

Recyclable, remendable and healing polyurethane/acrylic coatings from UV curable waterborne dispersions containing Diels-Alder moieties

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Abstract

The aim of the present work is to increase the sustainability of UV curable waterborne polyurethane dispersions using the Diels-Alder chemistry. In this way, the obtaining of crosslinked polyurethane coatings presenting healing and recycling properties is proposed.

Thus, waterborne polyurethanes were obtained by the acetone process replacing the chain extender by a diol containing the Diels Alder adduct and using acrylic chain ends that allowed the UV cross-linking. Photo-DSC results showed that the Diels Alder adduct did not prevent the UV cross-linking of the coating. In addition, FTIR, DSC and rheological experiments confirmed the occurrence of the DA and retro DA reaction (at 60°C and 120°C respectively) in the cross-linked polymer. Thanks to this reaction, the materials obtained by this methodology could be healed and reprocessed when increasing the temperature as shown by the maintenance of the mechanical properties and carbon dioxide permeability after repairing. These results can be of great interest towards the development of more sustainable waterborne polyurethane coatings.

Keywords: Waterborne polyurethanes, UV crosslinking, Diels Alder Chemistry, Healing, recycling

Highlights: UV curable cross-linked waterborne polyurethanes containing Diels Alder adduct, effective cross-linking in presence of the adduct, Cross-linked samples can be repaired with temperature, possibility of recycling the samples containing high DA adduct concentration

1. Introduction

Because of the increasing environmental conscious, waterborne polyurethane (WPU) production is experiencing a great development [1]. The vast majority of WPUs are linear polymers dispersed in water thanks to the addition of a functionalized diol that acts as internal emulsifier [2, 3]. This compound is needed to have good colloidal stability, however it is responsible for the poorer solvent resistance that present WPUs when comparing with solvent based systems. One way to improve the properties of these polymers can be via cross linking [4]. Thus, different functionalities have been introduced in the polymeric backbone in order to induce the cross linking of the polymer by means of different reactions [5,6].

One of the most employed methods to crosslink the polyurethane dispersions is based on the introduction of acrylic double bonds that allow the UV curing via chain polymerization [7,8]. The UV curable waterborne polyurethane dispersions (UV-WPUs) do not contain volatile organic compounds (VOCs) and have a promising future in the coatings industry [9,10,11,12, 13].

It is clear that after UV curing, the cross-linked polyurethanes show better mechanical and chemical performance when comparing with the linear ones. However, the covalently cross-linked networks are unable to change their shape and this becomes a problem in the frame of the circular economy concept because they cannot be neither repaired nor recycled [14]. One way to overcome this problem can be introducing reversible covalent linkages in the polymer backbone. Currently, the development of these types of systems, named as Covalent Adaptable Networks (CANs), is gaining a great attention because the cross linking can be reverted under a stimulus [15, 16].

A great number of reversible reactions have been described in literature that can be useful to get an efficient reversible cross-linking. However only a few ones are able to fulfil the efficiency characteristics needed. One of them is the well-known Diels Alder (DA) reaction [17, 18]. The reaction between the furan and maleimide (DA reaction) is thermally reversible and gives rise to the formation of a cyclohexene ring (DA adduct). Thus, if this adduct is introduced in a cross-linked polymer network, the retro DA reaction will induce a reduction of the cross linking density which will increase the sample diffusion rate allowing both, the sample healing and the recycling [19].

In Polyurethane chemistry, the DA reaction has been used to obtain recyclable and healing materials. Some authors report the formation of furan-capped polyurethanes cross-linked with maleimide compounds [20,21,22,23]. There are also works where, using a similar strategy, a maleimide capped polyurethane is cross linked by means of a furan compound [24, 25, 26] or maleimide and furan capped polyurethanes are mixed [27]. The DA adduct can be also directly introduced in the polyurethane structure by means of a functionalized diol (using one pot strategy) [28, 29, 30, 31, 32].

As reported in the preceding paragraphs, it is clear that reversible polyurethane networks have been successfully obtained via DA reaction [33,34]. However, the works describing the introduction of DA moieties in waterborne polyurethanes are scarcely found, probably because of the hydrolysis of maleimide in basic medium

[35]. In addition, no works can be found about the synthesis of UV cross-linked waterborne polyurethanes containing DA groups and it is not clear if the presence of acrylic bonds can be an obstacle for obtaining this goal. Bearing this in mind, the aim of our work is to increase the sustainability of waterborne UV cross linked polyurethanes by introducing DA moieties that are supposed to impart repairing and recycling properties to the obtained dispersions. For this, purpose we introduced in a conventional waterborne polyurethane formulation a diol containing the DA adduct and acrylic double bonds as chain ends. After UV cross-linking we studied the DA reaction and its effect in the repairing and recycling properties of the obtained coatings.

2. Experimental

2.1. Materials

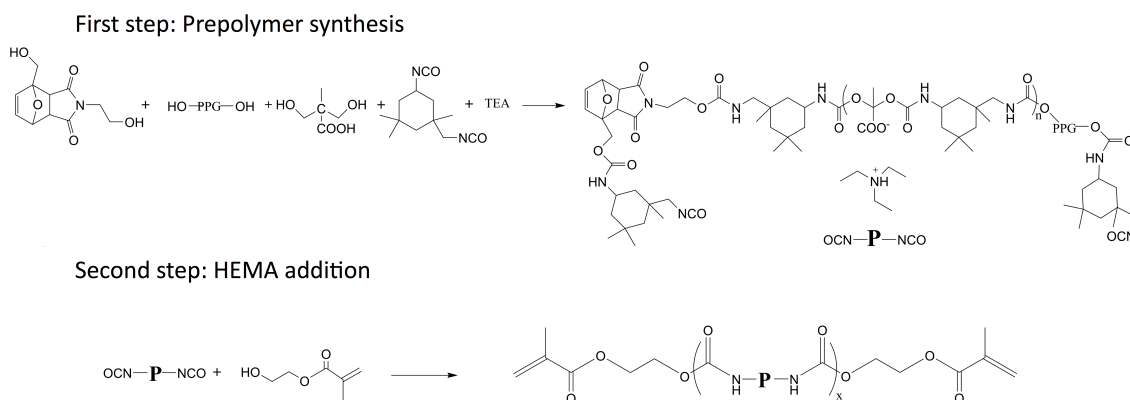
2-bis (hydroxymethyl) propionic acid (DMPA), triethylamine (TEA), dibutyltin diacetate (DBTDA), Isophorone diisocyanate (IPDI), 2-hydroxyethyl methacrylate (HEMA), polypropylene glycol (PPG) (M_n 1000 g/mol), 1-hydroxycyclohexyl phenyl ketone, ethanolamine, furfuryl alcohol (FA), 1,4 butanediol (BD), acetone, methanol, ethanol, tetrahydrofuran and toluene were purchased from Sigma-Aldrich Chemical Corporation. Exo-3,6-Epoxy-1,2,3,6-tetrahydrophthalic Anhydride was purchased from TCI Europe N.V.

