continuous mechanical stirring at 200 rpm and without using any catalyst. The reaction was cooled down and the polymer stored. In figure 5 the product obtained can be seen.

All reactions were carried out in the same way, adjusting quantities of PPGdiCC and RdiCC or BdiCC according to the ratios shown in Table 2. In all cases diamine was kept at 1.25 equivalents regarding to total equivalents of cyclic carbonate.
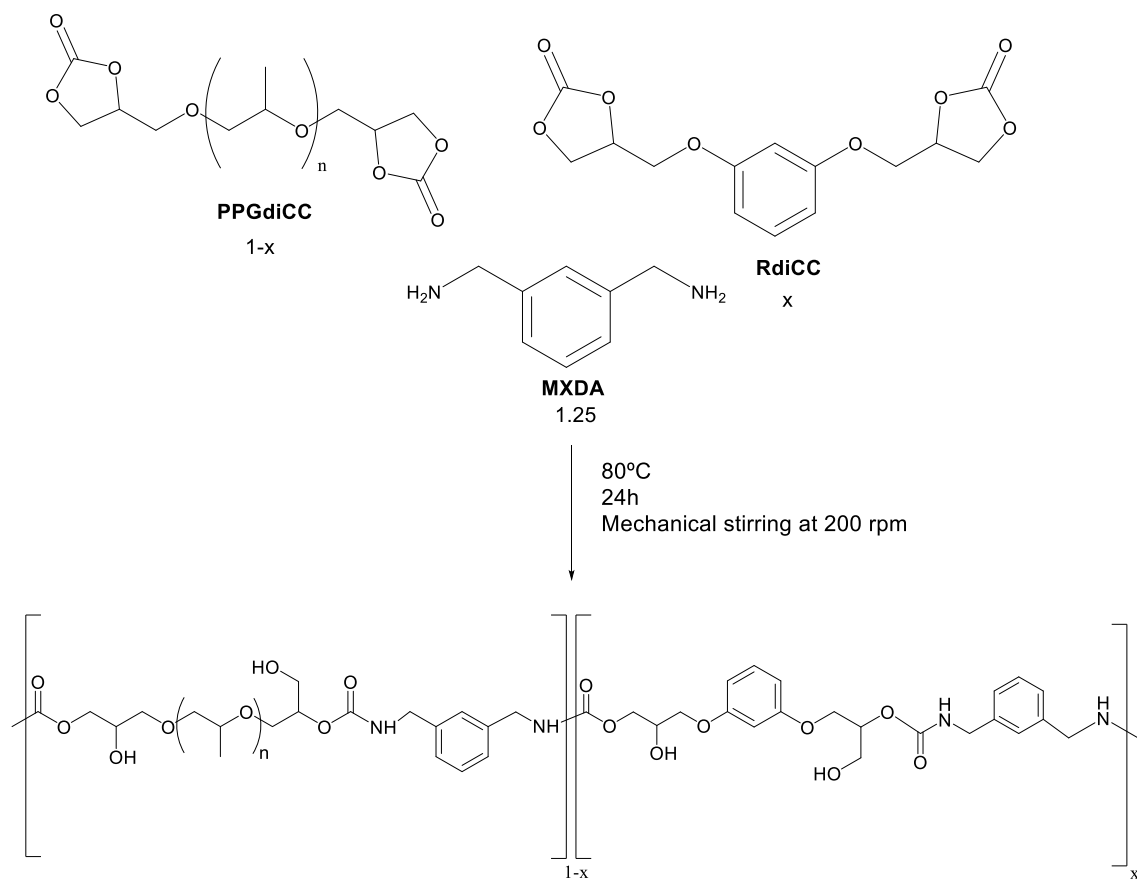
Figure 5. Synthesis of NIPU adhesives based on polyaddition reaction, combining two dicyclic carbonates and a diamine.

Table 2. All the reactions and their compositions.

Code	Diamine	Dicyclic carbonates	Molar ratio of the diclyclic carbonates
0/100-MXDA	MXDA	PPGdiCC/RdiCC	0/100
100/0-MXDA			100/0
70/30-MXDA			70/30

60/40-MXDA			60/40
50/50-MXDA			50/50
50/50-DAD	1,12-DAD		
50/50-HMDA	HMDA		
50/50-CBMA	CBMA		
50/50B-MXDA	MXDA	PPGdiCC/BdiCC	

Characterization and Methods:

- *Nuclear Magnetic Resonance (NMR) Spectroscopy:*

This technique can be defined as a highly useful tool which applies a magnetic field to an atomic nucleus (the most common stable isotopes are[1]H and ^{13}C) as well as radio frequency pulses, to characterise the nuclear magnetic resonance frequency of that atomic nucleus according to its chemical or environmental surroundings. When the magnetic field is applied, the electrons surrounding the nucleus start to circulate along the direction of the applied magnetic field, causing a small opposing magnetic field at the nucleus. As a consequence, variations in electron density around each nucleus will cause each nucleus to experience a different magnetic field, and that differences are measured by the chemical shift, which gives us significant information to characterize a molecule.[17]

In this study, ^{1}H spectra were recorded on a Bruker AdvanceDPX 300 spectrometer at 25 °C. The samples were prepared by weighting around 10 mg of each polymer and dissolving that quantity in 0.5 mL of DMSO-d_6.

- *Fourier Transform Infrared (FT-IR) Spectroscopy:*

IR spectroscopy is an absorption technique where molecules are irradiated with infrared radiation causing molecular vibrations. When the irradiated energy corresponds to a specific vibration, the molecule absorbs the energy. However, a change in electric dipole moment must occur during the vibration. Therefore, this technique measures the absorbance of the infrared radiation at different wavelengths to characterize different molecules. This procedure is also useful for following reactions and for making sure that the reaction is complete.[15]

In this study, FT-IR spectra were obtained using an FT-IR spectrophotometer (Nicolet iS20 FT-IR, Thermo Scientific Inc.) equipped with Diamond Crystal Plate for Smart iTX/iD7/Everest ATR 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 16 scans.

- *Rheology measurements*:

Rheology explores the flow and the strain of a material, and it is useful for knowing how our material will behave under specific conditions. The behavior of a material is different depending on the experimental time. According to 2.equation, where D_e is Deborah number, λ is relaxation time and t_{exp} is the experimental time, when experimental time is low or relaxation time is high, D_e is high and the material behaves as an elastic solid. On the other hand, when experimental time is high and relaxation time is low, D_e is low and the material has the behavior of a viscous liquid. Regarding polymers, they show an intermediate state called viscoelastic behavior, that is to say, they have elastic as well as viscous characteristics and depending on the experimental time they act like solids or like liquids. This characteristic is hugely important with regard to processing.[18]

$$D_e = \frac{\lambda}{t_{exp}}$$

Equation 2. Deborah number.

Viscoelasticity is measured using devices called rheometers which can do dynamic measurements applying oscillatory flow, meaning that they put on sinusoidal stress.[19]

In this case, rheology measurements were done using a stress-controlled Anton Paar Physica MCR101 rheometer, and all the experiments were carried out using 15 mm parallel plate geometry. Firstly, strain sweep experiments were performed at room temperature, at a frequency of 1Hz and at a variable strain between %0.01-10, to determine the linear viscoelasticity of the materials. Secondly, temperature sweep experiments were carried out from -10 to 200°C, at a frequency of 1Hz and a strain in the range of linear viscoelasticity of the materials. This type of dynamic measurement is useful for determining thermal transitions such as T_g (glass-transition temperature) or T_m (melting temperature).

To prepare each sample, around 190 mg of the polymer were shaped in the oven applying pressure between two substrates with a spacer to control the thickness (~0.6-0.8 mm), at a temperature in which the sample could be easily shaped. The size of the sample was around15mm and it had circular form, to cover all the plate.

- Dynamic Mechanical Thermal Analysis (DMTA):

Dynamic Mechanical Thermal Analysis is a technique where a sinusoidal deformation is applied to a solid sample in a cyclic manner.[20] It is used for analyzing the mechanical properties of different materials using several deformation modes, such as tension, compression, dual cantilever bending, 3-point bending and shear modes, and the most suitable type should be selected depending on the sample shape, modulus and measurement purpose.[21]Viscoelastic properties such as storage modulus, loss modulus and loss tangent can be measured, and their dependence on temperature and frequency can be analysed. In these measurements, the glassy zone and rubbery plateau of the polymers are seen, as a consequence, T_g can be measured.

In this case, a Dynamic Mechanical Thermal Analyzer, Triton 2000 DMA from Triton Technology, was used in a single cantilever bending deformation mode to carry out each analysis. Each sample had a different length, width and thickness, and they were heated from −50 to 150 °C at a constant heating rate of 4 °C/min, and a frequency of 1 Hz was employed. The glass transition temperature (T_g), given by the maximum peak in the loss tangent ($\tan\delta$) was determined for all samples.

- *Differential Scanning Calorimetry (DSC):*

Differential Scanning Calorimetry (DSC) is a thermal analysis technique in which the heat flow into or out of a sample is measured as a function of temperature or time, while the sample is exposed to a controlled temperature program. Actually, the amount of heat required to increase the temperature of a sample is compared with the one needed to heat a reference, and the difference is measured while the temperature of the reference and the sample is maintained equal. This is a very powerful technique to evaluate material properties such as

glass transition temperature, melting, crystallization, specific heat capacity, cure process, purity, oxidation behavior, and thermal stability.[22]

In this study, a differential scanning calorimeter (DSC-Q2000, TA Instruments Inc., USA) was used to analyse the thermal behaviour of the samples. A total of 6–8 mg of each sample was scanned from −80 to 150 °C at a heating rate of 20 °C min^{-1}. A first scan is done for removing the thermal background of the polymer, then the sample is cooled down and finally, a second scan is done to obtain the real properties of the material, as we know exactly how it was cooled down. By doing that, heat flow versus temperature curves were obtained, and the glass transition temperatures (T_g) were taken from the inflection point in the curve.

- *Adhesive properties:*

    1. Probe tack:

Tack is related to the bond formed when another surface is pressed against the adhesive surface for a brief period of time.[23]The quality of the bond is influenced by numerous factors including the surface energies of the adhesive and substrate, dwell time, contact pressure, mechanical properties of the adhesive, temperature and humidity[24]The aim of these tests is to probe the stickiness of the adhesives. In this study, circular samples were prepared by shaping around 100 mg of the polymer in the oven at 80ºC applying pressure manually. Thickness was controlled to 0.6 mm using spacers. Diameter of the samples was higher than 5 mm. Then, each sample was placed in the middle of a stainless steel substrate and each substrate was entered in the oven, which is part of the probe tack equipment, at a temperature chosen depending on the rheology. Each test was done by bringing into contact a cylinder of 5 mm diameter with the adhesive surface, at a test speed of 300 mm min^{-1} and a contact time of 10 seconds (Figure 6). In these tests, a force-displacement curve was obtained and it can be converted into a stress-strain curve.
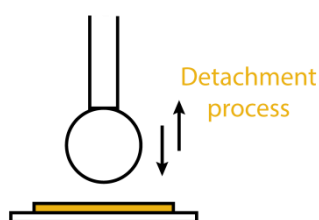
Figure 6. General representation for probe tack using a ball geometry to address tack behavior of the adhesive. In our case, 5mm diameter cylinder was employed.

2. Lap-shear tests:[14]

The adhesive properties of the NIPUs were evaluated at 298K and 50% R.H. (relative humidity) using an Instron 5569 and applying a parallel force to the adhesive bond with a displacement rate of 50 mmmin^{-1} (Figure 7). Stainless steel AISI 316 substrates with dimensions of 100 mm x 25 mm x 1.95mm were used for 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 and the error was calculated as standard deviation of the measurements. The lap-shear strength was calculated by the 3.equation, 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 mm^2).

$$\tau\tau = \frac{P}{A}$$
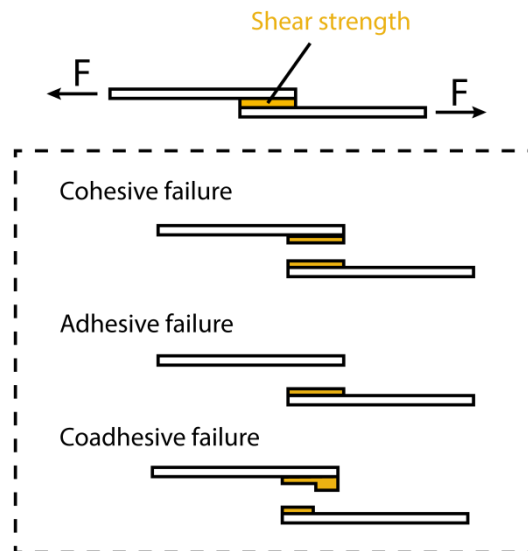
Equation 3. Calculation of the lap-shear strength.

Figure 7. Representation of lap-shear tests and the possible nature failure when adhesive bond line is broken.