2.2. Synthesis of temperature stimuli responsive waterborne polyurethanes (WPU)

The synthesis of waterborne polyurethanes was carried out by means of the “acetone process”, which consists in a two step procedure. In the first step, the polymer is synthesized in acetone, and a diol containing acid groups (that acts as internal emulsifier) is incorporated in the polymer backbone. In order to produce the dispersion water is added in a controlled way and finally, acetone is removed. The acid groups of the internal emulsifier incorporated during the polymerization process, allow the obtaining of stable dispersions.

The diol containing the DA adduct (2-(2-hydroxyethyl)-4-(hydroxymethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione (DA2OH) was synthesized as previously described [34]. Scheme 1 resumes the synthetic way to obtain the polyurethanes with the DA adduct and final acrylic double bonds (PUDAHEMA) and table 1 summarizes the reagent amounts used in the different reactions. Briefly, DA2OH, Polyol (PPG, 18g, 18mmol), internal emulsifier (DMPA, 1.18g, 8.8mmol), triethylamine (TEA, 12mmol), DBTDA (25mg, 800ppm) and acetone were introduced into a 250-mL jacket glass reactor and stirred mechanically. When the temperature of the reaction mixture was 57°C, IPDI (10 g, 113 mmol) was added to the flask. The reaction mixture was maintained at 57°C for 24 hours. Afterwards, 2-hydroxyethyl methacrylate (HEMA) was added to the reaction (stoichiometric ratio of OH and NCO) groups. Fourier transform infrared spectroscopy (FTIR) was used to follow periodically the reaction conversion. When the infrared absorbance of the NCO groups (around 2260 cm^{-1}) was negligible the reaction was stopped.

The reaction mixture was cooled at room temperature and the solid content was adjusted to 70 % using acetone. The reaction mixture was mechanically stirred at 300 rpms and in order to obtain the dispersion water was added drop-wise at $1.5 \text{ mL}\cdot\text{min}^{-1}$. Finally, acetone was removed under vacuum using a rotary evaporator at $30 \text{ }^\circ\text{C}$. The solid content of the resulting dispersion was 20 wt %. Two different polymers were obtained varying the functionalized diol and HEMA amounts (table 1). For comparison reasons, a polymer without the DA adduct was also synthesized replacing the DA adduct by 1,4 butanediol.



Scheme 1: Synthetic way to obtain acrylic capped polyurethanes.

Polymer	HEMA (mmol)	DA2OH (mmol)	DA2OH (wt%)	HEMA (wt%)	BD (mmol)
PUDA9HEMA5	12.8	12	9.3	4.9	0
PUDA11HEMA3	6.8	15	10.6	2.9	0
PUHEMA5	12.8	0	0	5.1	12

Table 1: Nomenclature and reagent amounts used in the reactions.

2.3. Crosslinking of the WPU dispersions

The required amount of the photoinitiator (1-hydroxycyclohexyl phenyl ketone) was dissolved in acetone and was mixed with the dispersion. The mixture was poured on a Teflon mould and left for one week in dark with the objective of evaporating the water but avoiding the radical polymerization. Afterwards, the samples were cured in the photo DSC or during 20 minutes with a Thorl Labds M365LP1 Led lamp with an intensity of $2 \text{ mW}/\text{cm}^2$ that had a wavelength of 365 nm. For the samples used in the FTIR studies the same procedure was followed but the casting was performed over KBr windows. The gel content of the samples was measured gravimetrically after soxhlet extraction using THF as solvent.

2.4. Instrumentation

A Nicolet 6700 spectrometer (Thermo Scientific) was used to record the spectra. The samples were prepared by casting onto KBr pellets. The spectra were obtained at a resolution of 4 cm^{-1} and 10 scans were recorded. For obtaining the spectra at high temperature a heater accessory (SPECAC) was used.

A Fourier Transform Bruker 300 MHz spectrometer (model Avance 300 DPX) was employed to obtain the ^1H liquid Nuclear Magnetic Resonance (NMR) spectra using deuterated chloroform (CDCl_3) as solvent.

The diameter of the particles was measured by Dynamic Light Scattering (DLS) in a 90Plus (Brookhaven) particle Size Analyzer.

Differential Scanning Calorimetry (DSC) study was performed from -80 to 180 °C at a heating and cooling rate of 10°C min⁻¹ and 50°C min⁻¹ respectively under nitrogen flow in a TA Instruments Q 2000. The sample size was about 7 mg.

Photo-DSC experiments were performed using the aforementioned DSC equipped with a photocalorimetric accessory (Omicure S2000) with a 200W mercury lamp, giving an optical range from 320 to 500nm with intensity between 1 and 2 mW/cm². The sample area was 0.2 cm².

The rheological measurements were carried out in a TRITEC 2000 DMA. The device presents stress controller characteristics and the experiments were performed in compression mode.

Stress strain measurements were performed at room temperature in an Insight 10 electromechanical testing system (MTS) using a load cell of 250 N and pneumatic grips, an initial distance between gags of 30 mm and a test speed of 5 mm/min. Elastic modulus (E), tensile strength at break (σ) and percentage elongation at break (ϵ) were averaged from five test specimen data.

Crack filling measurements were performed using a Leitz Aristoment optical microscope with a Mettler FP82Ht temperature controller.

The permeability to CO₂ was measured at 25°C and 1 Atm in a manometric permeation cell. This cell contained two parts connected to a pressure transducer (MKS Instruments Baratron 762 (in the high pressure part) and 740B (in the low pressure part)). The pressure was registered in a computer using the Press Aquirer V0.2 software. Circular films of 1.8 cm² were used to perform the measurements.

3. Results and discussions

3.1. Characterization of PUDAHEMA

Figure 1 shows the infrared spectra obtained for sample PUDA9HEMA5 at the beginning of the reaction (initial), just after the addition of the acrylic component (HEMA addition) and the final spectrum.

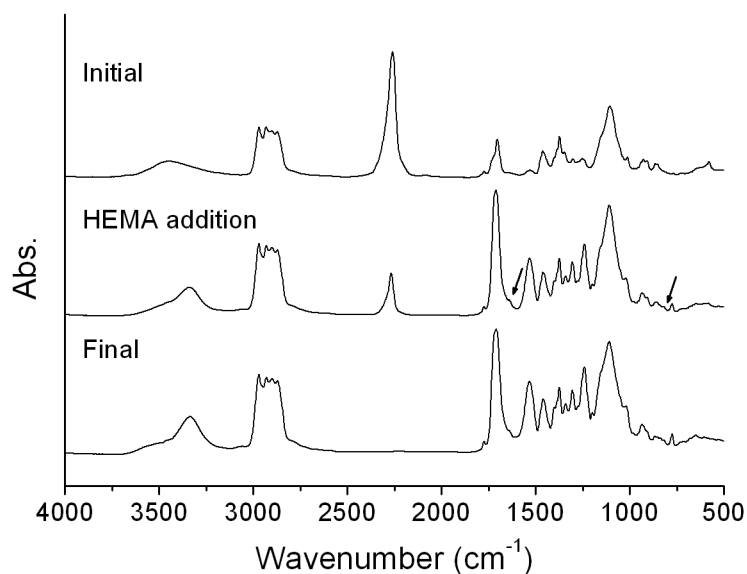


Figure 1: FTIR spectra obtained during the synthesis of PUDA9HEMA5.

As can be observed, as the reaction progressed the absorbance of the band related to the isocyanate stretching at 2220 cm^{-1} decreased while the bands due to the urethane moieties (mainly the carbonyl stretching at 1705 and the N-H bending at 1550 cm^{-1}) increased. As expected, after HEMA addition, the bands at 1650 (C=C stretching) and 810 (=CH out of plane bending), marked in the spectrum with arrows, could be observed.

The ^1H NMR spectrum of the same sample and the assignment of the different protons are shown in figure 2.

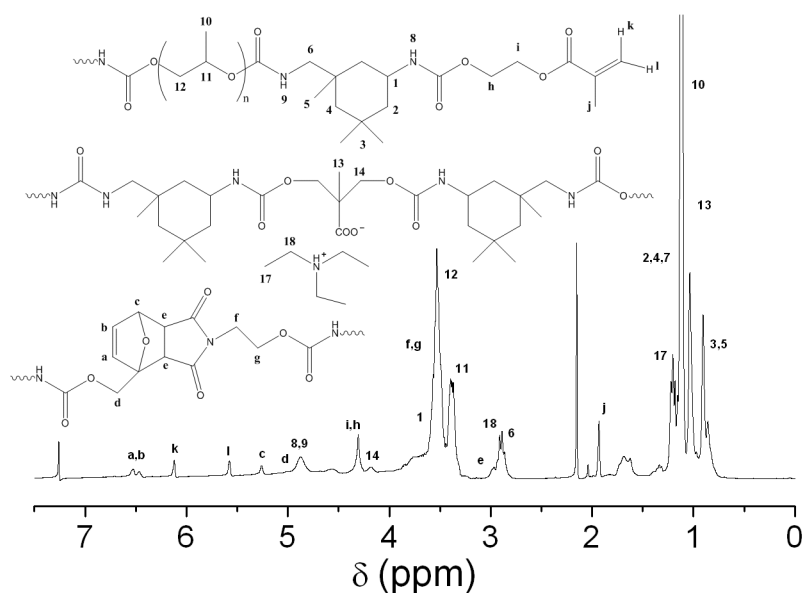


Figure 2: ^1H NMR spectrum of sample PUDA9HEMA5.

As observed, in addition to the signals due to the polyurethane, the spectrum presented bands assigned to both, the DA adduct and the acrylic double bond. The

presence of signals of protons d, and h allowed to verify that the adduct and HEMA were covalently linked to the urethane backbone. All these observations demonstrated that the reaction was successfully performed. **NMR was also used to calculate the molecular weight of the prepolymers. The results are shown in table 2. As expected, the calculated molecular weight was very close to the predicted using the stoichiometry, which confirmed the occurrence of the reaction.**

The particle size of the dispersions is reported in table 2. Particle size of sample PUHEMA 5 was not measured because as it was synthesized as a reference material the phase inversion process was not performed.

Polymer	PUDA9HEMA5	PUDA11HEMA3
Mn (NMR)	6485	10140
Mn (predicted)	5270	9905
Dp (nm)	44±4	43±1

Table 2: Particle size of the dispersions.

As reported in table 2, both dispersions showed similar particle sizes around 44 nm.

3.2. Study of the curing process

Different photoinitiator amounts were added to the dispersions and after casting in dark the film was introduced in the photo DSC. Figure 3 shows the obtained curve for the sample PUDA9HEMA5 after adding 0.5% of the photoinitiator.