The nature of adhesion failure was also recorded based on visual inspection of the sample following the test. The failure can be of two types. On the one hand, an adhesive failure can happen, this means that the linkage between the adhesive and the substrate breaks, as the internal forces of the adhesive are strong enough to keep the adhesive together. On the other hand, if the adhesive breaks, a cohesive failure occurs, and this happens because the forces between the adhesive and the substrate are higher than the internal forces of the adhesive. A mixture thereof is considered as coadhesive failure (Figure Y).In the case of the adhesives, a cohesive failure is preferable, as it measures the real force of the adhesive whereas regarding the adhesive failure, the break can happen for some external reason which is not related to the adhesive. For example, if the substrate is not correctly cleaned, the lap-shear strength value is going to be lower due to that and not due to the quality of the adhesive.

Lap-shear test specimens were prepared as follows. At first, the surfaces of the substrates were cleaned this way: 10 substrates were introduced in an acetone/isopropyl alcohol mixture (1:1, V/V) for 5 minutes, and then, they were introduced in water for 2 minutes. The procedure was repeated three times, and after that, each substrate was wiped with tissue paper and dried at room temperature for 2 h. In the case of oak wood, the substrates were dried at 70ºC during 24h, to get rid of humidity.To prepare each sample, around 250 mg of the polymer were shaped in the oven applying pressure between two substrates with a spacer to control the thickness (~0.6-0.8 mm), at a temperature in which the sample could be easily shaped. The size of the sample was 25x12.5 mm^2. On the other hand, to prepare the adhesive joints, at first the previously prepared sample was stuck on half of the cleaned substrates applying light pressure manually. Then, the substrates were placed into the oven separately to allow the softening of the polymer for 5 minutes at a certain temperature. After that, the second substrate was placed in contact with the first one applying light pressure manually and the substrates were placed again into the oven. 80 ºC and 100 ºC were the selected temperatures. The overlapping area was in all cases 312.5 mm^2.

After finishing the lap-shear test, the thermoreversible adhesion of the adhesives was tested, to prove the efficiency of the material for repeated use. A first rebounding was done to see if once the adhesive was unglued could be glued again without decreasing hugely the lap-shear strength. Firstly, each pair of substrates was stuck again at room temperature. Then, they were

placed into the oven at the same temperature and twice the time that they were in the first lap-shear test. Finally, lap-shear was repeated in the same conditions as before.

Subsequently, a second rebounding was done. At first, while the stainless steel substrates were in the oven, the adhesive was removed using a PMMA substrate. As a result, I had again 5 adhesive samples. Then, substrates were cleaned with acetone and each sample was prepared again as in the first lap-shear tests. Finally, lap-shear test were repeated in the Instron 5569. This procedure is useful for finding out if the adhesives can be reused maintaining their adhesive properties.

3. Shear adhesion failure temperature (SAFT) experiments:

This procedure was done with the aim of knowing how many degrees could be held by the adhesives while they supported a weigh of 1 Kg. The experiments were performed on stainless steel panels using SAFT equipment and the overlapping area of the panels was 625 mm^2 (25 mm × 25 mm). At first, the substrates were cleaned following the procedure explained for lap-shear tests. Afterwards, samples were prepared following the procedure described for lap-shear tests but using 500 mg of each polymer instead of 250 mg, and in this case, the samples obtained had a size of 25 mm. Then, the adhesive joints were prepared as explained for lap-shear tests and the temperature of the oven was chosen depending on the lap-shear tests results. Finally, the adhesive joints were placed into the oven which is part of the SAFT equipment, and the temperature was increased from 20°C to 200°C at 1°C/min rate until the substrates fell off. The temperature of failure was reported as an indication of temperature service of adhesives and the nature of adhesion failure was also recorded based on visual inspection of the sample following the test.
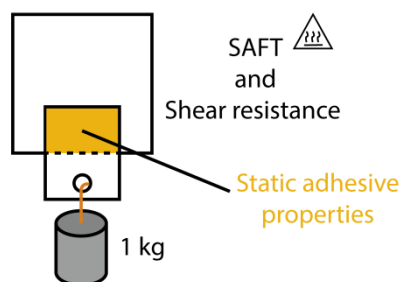
Figure 8. Sketch of the SAFT and shear resistance experiments carried out in an oven with a ramp of temperature and a constant temperature, respectively.

4. Shear Resistance:

These tests were performed following the same procedure and using the same equipment as the one described for SAFT experiments (Figure 8). However, in this case, the aim was to determine how much time could tolerate the adhesives at a constant temperature. The nature of adhesion failure was also recorded based on visual inspection of the sample following the test.

RESULTS AND DISCUSSION:

1. *Homopolymer synthesis and rheology:*

Polyaddition of m-xylylenediamine (MXDA) and poly(propyelene glycol) dicycliccarbonate (PPGdiCC) or MXDA and resorcinol dicyclic carbonate(RdiCC) were carried out to prepare 100/0-MXDA and 0/100-MXDA formulations, respectively. Selection of the monomers was based on previous work of the group since good adhesive performance was obtained.[25]Completion of the reaction was followed by FTIR-ATR, observing the disappearance of the carbonyl stretching vibration band of the carbonates at 1782cm^{-1}and 1791 cm^{-1},associated to RdiCC and PPGdiCC, respectively, and the appearance of the carbonyl stretching vibration band of the urethane at 1694 cm^{-1}in (0/100-MXDA) and 1699 cm^{-1} in (100/0-MXDA) (Figure 9).Moreover, these signals can be observed in both cases: at 3320 cm^{-1} –OH stretching, around 2930-2970 cm^{-1} C-H stretching, C=C stretching of the aromatic rings at 1592, 1491 and 1450 cm^{-1}, N-H bending at 1531 cm^{-1}, C-O stretching at around 1240 cm^{-1}, out of plane bending vibrations at 775 and 700 cm^{-1} which indicate that the aromatic ring is disubstituted at meta. Additionally, in 100/0-MXDA,CH$_3$ bending (umbrella band) can be seen at 1374 cm^{-1}, at 1086 cm^{-1} C-O-C stretching and secondary alcohol bands are overlapped, and at 1013 cm^{-1} the band corresponding to the primary alcohol can be seen. In 0/100-MXDA, C-O-C stretching at 1181 cm^{-1}, secondary alcohol band at 1131cm^{-1} and primary alcohol band at 1038 cm^{-1}can be observed.
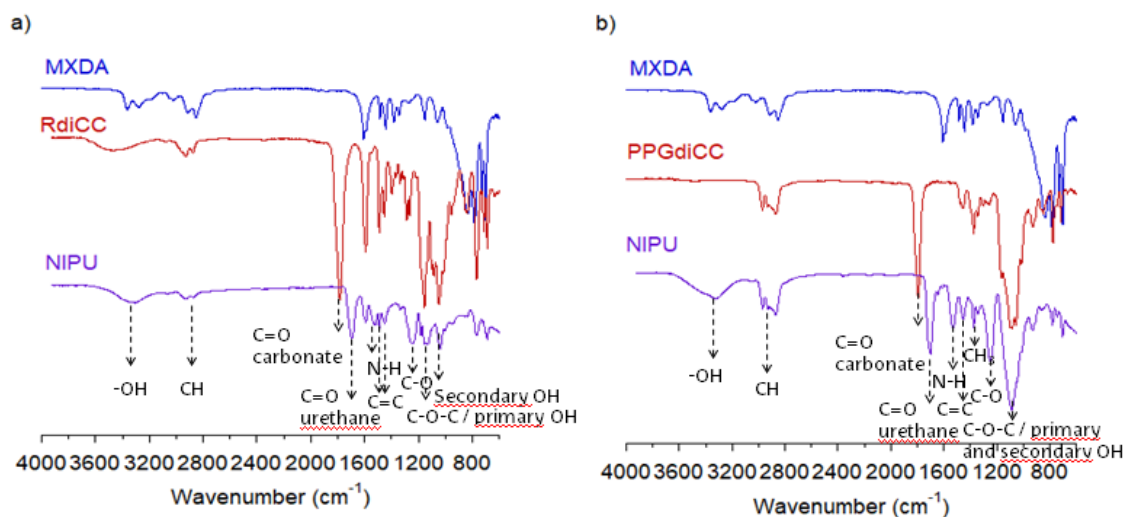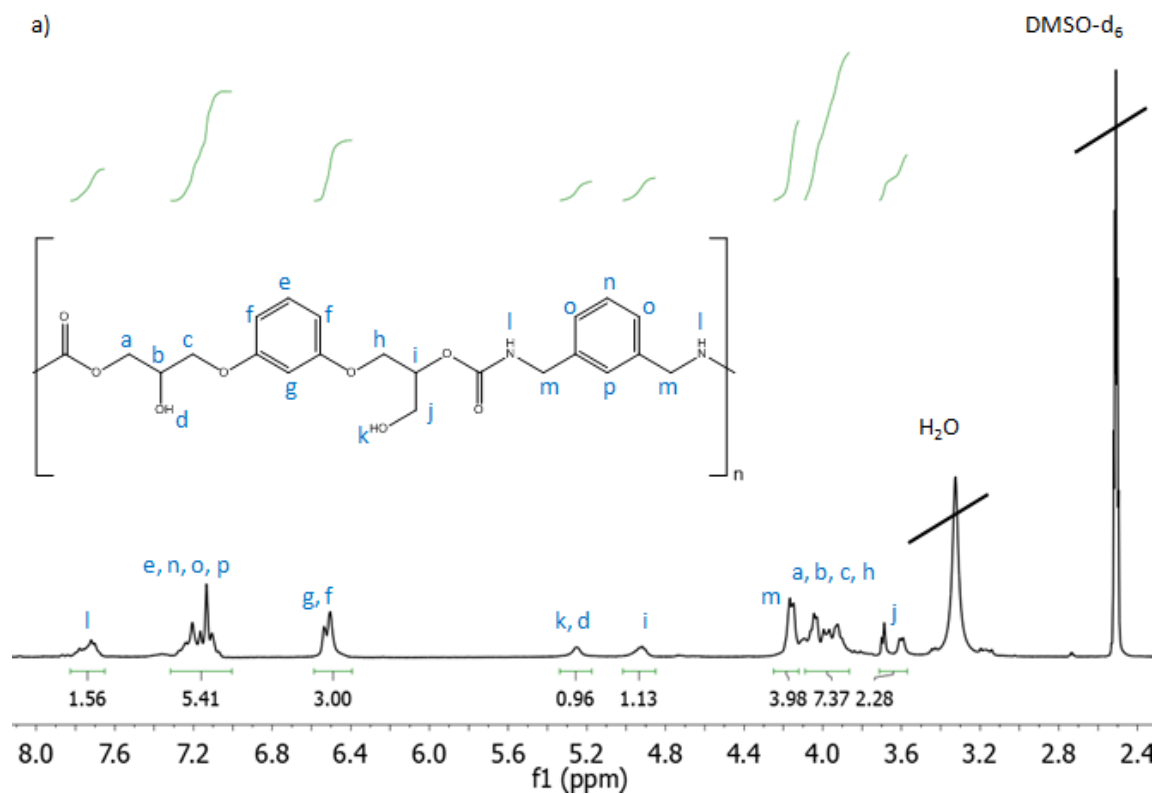
Figure 9. a) FTIR-ATR of 0/100-MXDA. b)FTIR-ATR of 100/0-MXDA.