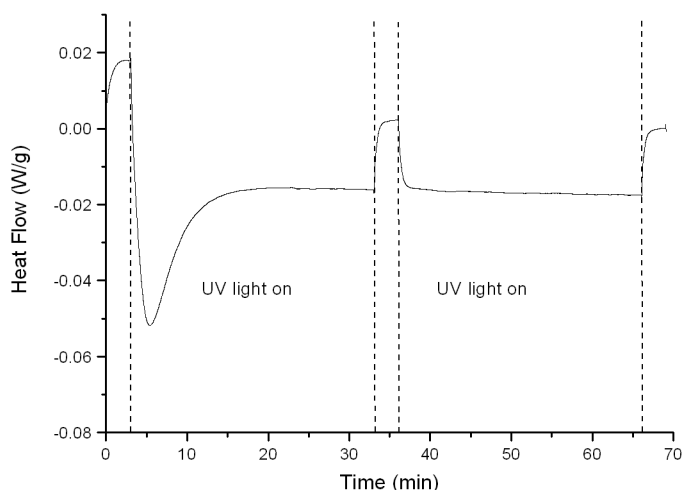


Figure 3: DSC thermogram of sample PUDA9HEMA5 containing 0.5% of photoinitiator.

As observed in figure 3, an exothermic peak was obtained with a minimum at 5 minutes of UV irradiation. This peak is a consequence of the acrylic double bond photopolymerization. In the second irradiation, no peak was observed. According to this it could be concluded that 15 minutes irradiation was enough to perform all the polymerization process.

From the data of figure 3, and integrating the curve, the conversion of the reaction can be calculated using equations 1 and 2.

$$\alpha = \frac{\Delta H_t}{\Delta H_0^{\text{theor}}} \quad (1)$$

$$\Delta H_0^{\text{theor}} = \frac{2 * 54.7}{M_w^{\text{theor}}} \quad (2)$$

where ΔH_t is the enthalpy of the $\Delta H_0^{\text{theor}}$ reaction at time t, and $\Delta H_0^{\text{theor}}$ is the theoretical enthalpy for the complete conversion, 54.7 kJ/mol is the molar enthalpy of methacrylate group and M_w^{theor} is the molecular weight of the polymer (calculated using the reaction stoichiometry) [36].

Figure 4 shows the reaction conversion calculated by photo DSC for samples PUDA9HEMA5 and PUDA11HEMA3 containing 0.5 and 1 wt% of photoinitiator.

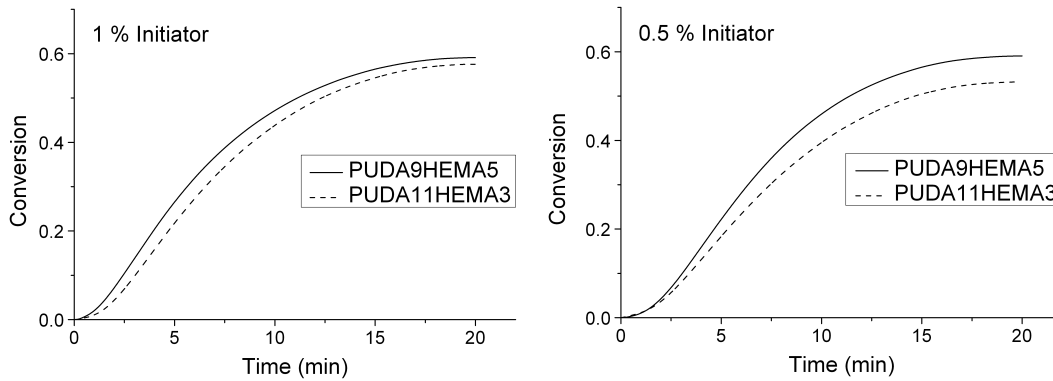


Figure 4: Conversion vs time for samples PUDA9HEMA5 and PUDA11HEMA3 containing 0.5 and 1 wt% of photoinitiator.

Table 3 shows the values of the final conversion obtained for the different samples.

Polymer	%DA adduct	%Photoinitiator amount	
		1%	0.5%
PUDA9HEMA5	9	0.59±0.04	0.58±0.05
PUDA11HEMA3	11	0.63±0.07	0.55±0.05
PUHEMA5	0	0.80±0.04	0.80±0.05

Table 3: Final conversion of the curing reaction measured by DSC.

As observed, the photoinitiator amount did not have a significant effect in the final conversion. In addition, in all the formulations containing DA adduct, the final conversion was around 60%, clearly lower than the values obtained for the samples that did not contain the DA adduct (that showed a final conversion of 80%, similar to the literature data for acrylic systems [36, 8]). In addition, if the curves of the samples with the same photoinitiator amount are compared, it is clear that the presence of the DA adduct decreased the reaction rate. All these results suggested that the DA adduct hindered the acrylic double bond

polymerization. The reason of this reduction in the conversion was related to the occurrence of autoinhibition reaction of the DA adduct. Thus, DA adduct is an allylic monomer and proton c (figure 2) can give rise to degradative chain transfer [37]. The reduction of the radical polymerization rate because of the presence of the DA adduct is not reported in literature, probably because in these papers the conversion was measured by FTIR that it has no a high precision, especially at high conversion [29,32].

In order to check the crosslinking degree of the UV cured samples, the gel content of the formulations was measured. The obtained results can be seen in figure 5.

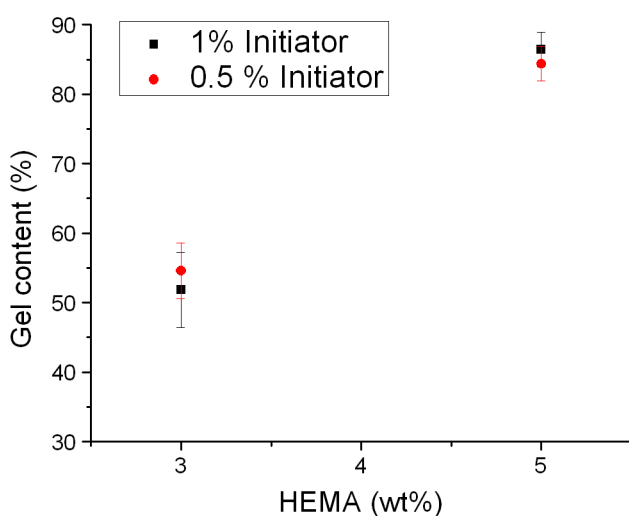


Figure 5: Gel content of the samples.