0/100-MXDA and 100/-MXDA polymers were characterized by ^{1}H-NMR spectroscopy (Figure 10).Signals corresponding to the -NH-C(O)O- of the urethane group (7.6-7.7 ppm) as well as to the –CH$_2$NH-of the diamine (4.1-4.2 ppm) confirmed the formation of the polymers.

b)

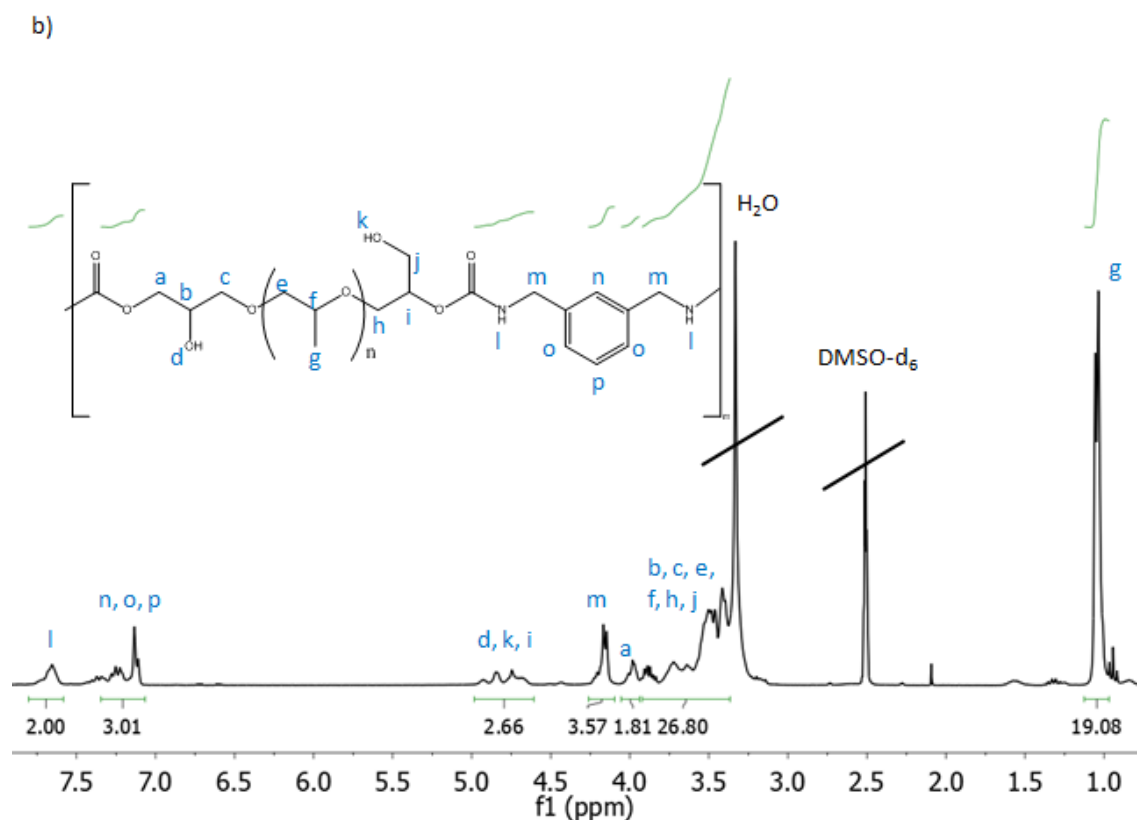Figure 10. a) ^{1}H-NMR of 0/100-MXDA. b) ^{1}H-NMR of 100/0-MXDA.

Afterwards, the thermal characterization of the materials was performed by differential scanning calorimetry (DSC). In figure 11 are depicted the curves from -70 to 110 ºC for the compositions. T_g were calculated from the second heating scan. 0/100-MXDA showed a high $T_g$at51 ºC, while 100/0-MXDA presented a low T_g at -11 ºC confirming its viscous behavior at ambient conditions. Therefore, none of the compositions was useful as an adhesive, as 100/0-MXDA was excessively soft, whereas 0/100-MXDA was too rigid. As a result, it was decided to mix both dicyclic carbonates in order to get an intermediate product. The balance between hard and soft segments is well established for designing adhesives with optimal properties.[13]
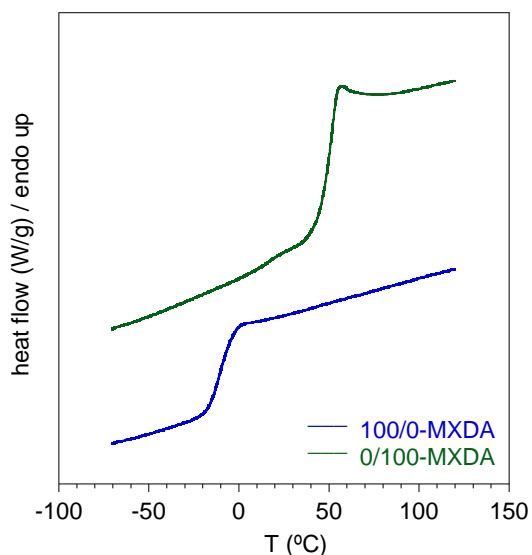
Figure 11. DSCs of the compositions0/100-MXDA and 100/0-MXDA.

2. *Copolymers compositions:*

2.1. Synthesis:

PPGdiCC and RdiCC were reacted in different molar ratios with MXDA to prepare three different formulations:70/30-MXDA, 60/40-MXDA and50/50-MXDA.The reaction was followed by FTIR-ATR. Disappearance of the carbonyl stretching vibration band of the cyclic carbonate at 1780-1790cm^{-1}and the appearance of the carbonyl stretching vibration band of the carbonyl of the urethane bond at 1698 cm^{-1}, confirmed the completion of the reaction. Additionally, the appearance of O-H stretching bands at 3320 cm^{-1}supported the ring opening of the cyclic carbonate. In Figure 12 the FTIR of the 60/40-MXDA is showed and signals are assigned as follows: below 3000 cm^{-1} C-H stretching, C=C stretching of the aromatic rings at 1592, 1491 and 1450 cm^{-1}, N-H bending at1531 cm^{-1}; CH$_3$ bending (umbrella band) at 1374 cm^{-1}; C-O stretching at 1248 cm^{-1}; C-O-C stretching, primary alcohol and secondary alcohol around 1086 and 1043 cm^{-1}; out of plane bending vibrations at 775 and 700 cm^{-1}which indicate that the aromatic ring is disubstituted at meta.
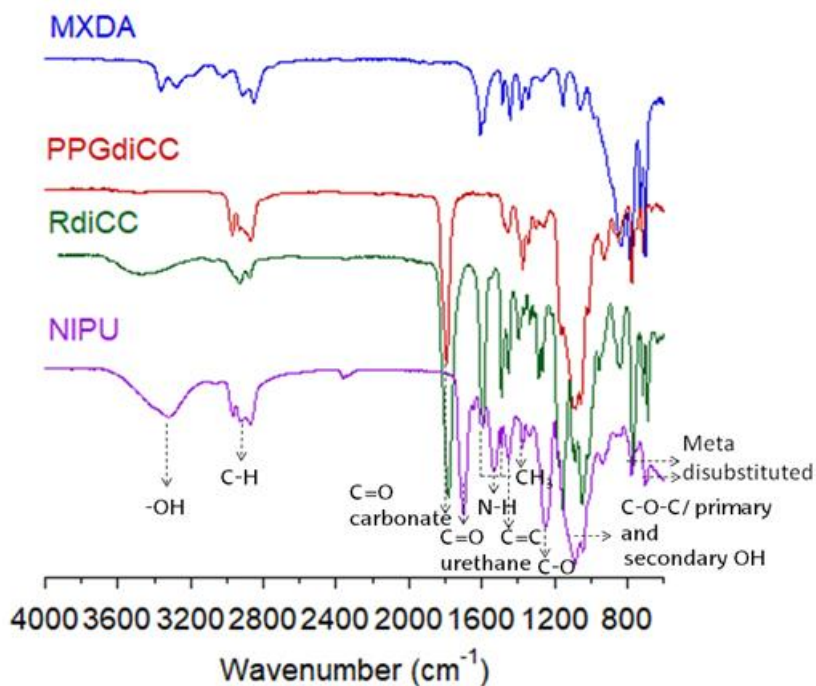
Figure 12.FTIR-ATRused for the following of the reaction.

The synthesized product was characterized by ^{1}H-NMR spectroscopy. Figure 13 shows the ^{1}H-NMRobtained for 60/40-MXDA and the corresponding assignation of the signals. Formation of urethane bond was confirmed by the appearance of a signal at 7.6-7.8 ppm, which corresponds to the proton of the -N<u>H</u>-C(O)O of the carbamate linkage. Additional signals at 5.3 ppm, which belong to OH groups confirmed the opening of the cyclic carbonates.
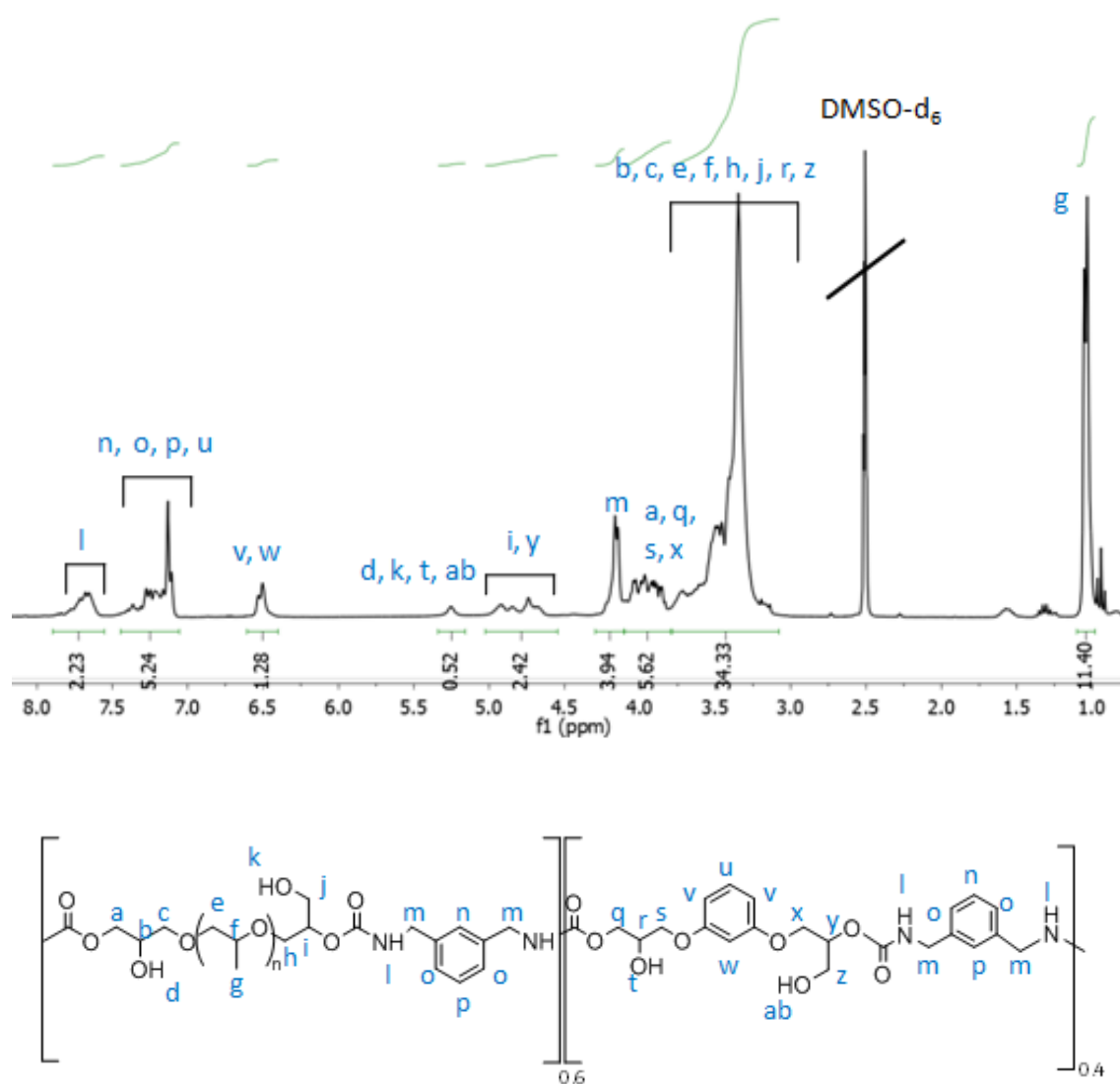
Figure13. ¹H-NMR of 60/40-MXDA.[26]

2.2. Rheology:

With the aim of knowing the behavior of the materials, temperature sweep measurements in parallel plates were performed. Figure 14 shows the storage and loss moduli for the compositions as a function of temperature and the corresponding tanδ. Analyzing the tanδ curve, two peaks can be differed. On the one hand, the smallest peak indicates that there was a T_g around 10-30ºC. On the other hand, it can be seen a higher peak which corresponds to a T_g around 100-110ºC.The glass transition temperature increased while the proportion of RdiCC increased in the composition. This happened because as long as the hardness of the polymer

chain increased, the value of the glass transition temperature also became higher. The mobility of the chain decreased and a higher temperature was needed to reach the T_g and to start the movement of the polymer chains. The presence of two different T_g indicated the phase separation of the materials.
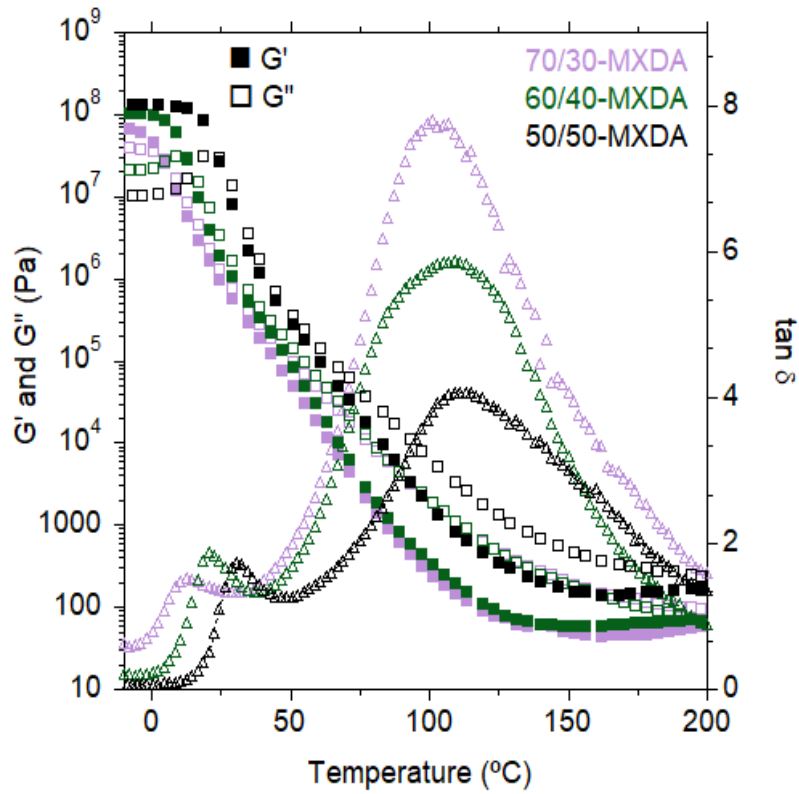

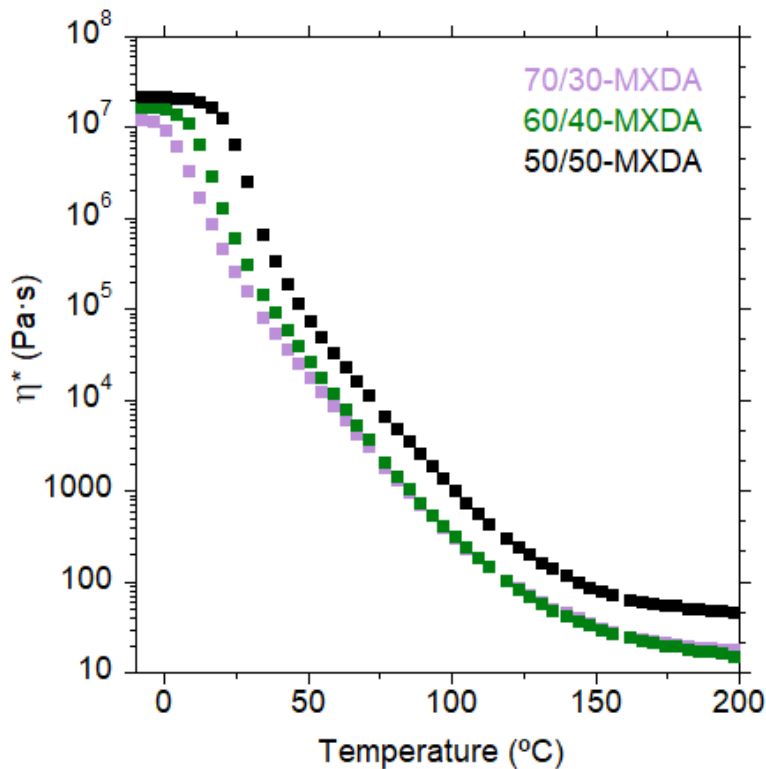Figure 14. Temperature sweep experiments for the three formulations.

Figure 15. Complex viscosity as a function of temperature.

2.3. Evaluation of the adhesive properties:

Adhesive properties of the formulations were evaluated by different experiments. Firstly, probe tack was performed to evaluate the stickiness of the materials at different temperatures. Then, lap-shear strength measurements were fulfilled on stainless steel substrates, and afterwards, two rebounding were carried out to address the thermoreversible behavior of the materials. Finally, Shear Adhesion Failure Temperature (SAFT) and Shear Resistance experiments were conducted.

2.3.1. Tack:

Tack is defined as the ability of a material to form an instant bond when it is brought into contact with a surface. In this case, the surface used was a cylinder of 5mm. In figure 15, the complex viscosity curve can be seen, and the temperature of the tests was chosen taking into account the temperature when the complex viscosity of the materials was in the range of 1000-2000Pa·s. In figure 16, the stress-strain curves obtained are depicted.
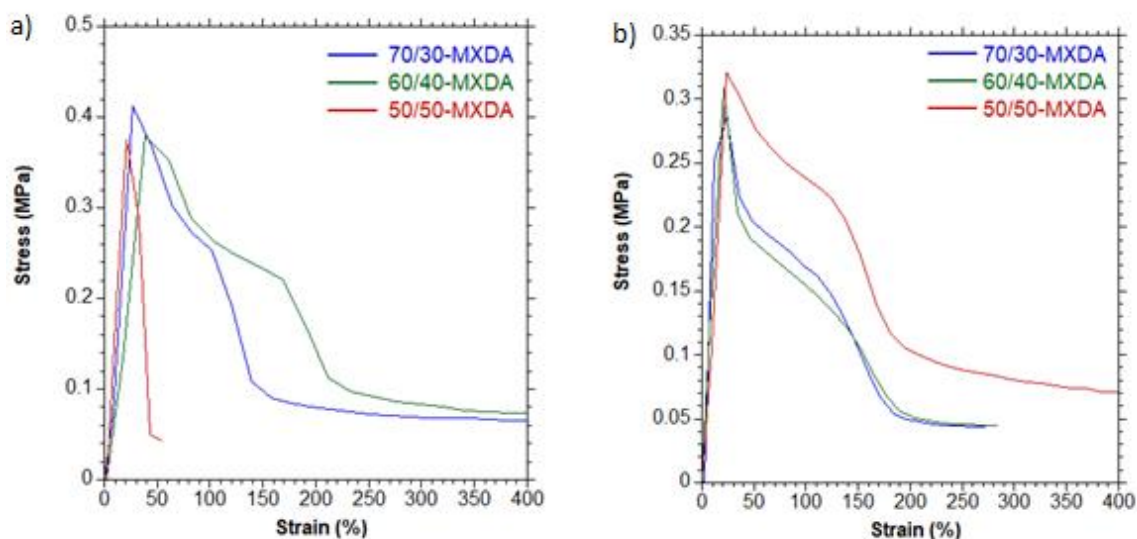
Figure 16. Probe tack stress-strain curves of the three formulations. a) Test temperature 80ºC b) Test temperature 100ºC.

The three formulations had a similar maximum stress (Figure 16a). That peak was then followed either by a sharp decrease or by a stabilization of the stress at a nearly constant value. In the case of the sharp decrease, the adhesive layer debonds rapidly from the probe and the adhesion energy is low. On the contrary, a stabilization of the stress (plateau) is a signature of the creation of a fibrillating structure. In the case of 50/50-MXDA, an interfacial failure was obtained. The sharp maximum and the very small area under the curve revealed the low capacity of the adhesive to wet the surface. As a result, the material was detached from the probe without leaving any residue. Regarding 60/40-MXDA as well as 70/30-MXDA, liquid-like or cohesive failure happened, as cohesive forces of the polymer were less strong than the adhesion to the probe. The capacity for fibrillation was slightly higher in 60/40-MXDA than in 70/30-MXDA, since a greater plateau was achieved. Otherwise, in figure 16bwe can observe that a liquid-like or cohesive failure was obtained with the three formulations. 60/40-MXDA and 70/30-MXDA had very similar behaviours, while 50/50-MXDA was able to retain a bit more the cohesion, which correlated with the higher G' at 100 ºC in the rheological experiments.

2.3.2.   Lap-shear:

Lap-shear specimens were prepared as described in experimental part. Adhesion performance of the copolymers was evaluated on stainless steel substrates. Lap-shear strength was calculated dividing the force at break of the bond line by the area of gluing.
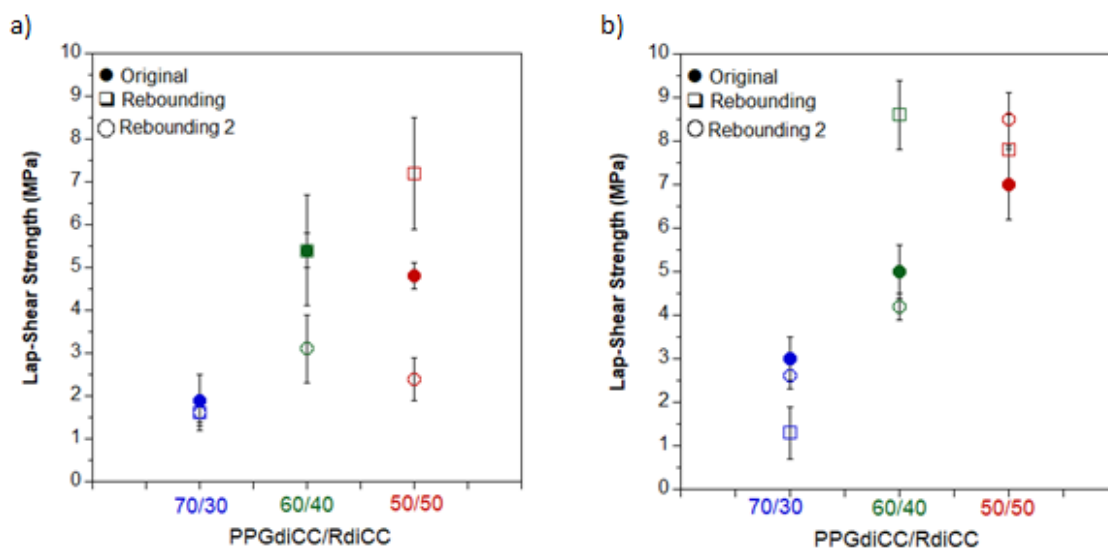

Figure 17.Comparison of the three formulations regarding lap-shear tests and both reboundings, taking into account the average lap-shear strength value and the error. a) Samples were applied onto the substrates at 80ºC. b) Samples were applied onto the substrates at100ºC.

Lap-shear strength values for compositions applied at 80 ºC and 100 ºC are depicted in Figure 17a and 17b, respectively. When materials were applied at 80 ºC 60/40-MXDA and 50/50-MXDA compositions showed similar and better performance than 70/30-MXDA, while when adhesives were applied at 100 ºC, lap-shear strength of 50/50-MXDA increased. This is correlated with the results obtained in tack measurements. The higher temperature, the greater liquid behavior of the PHU having a better ability to wet the surface of the adherends and improving adhesive performance. Thermoreversible adhesion of the polymers was addressed by rebounding adhesives two times (rebounding and rebounding 2 in Figure 17) after breaking the bond line. In a first rebounding, substrates were joined together again directly and put into the oven at 80 or 100 ºC to allow the breaking of interactions and rebuild the bonding. In a second rebounding, adhesives were removed totally from the substrates and applied into new specimens. Similar lap-shear strength values confirmed the efficiency of the materials for a second or third used.

After performing lap-shear tests, the nature of adhesion failure was recorded based on visual inspection of the substrates (Figures 18 and 19).In almost all cases an adhesive failure was observed. Adhesion forces with the substrates were lower than cohesive forces of the polymer. In some cases, the adhesive remained in both substrates, presenting a coadhesive failure since both pieces fitted perfectly together.

Figure 18. Photos of the representative adhesion failure of the adhesives applied at 80ºCfor a) 70/30-MXDA; b) 60/40-MXDAand c) 50/50-MXDA.
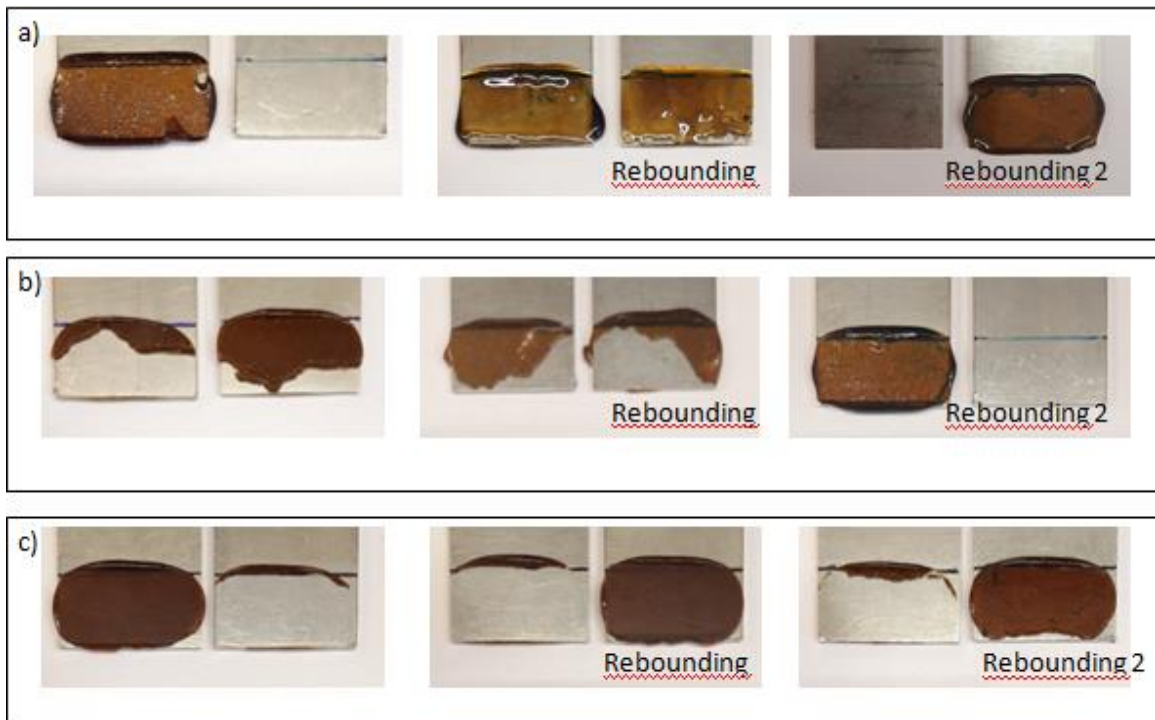
Figure 19. Photos of the representative adhesion failure of the adhesives applied at 100ºC for a) 70/30-MXDA; b) 60/40-MXDA and c) 50/50-MXDA.