As expected, the gel content increased with the HEMA content and **and therefore with decreasing the molecular weight of the prepolymer**. No effect of the photoinitiator amount was observed. This result indicated that the samples were crosslinked even with the occurrence of the autoinhibition provoked by the DA adduct.

3.3. Study of the DA reaction and its thermal reversibility

It is clearly stated in literature that the DA reaction is a reversible process. Thus if the prepared samples are exposed at high temperature, the DA adduct will be broken. According to previous results 120°C was selected as an appropriate temperature to the DA reaction took place [34,19]. Scale expanded FTIR spectra of the UV cured (1% of photoinitiator) PUDA9HEMA5 sample obtained at this temperature and different times are shown in figure 6 (left).

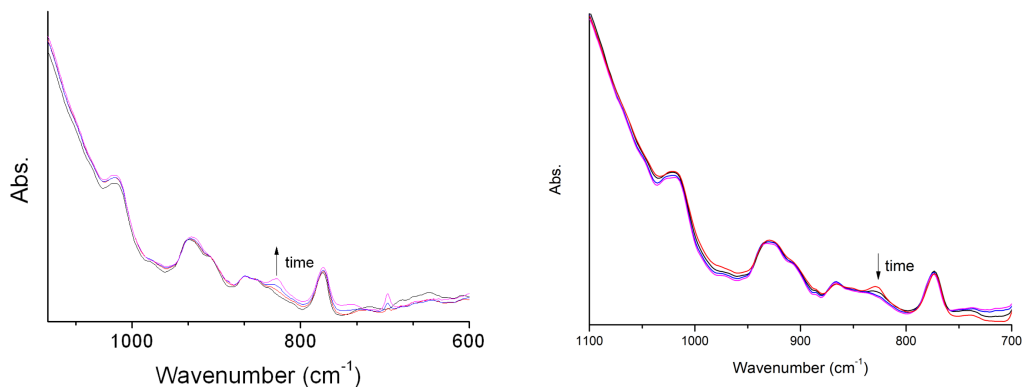


Figure 6: Scale expanded infrared spectra of cured PUDA9HEMA5 at different times (0, 5, 7 and 10 minutes) at 120°C (left) and after cooling the sample at room temperature for (0, 10, 70 and 140 minutes) (right).

As observed, the absorption of the band at 830 cm^{-1} (attributed to the out of plane bending of the olefinic protons of maleimide) increased with the time at 120°C. No more changes in the absorption were detected after 10 minutes. The increase of this band was a clear evidence of the occurrence of the retro DA reaction as the double bond of the maleimide is recovered as a consequence rupture of the DA adduct. This band decreased when cooling the sample at room temperature (Figure 6, right) which demonstrated the reversibility of the DA reaction. Therefore it was clear that at least one part the DA adduct did not suffer changes during the UV irradiation and therefore the samples could show temperature responsive properties. Unfortunately, the FTIR spectra did not allow the calculation of the conversion of the retro DA reaction, because the absorption of the totally broken adduct was unknown.

The DSC run (first and second scan) of sample PUDA9HEMA5 (1% photoinitiator) after curing are shown in figure 7.

As observed, in both runs the sample showed a glass transition at -60°C assigned to the polyurethane soft segment. However an endothermic peak at 150°C was observed in the first scan. According to literature [25,19] this peak can be attributed to the retro DA reaction. Therefore it was clear that the cured samples contained the DA adduct and that this adduct was opened during the first scan. **Afterwards the sample was cooled at 50 °C/min to -80°C. As the cooling rate was very fast, there was no time for the DA reaction occurrence (at 25°C it lasts more than 5 hours to obtain total conversion [34]) and therefore in the second run we did not see any peak related to this reaction.**

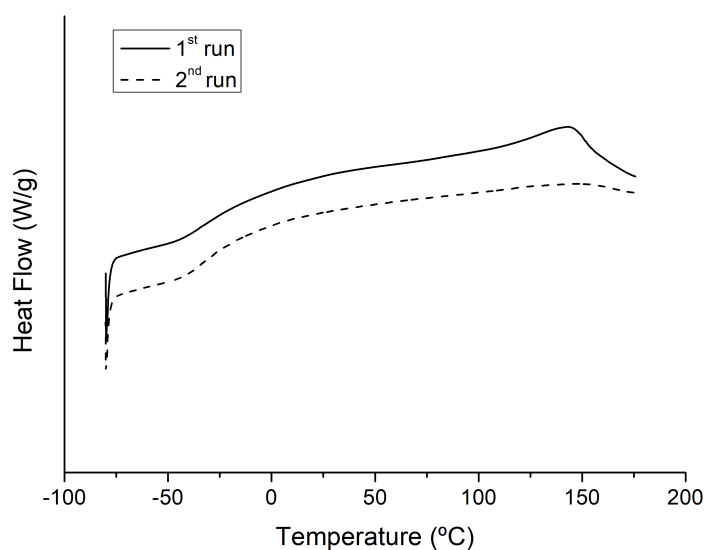


Figure7: DSC scan for sample PUDA9HEMA5.

DSC was also used to study the reversibility of the DA reaction. For this purpose the cured samples were exposed in an oven to three thermal cycles that in previous studies have proved to be appropriated to provoke the DA and retro DA reactions [19]. Thus, the samples were heated at 120°C for 20 minutes and as a consequence, the retro DA reaction occurred. Afterwards, they were maintained at 60°C for 5 hours (sample 1DA). During this heat treatment, the DA adduct was formed again. These samples were analysed by DSC where the retro DA reaction happened during the heating and as a consequence a peak was observed at 150 °C. These results evidenced the reversibility of the reaction. This cycle (heating at 120°C for 20 minutes and maintaining at 60°C for 5 hours) was repeated two more times (samples 2DA and 3 DA) and DSC runs were performed after each cycle. In all cases a peak related to the retro DA reaction was observed at 150°C. The values of the enthalpy of this peak in the different samples and cycles are shown in table 4.