2.3.3. SAFT and Shear Resistance:

SAFT and Shear Resistance specimens were prepared as described in experimental part. In these tests, service temperature (SAFT) and creep resistance (Shear) of the adhesives were addressed, and in figure 20 the obtained results can be seen. Higher service temperature as well as creep resistance values were achieved while the proportion of the hard segment increased, as it increased the rigidity of the polymer chain, so that it needed greater temperatures and times for falling. On the other hand, better results were obtained when the adhesives were applied onto the substrates at 100ºC than when they were applied at 80ºC, due to the fact that when the material is more rigid, a higher temperature is needed for a greater adhesion.
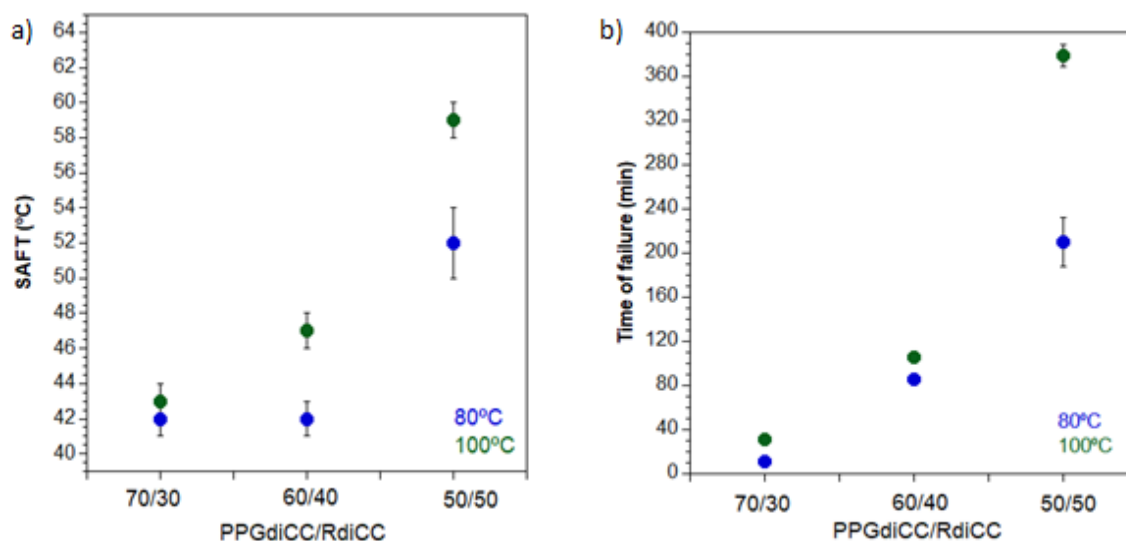
Figure 20. a) Average value of the results for SAFT experiments of the three formulations at 80ºC and 100ºC. b) Average value of the results for Shear Resistance experiments of the three formulations at 80ºC and 100ºC.

After performing these tests, the nature of adhesion failure was recorded based on visual inspection of the substrates. In all cases a cohesive failure was observed. Adhesion forces between the adhesives and the substrates were higher than the cohesive forces of the polymer, which were lower as the hard segment decreased in the composition.

3. *Influence of the diamine:*

The influence of the aromatic ring of the diamine was studied by changing the aromatic diamine to an (cyclo)aliphatic one (Figure 21). In the three formulations mentioned before, the best results were obtained using a 50/50 molar ratio of dicyclic carbonates (PPGdiCC/RdiCC). This is why these formulations were also synthesised with that molar ratio of dicyclic carbonates. Materials were characterised as previously.
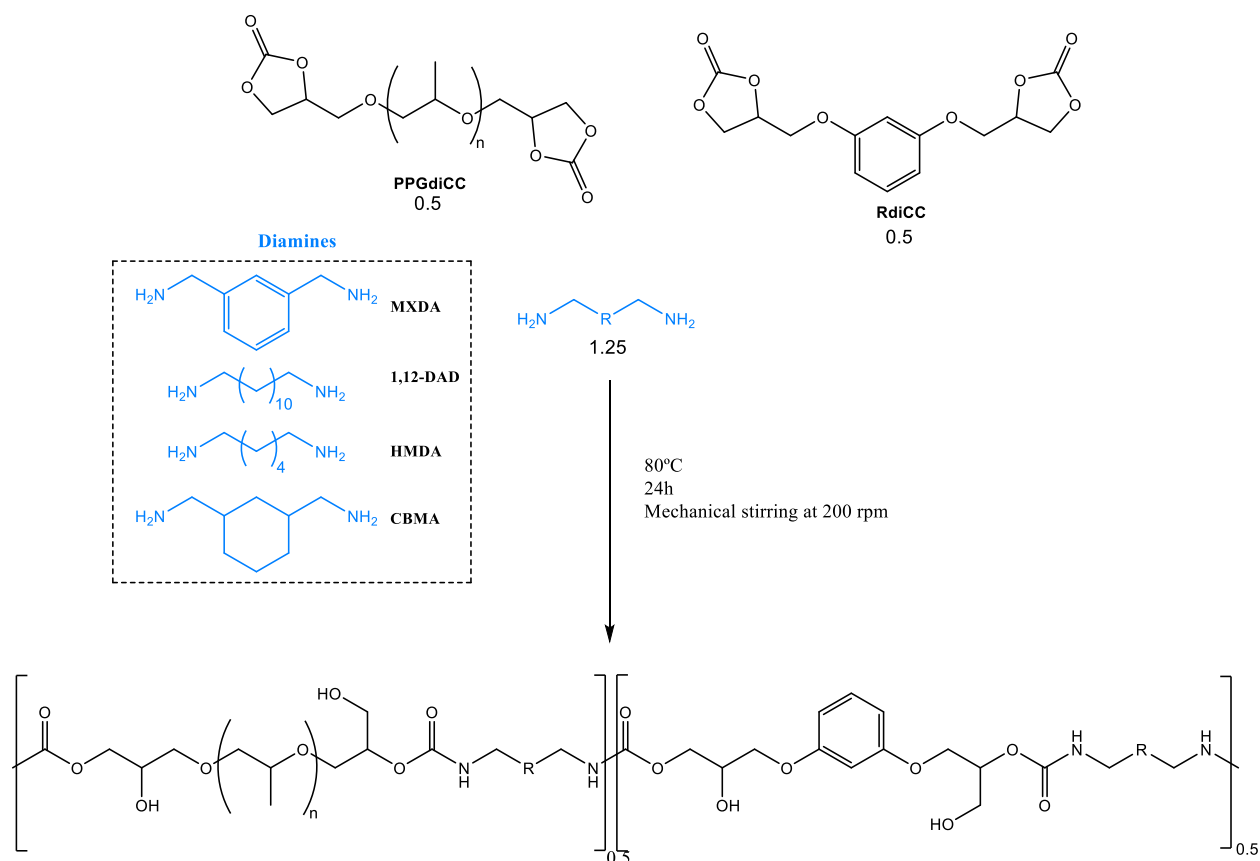
Figure 21. Synthesis of PHU adhesives based on polyaddition reaction, changing the diamine.

3.1.   Rheology:

After the synthesis, rheology measurements were performed to study the behaviour of the materials. In the case of 50/50-HMDA a temperature sweep experiment in parallel plates was performed, whereas a DMTA was performed with 50/50-DAD. Figure22 shows the storage moduli, loss moduli as well as $\tan\delta$ of each material as a function of temperature. In both cases, the storage moduli was higher than the loss moduli between the temperature range of the tests, meaning that the materials did not flow. Therefore ,these two formulations were left aside as they did not present a region with adhesives properties.
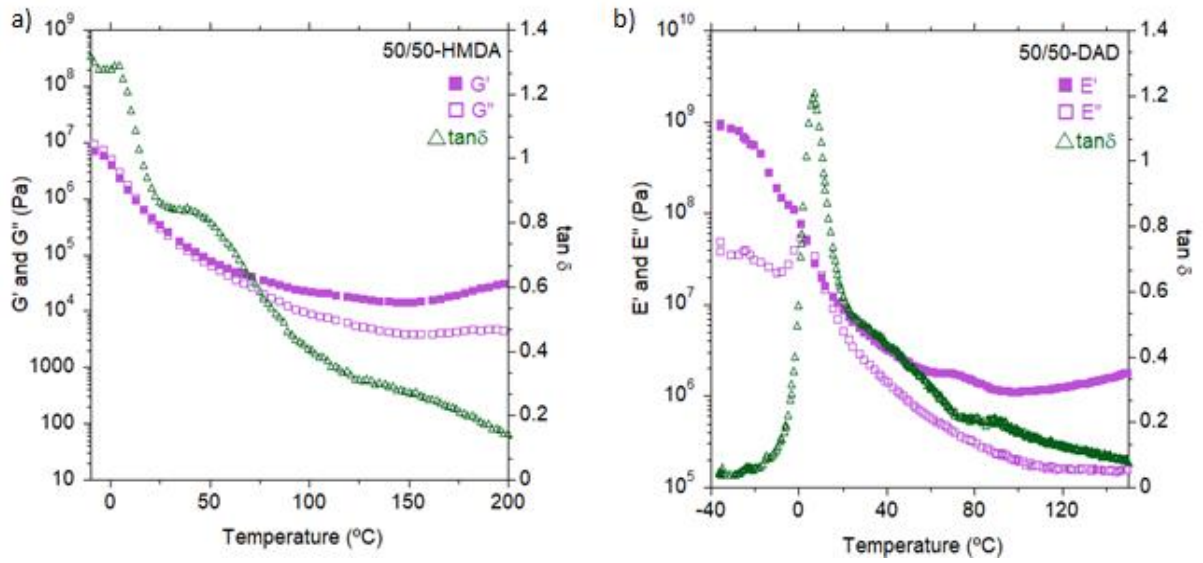
Figure 22. a) Temperature sweep experiment of 50/50-HMDA. b) DMTA of 50/50-DAD.