Sample	1DA (J/g)	2DA (J/g)	3DA (J/g)
PUDA9HEMA5 (0.5% photoinitiator)	25	17	15
PUDA9HEMA5 (1% photoinitiator)	20	24	17
PUDA11HEMA3 (0.5% photoinitiator)	25	22	20
PUDA11HEMA3 (1% photoinitiator)	25	22	22

Table 4: Enthalpy of the retro DA reaction for the samples after each heating treatment.

The data showed that in the first cycle there was not a clear dependence of this parameter neither with the DA adduct amount nor with the photoinitiator amount. In addition, for each sample, the enthalpy of the retro DA reaction measured during the DSC run decreased when different heating cycles were applied, indicative of an efficiency loss in the DA reaction.

The enthalpy of the retro DA of these systems was compared with that of non cured polyurethanes reported in a previous work [34]. In that work a value of 30 J/g was given for the first cycle in a sample containing 12% of DA adduct. That

value was higher than the value obtained in the present work for the sample containing 11% of the DA adduct, which meant that the conversion of the DA reaction was lower in the UV crosslinked system. This fact was attributed to the previously mentioned chain transfer reaction to the DA adduct that can happen during the acrylic double bond UV polymerization. As a consequence of this reaction, a part of the adduct was destroyed and therefore the conversion of the DA reaction decreased.

3.4. Physical response characterization

The storage and loss modulus obtained by DMA for the different samples are shown in figure 8.

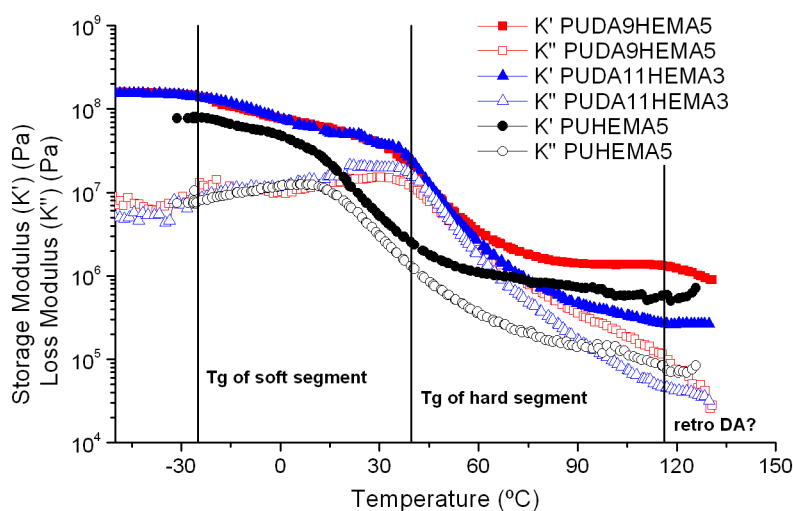


Figure 8: DMA results for the different samples (1% photoinitiator).

In all the curves two transitions could be detected: One close to $-25\text{ }^{\circ}\text{C}$ related to the soft segment glass transition and the other close to $40\text{ }^{\circ}\text{C}$ related to the hard segment glass transition. The samples that contained the DA adduct showed this transition at higher temperature than the sample without adduct which was related to the rigidity imposed by the introduction of the DA adduct in the polyurethane backbone. In addition, as expected, the value of the storage modulus at high temperature was lower in the sample containing less HEMA because the crosslinking degree of this sample was lower. Moreover comparing the storage modulus at high temperature of the two samples containing 5% of HEMA the lower value that was recorded in the sample containing the DA adduct confirmed that this sample had a lower crosslinking degree (because the DA adduct hindered the UV curing reaction). Finally, at $120\text{ }^{\circ}\text{C}$ a transition related to the higher mobility of the sample because of the retro DA reaction was hardly observed.

Measurements of the storage modulus and loss modulus at one temperature as a function of the frequency gives significant information about the crosslinked samples. Thus in permanent gels, both modulus do not present an important dependence with frequency. However, if the samples have reversible linkages the both modulus present a crossover point [38,39]. The values of the modulus at $120\text{ }^{\circ}\text{C}$ for one of the DA adduct containing sample (reversible crosslinking) at

different frequencies compared with the value of a sample that did not contain the adduct (permanent crosslinking) are shown in figure 9.

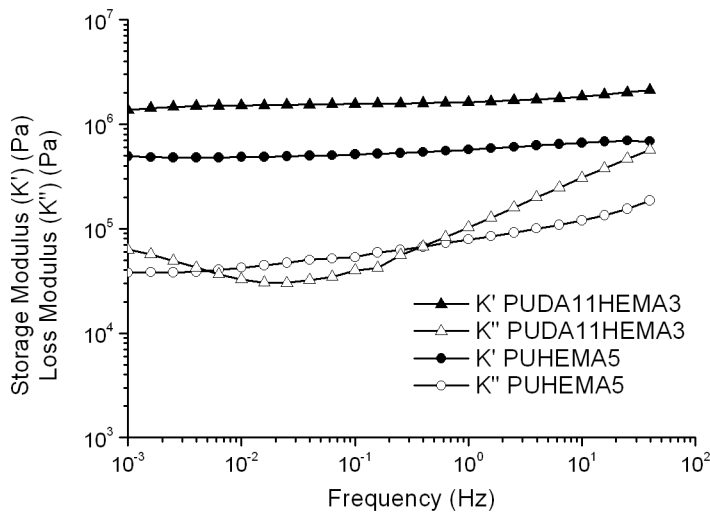


Figure 9: Storage and loss modulus of different samples at 120 °C as a function of the frequency (1% photoinitiator).

As observed, in sample PUHEMA5 both modulus did not present frequency dependence. This is related with the permanent character of the network that presented this sample. However, in the sample that contained the DA adduct, the network can be destroyed by temperature and therefore both modulus approached. It is interesting to note that the expected crossover point of both modulus was not observed, probably because the conversion of the retro DA reaction was not total and therefore not all the network was destroyed at 120°C.