On the other hand, in the case of 50/50-CBMA, a temperature sweep experiment in parallel plates was performed. In figure 23, the comparison between the results obtained with 50/50-MXDA and 50/50-CBMA can be seen. Analysing the $\tan\delta$ curve, two peaks can be differed in both cases. The value of the T_g was higher in 50/50-MXDA as the aromatic diamine increased the rigidity of the polymer and additionally can establish non-covalent interactions between different chains (π-π interactions). Nonetheless, there was not a huge difference between the rheological measurements of both formulations.
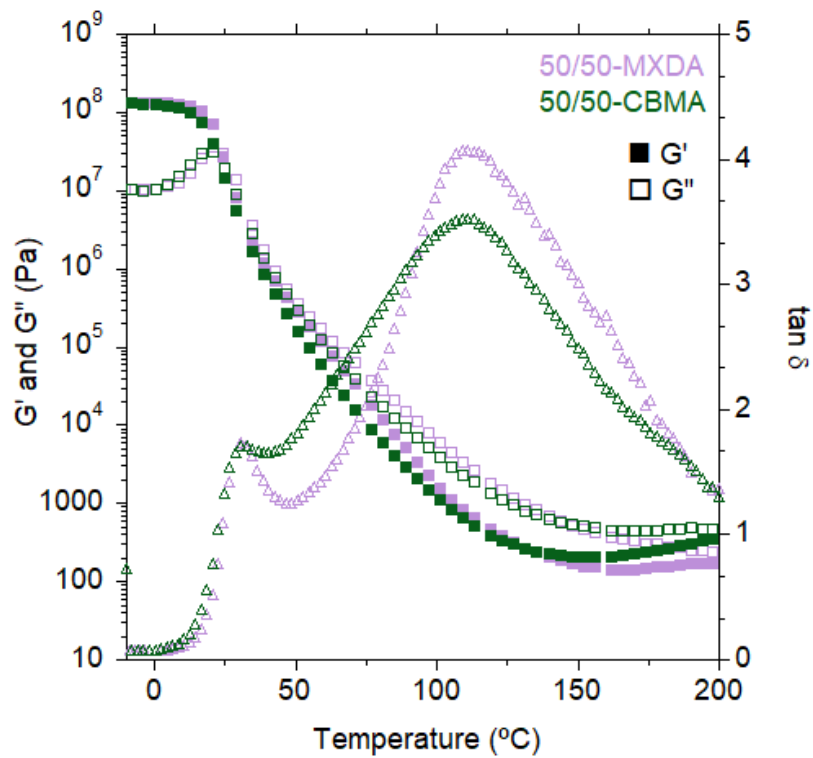
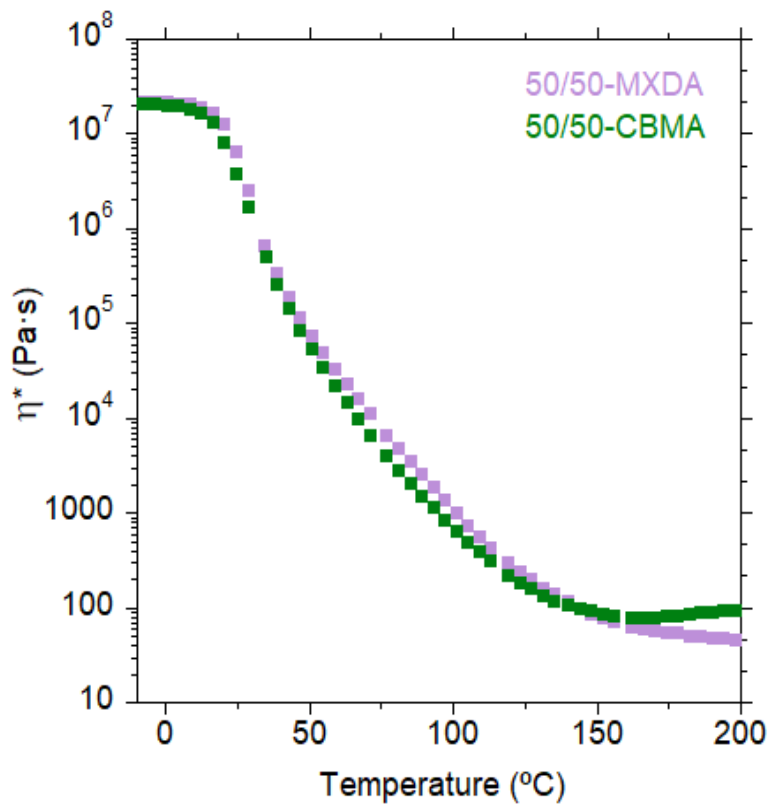Figure 23. Temperature sweep experiments for 50/50-MXDA and 50/50-CBMA.

Figure 24. Complex viscosity as a function of temperature.

3.2. Evaluation of the adhesive properties:

As previously, adhesive properties were evaluated by different experiments. Firstly, probe tack was performed to evaluate the stickiness of the materials at different temperatures. Then, lap-shear strength measurements were fulfilled on stainless steel substrates, and afterwards, two reboundings were carried out to address the thermoreversible behaviour of the materials. Finally, Shear Adhesion Failure Temperature (SAFT) and Shear Resistance experiments were conducted. In this case, comparisons between 50/50-MXDA and 50/50-CBMA were done, to assess the influence of the diamine.

3.2.1. Tack:

This test was performed to evaluate the stickiness of the materials. In figure 24, the comparison between the complex viscosity curve for 50/50-MXDA and 50/50-CBMA can be seen. As the rheological measurements obtained with 50/50-CBMA were similar to the ones obtained with 50/50-MXDA, the samples used for evaluating the adhesive properties were prepared at 80ºC and 100ºC. In figure 25, the stress-strain curves obtained can be seen.
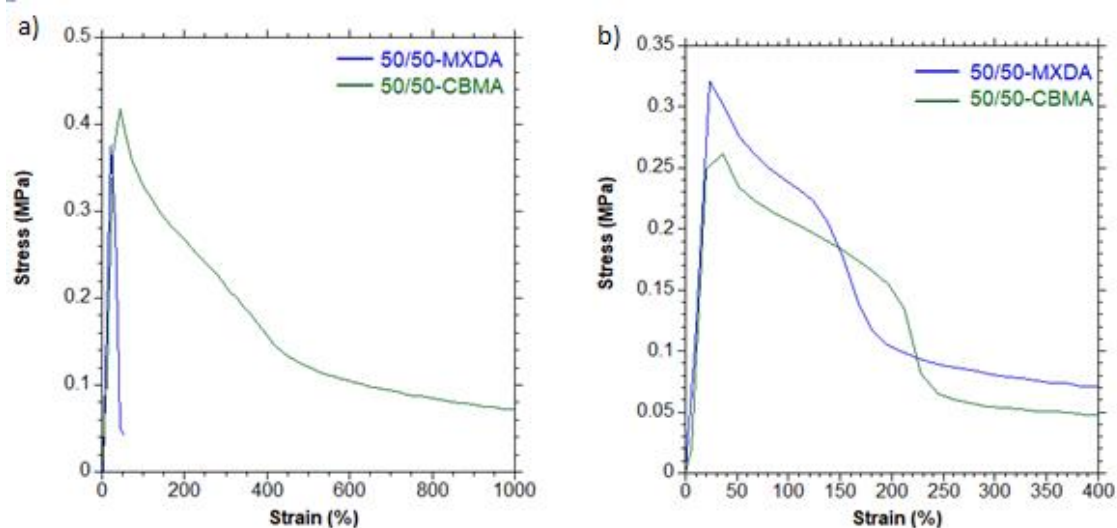

Figure 25. Comparison of probe tack stress-strain curves of 50/50-MXDA and 50/50-CBMA. a) Test temperature 80ºC b) Test temperature 100ºC.

The 50/50-CBMA presented a greater liquid-like behavior, as the adhesion forces to the probe were higher than the cohesive forces of the polymer. Otherwise, in figure 25b we can observe

that the behaviour of 50/50-MXDA changed, as a liquid-like or cohesive failure was obtained in both cases. Regarding 50/50-CBMA, the maximum stress decreased correlating with a decrease in the storage modulus from rheological measurements.

3.2.2. Lap-shear:

Lap-shear specimens were prepared as described in experimental part. Adhesion performance of the copolymers was evaluated on stainless steel substrates. Lap-shear strength was calculated dividing the force at break of the bond line by the area of gluing.
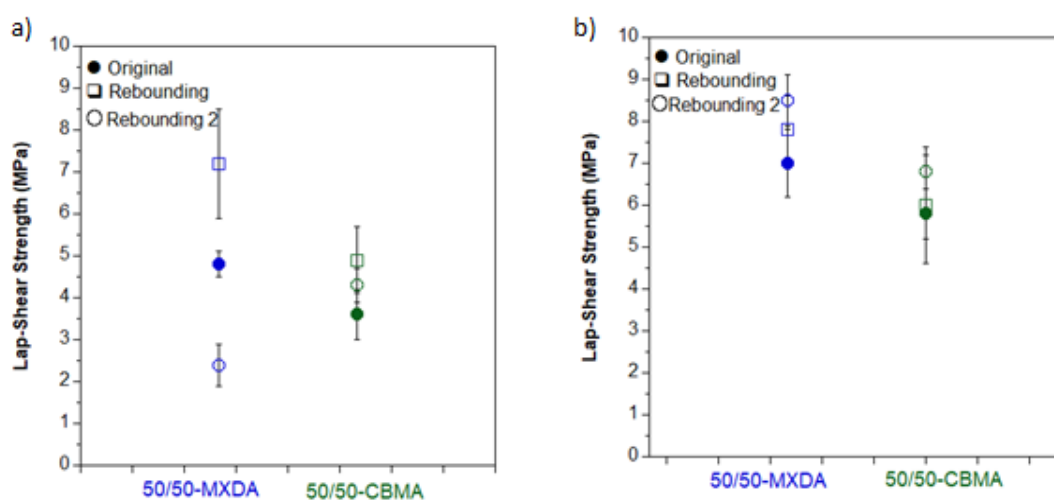

Figure 26. Comparison of 50/50-MXDA and 50/50-CBMAregarding lap-shear tests and both reboundings, taking into account the average lap-shear strength value and the error. a) Samples were applied onto the substrates at 80ºC. b) Samples were applied onto the substrates at100ºC.

Lap-shear strength values for compositions applied at 80 ºC and 100 ºC are depicted in Figure 26a and 26b, respectively. In both cases, better results were accomplished with 50/50-MXDA than with 50/50-CBMA. This happened because the aromatic ring increases the hardness of the polymer chain, increasing its adhesive properties. In addition, when adhesives were applied at 100 ºC, lap-shear strength values increased in both cases. The higher temperature of application, the greater liquid behavior of the NIPU, achieving a better ability to wet the surface of the adherends and improving adhesive performance. Thermoreversible adhesion of the polymers was addressed by rebounding adhesives two times (rebounding and rebounding

2 in Figure 26) after breaking the bond line. In a first rebounding, substrates were joined together again directly and put into the oven at 80 or 100 ºC to allow the breaking of non-covalent interactions. In a second rebounding, adhesives were removed from the substrates and applied into new specimens. Similar lap-shear strength values confirmed the efficiency of the materials for a second or third used.

After performing lap-shear tests, the nature of adhesion failure was recorded based on visual inspection of the substrates (Figure 27). In almost all cases an adhesive failure was observed. The cohesive forces of the polymer were higher than the adhesion forces with the substrates. In some cases, the adhesive remained in both substrates, presenting a coadhesive failure since both pieces fitted perfectly together.
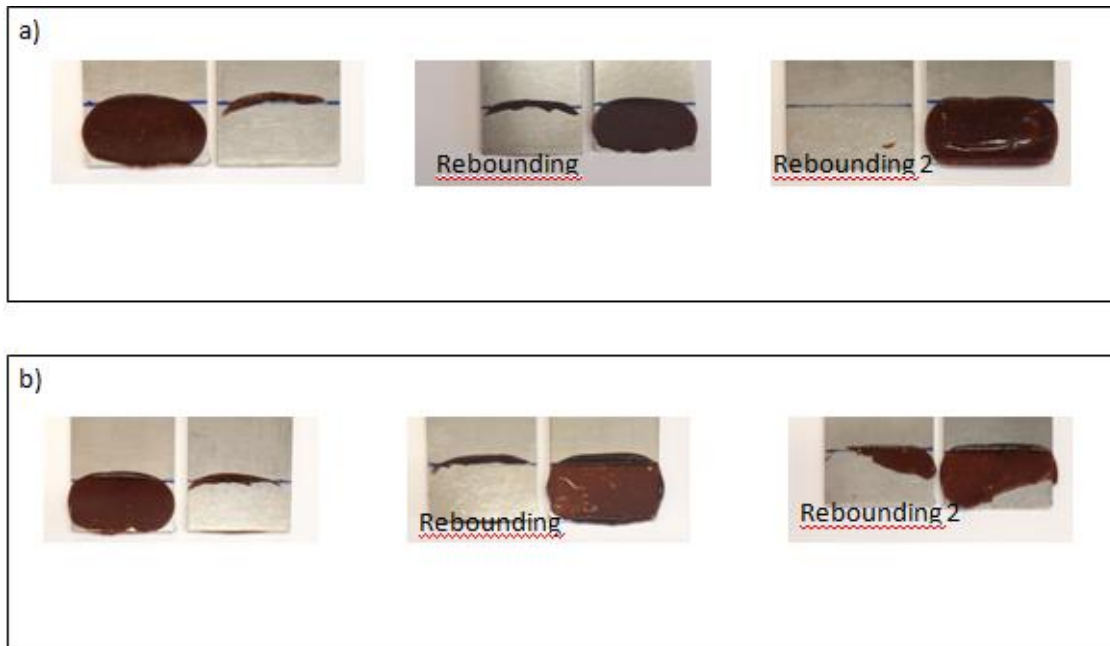

Figure 27. Photos of the representative adhesion failure of 50/50-CBMA. a) Adhesives applied at 80ºC. b) Adhesives applied at 100ºC.