In order to confirm this relaxation, a van Gorp-Palmen plot [40,41] was performed for the sample PUDA11HEMA3 (Figure 10).

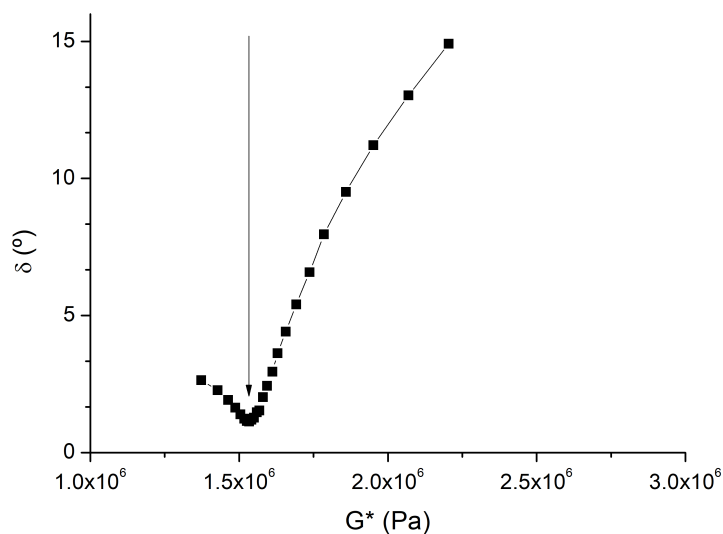


Figure 10: van Grup-Palmen plot for sample PUDA11HEMA3 (1% of photoinitiator).

As observed, the sample showed a clear minimum that could be related to the relaxation process provoked by the retro DA reaction.

3.5. Recycling of the material

From the results showed in previous paragraphs it is clear that the synthesized polyurethanes showed a temperature response originated by the DA reaction. So, this behaviour can be used to recycle the material and therefore increase its environmental sustainability. For this, the sample was broken in small pieces and introduced in a mould that was maintained at 130°C for 30 minutes. The images obtained for sample PUDA11HEMA3 (1% of photoinitiator) before and after recycling are shown in figure 11.

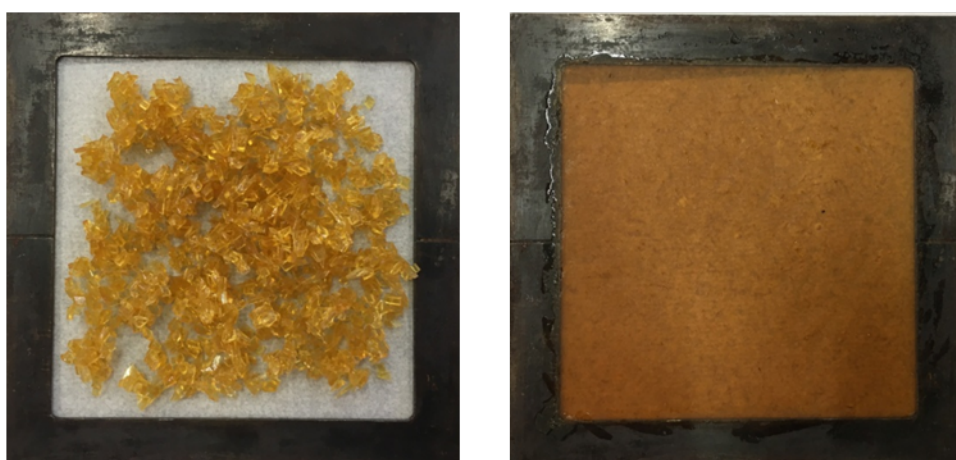


Figure 11: Image of sample PUDA11HEMA3 (1% photoinitiator) before recycling (left) and after recycling (right).

As observed, it was possible to obtain a good film after reprocessing the sample PUDA11HEMA3. However it is to worth mention that this was not possible with samples PUHEMA5 and PUDA9HEMA5. In the case of the sample PUHEMA5, it was clear that as it was permanently crosslinked it can not be melted and therefore reprocessed. However, in sample PUDAHEMA5 because of the occurrence of the retro DA reaction the material could show recycling abilities. The impossibility to recycle this sample was related to its lower DA adduct content in conjunction with its higher crosslinking density (motivated by a higher HEMA amount).

Sample PUDA11HEMA3 was reprocessed three times and in order to check the validity of the process, the mechanical properties were measured (Table 5).

Sample	Young Modulus (MPa)	Tensile Strength at break (MPa)	Deformation at break (%)
Virgin	0.41±0.05	1.3±0.36	509±137
1 recycled	0.32±0.03	1.1±0.21	455±56
2 recycled	0.80±0.06	2.0±0.17	462±29
3 recycled	0.93±0.08	1.6±0.21	560±49

Table 5: Mechanical properties of sample PUDA11HEMA3 (1 % photoinitiator) in the three recycling cycles.

In this sample, two different behaviours were observed. If the data of the virgin material are compared with the data of the material after the first recycling a small loss of the mechanical properties was observed. However, after the second and third recycling the Young Modulus and tensile strength increased and the deformation at break was reduced. It is clear that normally the materials loss mechanical properties after recycling. In literature, an increase of the mechanical properties has been described for polyurethane samples containing DA adduct [28]. According to this work, this increase was related to the phase mixing that happens during the recycling of the material. In our case this process can take place as a small increase of the glass transition was observed in the recycled samples. However, other processes such as the crosslinking can be in the origin of the increase of the Tg. The crosslinking reaction can happen as a consequence of the maleimide homopolymerization [42]. Although this process has been described at high temperatures it can happen if the material is at 120°C for long time (as the used during the recycling cycle). In addition, this reaction will provoke a reduction of the DA reaction efficiency in the different cycles as the observed in this work in the DSC data. According to this, the increase of the mechanical properties observed during the recycling was related to the maleimide homopolymerization.

3.6. Healing abilities

As stated in the previous section due to the presence of the DA adduct the waterborne polyurethanes synthesized in this work can be recycled. However in the circular economy concept repairing can be also interesting because it increases the material use time. In damaged materials, the cracks generate new surfaces and as a part of the repairing processes the material must be able to fill them. Thus, we measured the ability of the material for crack filling by optical microscopy. For this, a scratch was made to the material and the behaviour of the scratch was monitored by optical microscopy under heating.

Figure 12 shows the evolution of the crack with temperature in the sample PUDA9HEMA5 cured with 0.5% of photoinitiator.

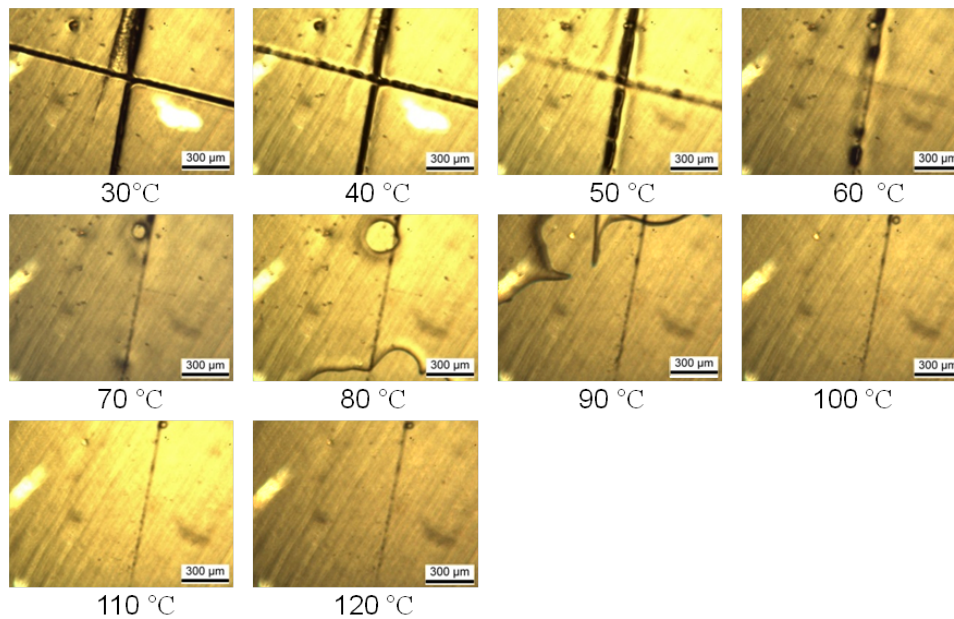


Figure 12: evolution of the crack with temperature in the sample PUDA9HEMA5 cured with 0.5% of photoinitiator.

As observed, the material started to fill the scratch at 60°C. This can be related with the glass transition of the hard segment that as the DMTA results showed took place at low temperature. However, when increasing the temperature the material was not able to fill all the crack. The same behaviour was observed when this sample was cured using 1% of photoinitiator. However, for the sample PUDA11HEMA3 cured with 0.5% and 1% of photoinitiator (figure not shown) the material was able to fill all the crack at high temperature. It should be remembered that in the previous section we demonstrated that it was not possible to recycle sample PUDA9HEMA5. So it is clear that the lower DA adduct content of this sample in conjunction with its higher crosslinking density (motivated by a higher HEMA amount) limits both the recycling and the healing of this sample.

After demonstrating the ability of the material to fill scratches the healing properties were tested. **For this purpose the circular films were cut in two symmetric parts of the same size and afterwards the two semi circle pieces were contacted and introduced in an oven for 20 minutes in order to provoke the retro DA reaction.** Afterwards, samples were introduced in an oven at 60°C for 24 hours in order the DA reaction took place. Samples were cooled at room temperature and the healing efficiency was tested qualitatively and also measuring the permeability to carbon dioxide before and after the healing process.

Qualitatively it is to remark that the samples PUDA9HEMA5 and PUDA11HEMA3, were successfully healed and they were able to maintain a weight of 500 g without breaking. However, as expected it was no possible to repair the sample PUHEMA5.

The permeability to carbon dioxide of the samples before and after repairing is shown in figure 13.

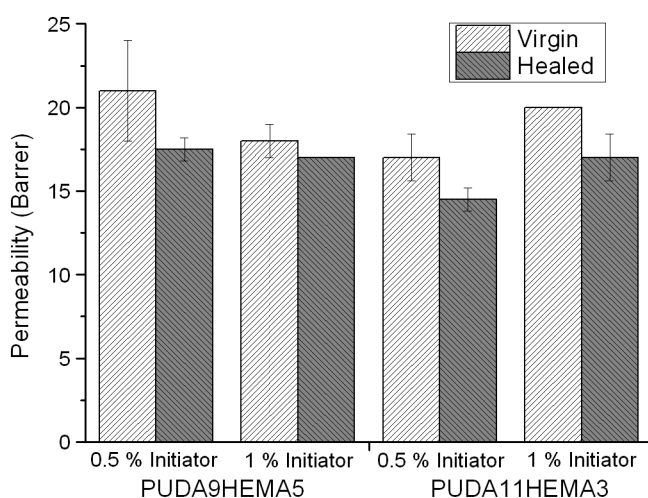


Figure 13: Permeability to carbon dioxide of virgin and healed samples.

As shown in figure 13, regardless the composition, all the samples showed similar permeability values. It is interesting to note that the values of the oxygen permeability did not show important changes after the healing process. Thus, it can be concluded that the repairing process was carried out correctly.

4. Conclusions

UV curable Waterborne polyurethane dispersions containing DA functions were successfully obtained. **The introduction of the DA adduct did not avoid the acrylate polymerization by UV as crosslinking of the samples was observed.** All the synthesized samples showed the ability to give rise to the retro DA reaction when putting at 120°C for 20 minutes and the DA adduct was recovered after heating at 60°C for 5 hours. As a consequence of this reaction, regardless the DA adduct content, all the samples could be repaired after breaking. **However, in order these samples were recycled there must be an appropriate balance between the amount of acrylic double bond component (that produces high crosslinking density and impedes the recycling) and the DA adduct amount that is the active healing material.**

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