3.2.3. SAFT and ShearResistance:

SAFT and Shear Resistance specimens were prepared as described in experimental part. Taking into account that the lap-shear strength values obtained at 100ºC were higher than the ones obtained at 80ºC, these experiments were done applying the adhesives onto the substrates at 100ºC. In these tests, service temperature (SAFT) and creep resistance (Shear) of the

adhesives were addressed and in figure 28 the obtained results can be seen. The service temperature as well as the creep resistance obtained was higher in the case of 50/50-MXDA, as the adhesives were able to stand higher temperatures and they resisted more time before falling. That had to do with the growth in the rigidity of the polymer chain when using an aromatic diamine.
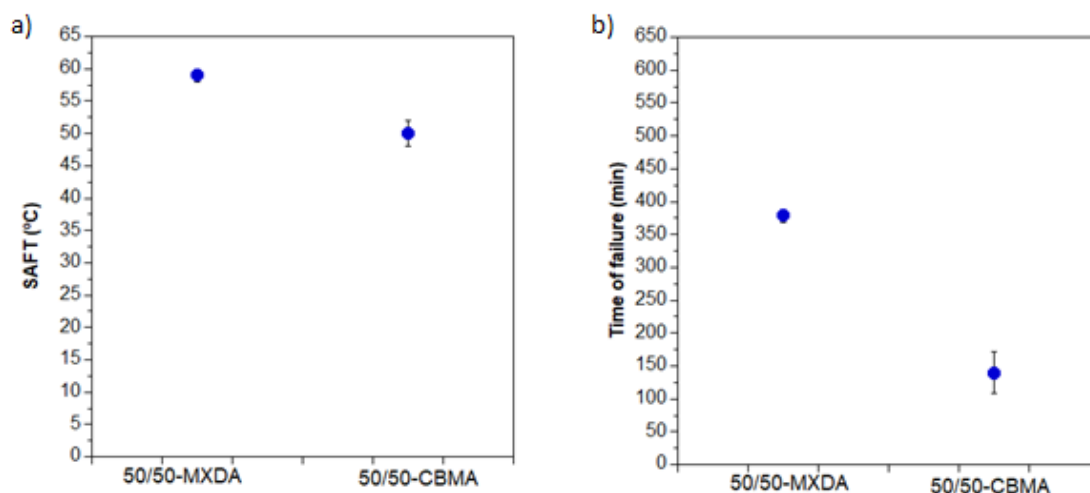

Figure28. a) Comparison of the average value of the service temperature of 50/50-MXDA and 50/50-CBMA at 100ºC. b) Comparison of the average value of the creep resistance of 50/50-MXDA and 50/50-CBMA at 100ºC.

After performing SAFT and Shear Resistance experiments, the nature of adhesion failure was recorded based on visual inspection of the substrates. In all cases a cohesive failure was observed. Meaning that adhesion forces between the adhesives and the substrates were higher than the cohesive forces of the polymer.

In all these tests done to evaluate the adhesive properties, better results were obtained when using MXDA than when using CBMA. So, it can be said that the hardness of the polymer chain is an important parameter regarding adhesive properties.

4. *Influence of the hard segment:*

To study the influence of the hard segment, the same synthesis was done but exchanging RdiCC for BdiCC (Figure 29). As for the moment the best results were obtained with 50/50-MXDA, the formulation using BdiCC was also synthesised with that composition.
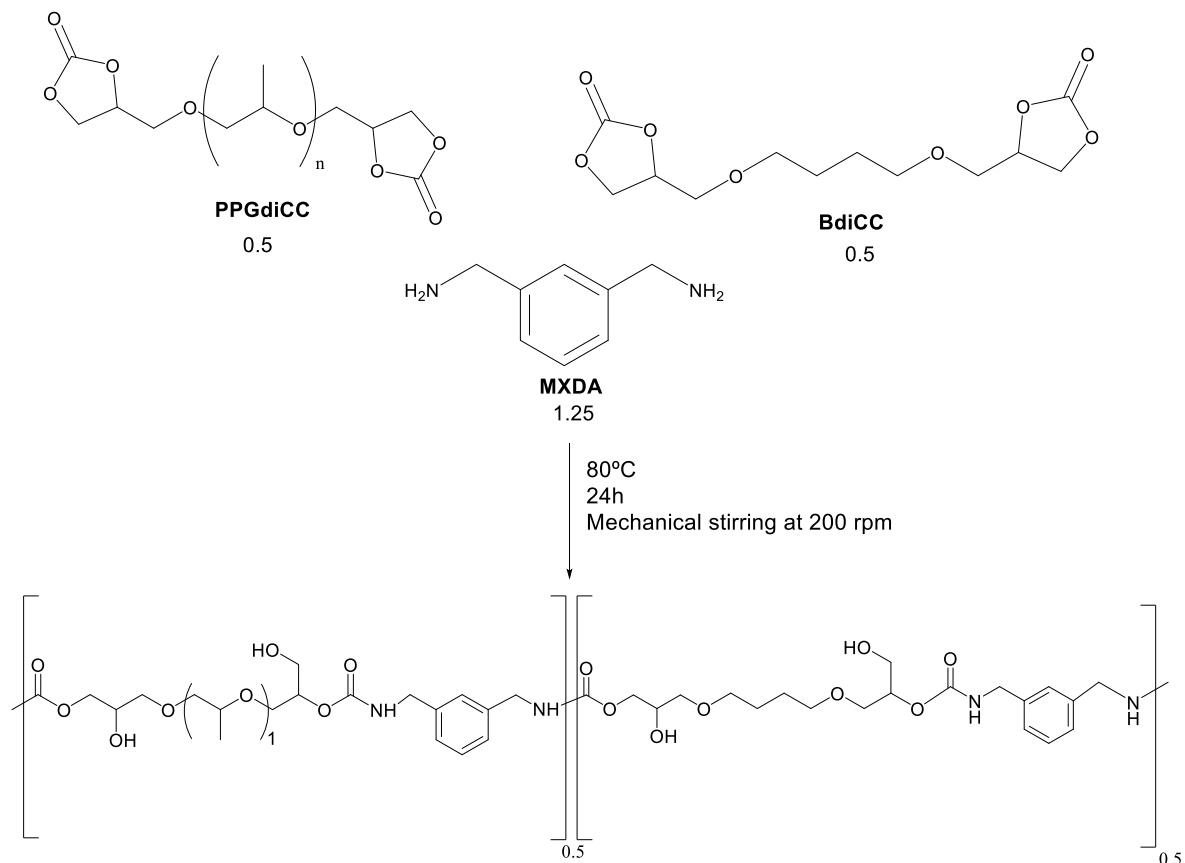

Figure 29. Synthesis scheme of the copolymer when BdiCC was employed as hard segment.

4.1. Rheology:

With the aim of knowing the behavior of the materials, temperature sweep measurements in parallel plates were performed. In figure 30 the comparison between the results obtained with 50/50-MXDA and 50/50B-MXDA can be seen. Analysing the $\tan\delta$ curve, two peaks can be differed in both cases. The value of the T_g was by far higher in 50/50-MXDA as RdiCC increased the rigidity of the polymer.
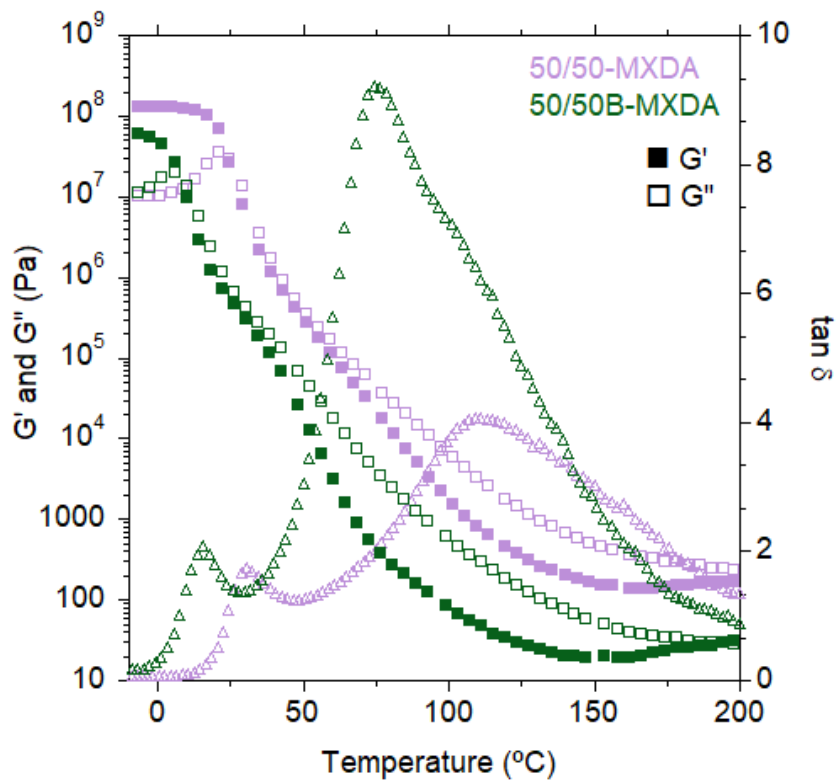
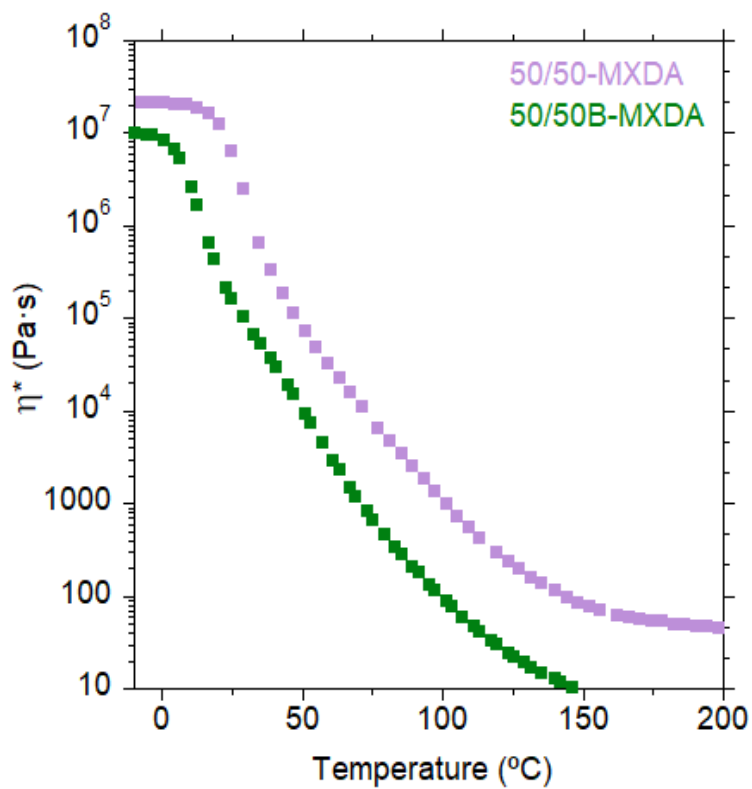Figure 30. Temperature sweep experiments for 50/50-MXDA and 50/50B-MXDA,

Figure 31. Complex viscosity as a function of temperature.

4.2.   Evaluation of the adhesive properties:

To evaluate influence of the hard segment on the adhesive properties we have followed and performed the same experiments as for the previous compositions.

4.2.1.   Tack:

This test was performed to evaluate the stickiness of the materials. In figure 31, the comparison between the complex viscosity curves of 50/50-MXDA and 50/50B-MXDA can be seen. There was a considerable difference between the complex viscosity in two cases. Tack probe test for the 50/50B-MXDA composition was only evaluated at 80 ºC since its complex viscosity at 100 ºC was quite below 1000 Pa·s, value that we established as criterion to measure tackiness. In figure 32, the stress-strain curves obtained are depicted.
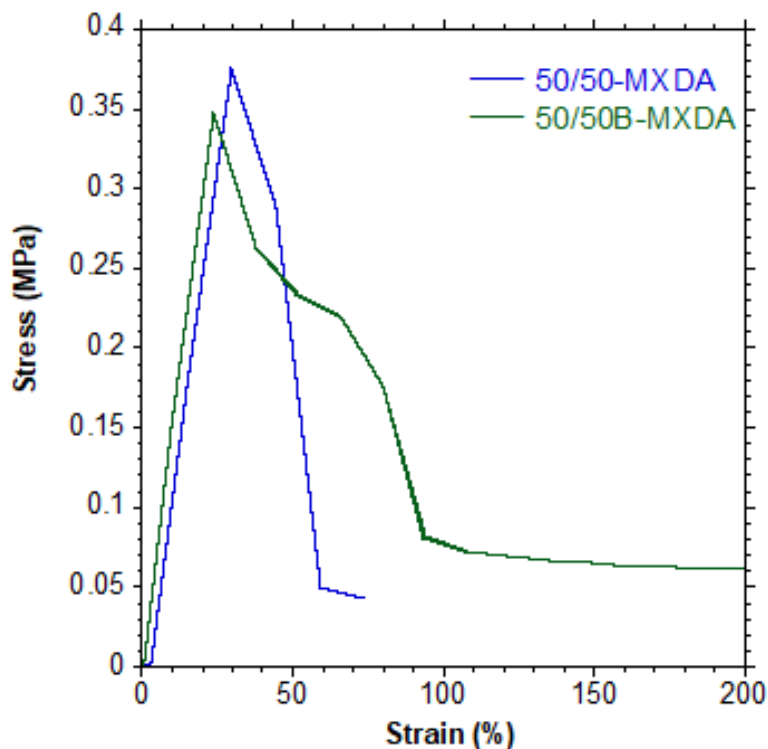

Figure 32. Stress-strain curves for 50/50-MXDA and 50/50B-MXDA compositions

It can be observed a slight greater liquid-like behavior when 1,4-butanediol dicyclic carbonate was employed as hard segment in the formulation. Stress fell rapidly because cohesive forces of the fibers were not enough strong to maintain together the adhesive.

4.2.2. Lap-shear:

Lap-shear specimens were prepared as described in experimental part. Adhesion performance of the copolymers was evaluated on stainless steel substrates. Lap-shear strength was calculated dividing the force at break of the bond line by the area of gluing.

Lap-shear strength values for compositions applied at 80 ºC and 100 ºC are depicted in Figure 33a and 33b, respectively. Far better results were accomplished with 50/50-MXDA than with 50/50B-MXDA, as RdiCC increased the hardness of the polymer chain, increasing its adhesive properties. The product synthesised in the case of 50/50B-MXDA, was soft. As a result, the lap-shear strength values purchased were reasonably low, since the composition of the hard and the soft segment was not correctly adjusted. Thermoreversible adhesion of the polymers was addressed by rebounding adhesives two times (rebounding and rebounding 2 in Figure 33) after breaking the bond line, as for the rest of the compositions. In a first rebounding, substrates were joined together again directly and put into the oven at 80 or 100 ºC to allow the breaking of non-covalent interactions. In a second rebounding, adhesives were removed from the substrates and applied into new specimens. Similar values for the 50/50B-MXDA were obtained after the reboundings confirming the thermoreversibility of the materials. Nevertheless, values were still low for adhesion purposes.
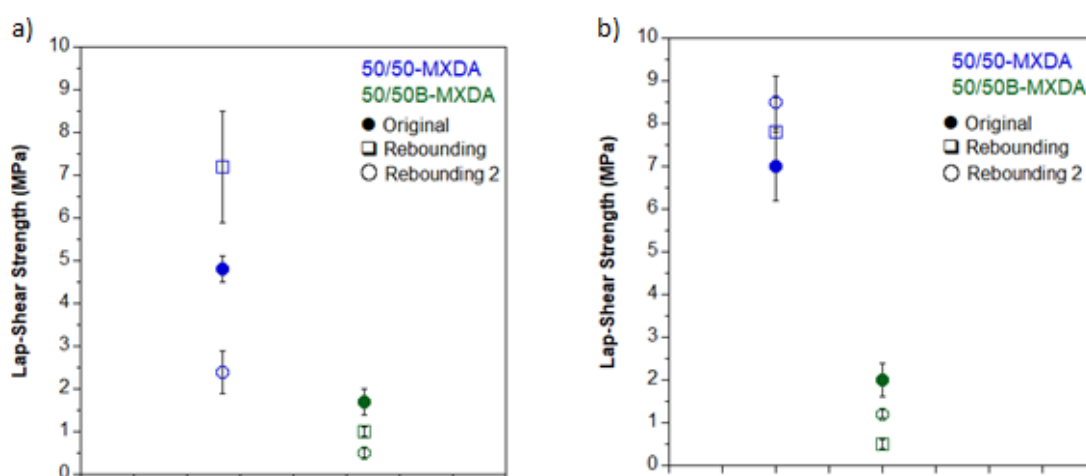
Figure 33. Comparison of 50/50-MXDA and 50/50B-MXDA regarding lap-shear tests and both reboundings, taking into account the average lap-shear strength value and the error. a) Samples were applied onto the substrates at 80ºC. b) Samples were applied onto the substrates at100ºC.

After performing lap-shear tests, the nature of adhesion failure was recorded based on visual inspection of the substrates (Figure 34). In all the cases, a cohesive failure was observed meaning that the cohesive forces of the polymer were lower than the adhesion forces with the substrates.
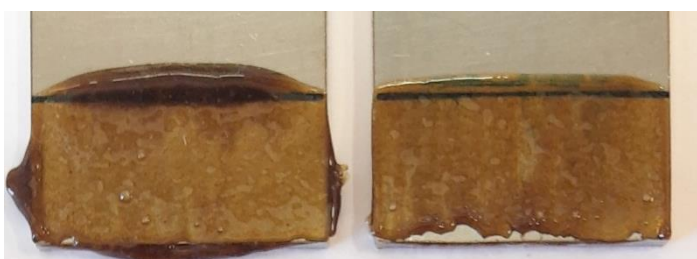

Figure 34.Photo of the representative cohesive failure of 50/50B-MXDA.

4.2.3. SAFT and Shear Resistance:

SAFT and Shear Resistance specimens were prepared as described in experimental part. Taking into account that the lap-shear strength values obtained at 100ºC were almost the same than the obtained data at 80ºC, these experiments were performed applying the adhesives onto the substrates at 80ºC. In these tests, service temperature (SAFT) and creep resistance (Shear) of the adhesives were addressed, and in figure 35 the obtained results can be seen. Higher service temperature as well as creep resistance values were achieved in the case of 50/50-MXDA as it resisted higher temperatures and withstood more time before falling. These results had to do with the softness of the synthesised product.
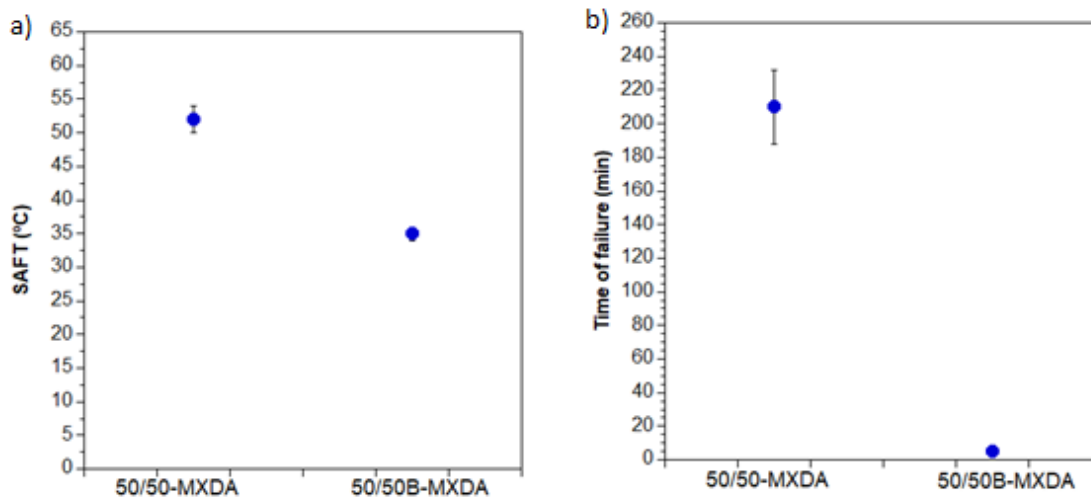
Figure 35. a) Comparison of the average value of the service temperature of 50/50-MXDA and 50/50B-MXDA at 80ºC. b) Comparison of the average value of the creep resistance of 50/50-MXDA and 50/50B-MXDA at 80ºC.

In all these tests done to evaluate the adhesive properties, better results were obtained when using RdiCC than when using BdiCC. As a consequence, it can be said that BdiCC seems to be too much soft for obtaining adhesive materials with optimal properties.

5. *Lap-shear in different substrates:*

Finally, the ability of the adhesives for gluing different substrates was addressed by performing lap-shear strength measurements on oak wood, HDPE and PMMA. These tests were performed using 50/50-MXDA, owing to the fact that the best results were achieved with that formulation. As it can be seen in figure 36, low lap-shear strength values were measured when polymeric substrates were glued. Nevertheless, PMMA showed stronger interactions with the adhesive than HDPE, due to its greater surface energy, as the higher surface energy, the easier wettability of the substrate and therefore stronger attractive forces were created between the adhesive and the substrate.[27] In addition, PMMA can establish hydrogen bonding interactions with the adhesive, while HDPE was not able to do it. For all polymeric substrates adhesive failure was observed showing the low affinity between adherend and adhesive. In contrast, when a polar substrate like oak wood was bonded, higher lap-shear strength values were

obtained. This demonstrates that the adhesives had a higher interaction with polar substrates, as the hydroxyl groups of the polymer chain had stronger interaction with these surfaces.
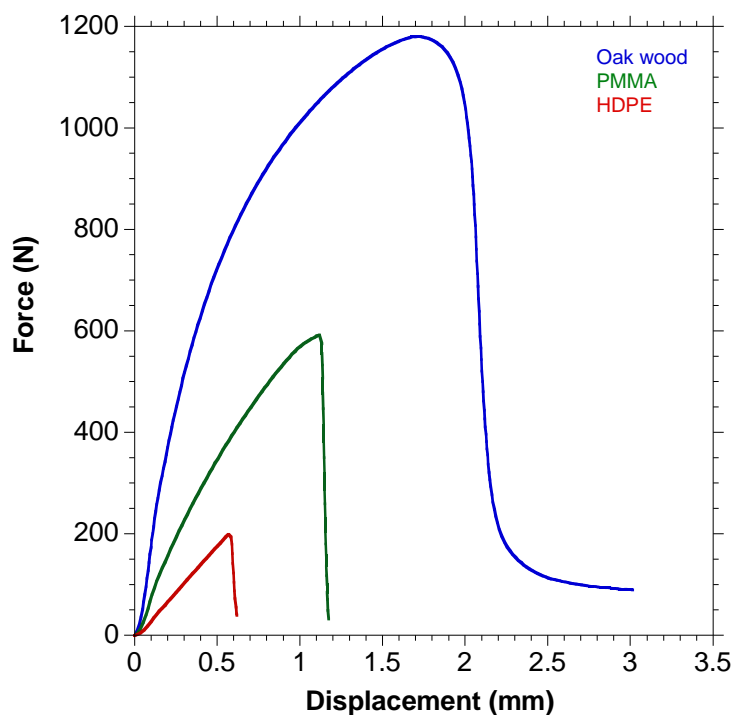

Figure36. Comparison of lap-shear strength curves for oak wood, PMMA and HDPE.

CONCLUSIONS:

Sustainable NIPU hot melt adhesives were synthesised by combining a diamine with two dicyclic carbonates, as one of them constituted the hard segment and the other one the flexible segment. Although several formulations were tried, the best results were achieved by mixing MXDA with PPGdiCC and RdiCC in a molar ratio of 50/50 of the dicyclic carbonates. In that case, lap-shear strength values from 4.8 to 7.0MPa were obtained. Regarding thermoreversible adhesion, values from 7.2 to 7.8MPa were obtained in the first rebounding, and in the second rebounding, values from 2.4 to 8.5MPa were obtained. Similar lap-shear strength values confirmed the efficiency of the materials for a second or third used. SAFT experiments addressed that the service temperature of this adhesive was between 52ºC and 59ºC, and Shear Resistance experiments probed that the time of failure was between 210

minutes and379 minutes. The comparison between 50/50-MXDA with the rest of the formulations, demonstrated the importance of balancing the proportion of the hard and soft segments as well as the importance of the rigidity of the polymer chain to obtain adhesives with optimal properties.

By doing the experimental part of the study, I have learned to manage in a laboratory as well as to organize my tasks. In addition, I have learned how to deal with the different issues that can appear through daily work. On the other hand, by performing the theoretical part of this work, I have assumed how to organize all the results obtained and how to write up all the work done in the laboratory.

CONCLUSIONES:

Combinando una diamina y dos carbonatos dicíclicos, mientras que uno de ellos forma el segmento rígido y el otro el segmento blando, se sintetizaron adhesivos hotmelt sostenibles de poliuretano sin isocianato. Se probaron diferentes formulaciones, pero los mejores resultados se obtuvieron al mezclar MXDA con PPGdiCC y RdiCC, con una proporción molar de 50/50 de los dicarbonatos cíclicos. En ese caso, se consiguieron valores de resistencia al cizallamiento entre 4.8 y 7.0MPa. Además, se estudió la adhesión termoreversible, obteniendo valores entre 7.2 y 7.8MPa en la primera repetición del pegado, mientras que, en la segunda repetición, se obtuvieron valores entre 2.4 y 8.5MPa. Los valores similares de resistencia al cizallamiento, confirmaron la eficacia de estos materiales para un segundo y tercer uso. La temperatura de servicio de estos adhesivos obtenida a través de experimentos de SAFT, se encuentra entre 52ºC y 59ºC, y el tiempo de caída obtenido mediante experimentos para analizar la resistencia al corte, se encuentra entre 210 y 379 minutos. La comparación de 50/50-MXDA con el resto de las formulaciones, demuestra la importancia de un buen balance entre las proporciones del segmento rígido y del segmento blando, así como la importancia de la rigidez de la cadena polimérica para obtener adhesivos con propiedades óptimas.

Durante el trabajo experimental de este estudio, he adquirido conocimientos para aprender a trabajar en un laboratorio y para organizar las diferentes tareas durante la semana. Además, he aprendido a sobrellevar los problemas que pueden aparecer repentinamente durante el

trabajo diario. Por otro lado, la parte teórica de este trabajo me ha servido para saber cómo organizar todos los resultados obtenidos y para saber cómo redactar todo el trabajo llevado a cabo en el laboratorio.

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