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Feasibility of polyamines and cyclic carbonate terminated prepolymers in polyurethane/polyhydroxyurethane synthesis

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Abstract

Polyurethanes are a well-established part of adhesive markets. However due to the toxicity of di-isocyanates used in the synthesis, finding an alternative route to synthetize polyurethanes is increasingly important. One strategy is to use cyclic carbonate terminated prepolymers with polyamines to yield polyhydroxyurethanes. This research highlights the possibility to use commercially available polyurethane prepolymers with different isocyanate chemistries for cyclic carbonate terminated prepolymer synthesis with the help of glycerol carbonate and a catalyst. These synthetized prepolymers were used in a screening study with different commercially available low toxic amines. It was observed that when secondary amines were used, the reaction advanced at room temperature with no further heating required. The development of lap shear strength over time on stainless steel, gel content, tensile strength and elongation were measured from room temperature cured polymers. The synthetized polyurethane/polyhydroxyurethane (PU/PHU) hybrid materials had high initial lap shear strength close to current industrial polyurethane adhesives. The strength development over time was negligible. Full conversions were seen within one month from the reaction. Tensile strength levels were slightly lower than typical industrial polyurethane adhesives. Even though the lap shear strength results and gel contents at room temperature were on a good level, curing at elevated temperature had a positive impact on them. The best performing combination was cyclic carbonate functionalised hexamethylene di-isocyanate prepolymer with multifunctional polyethyleneimine amine. In short, di-isocyanate free PU/PHU hybrid materials were successfully synthetized from commercial raw materials and their performance was comparable with current industrial polyurethane adhesives.

Keywords

Polyurethane, polyhydroxyurethane, polyethyleneimine, lap shear strength, tensile strength

1. Introduction

Polyurethanes (PUs) are widely used in the industry. In coatings, adhesives and sealants markets they combined for ca. 20% of the total revenue in 2016 [1]. In adhesives, polyurethanes have multiple application fields ranging from structural bonding to textile bonding [2,3]. Polyurethanes are typically manufactured by the reaction of a di-isocyanate with hydroxyl group containing polymers or oligomers [1]. Polyurethane consists of soft and hard segments [4] and by a careful selection of reaction partners, the mechanical properties of the final product can be tailored from very flexible to tough and hard. This enables applications in many areas and makes the polyurethanes so unique [1]. Polyurethanes can also be manufactured from isocyanate terminated prepolymers, which further react with polyols [1], polyamines [1] or moisture [5]. The prepolymer functionality, viscosity and free isocyanate content (NCO content) can be adjusted based on the application requirements [1]. However, these standard synthetic routes have some notable issues with the main concern being the toxicity of the isocyanate compounds [4]. Recently, many reports including the restriction proposal of European Chemical Agency (ECHA) [6] for di-isocyanates has increased the interest in the academic and industrial world for isocyanate free polyurethanes (NIPUs) [7]. Among the possible synthesis strategies, the most viable and user-friendly method seems to be the polyaddition reaction of cyclic carbonate with amine to yield polyhydroxyurethanes (PHU). They differ from polyurethanes by their pendant primary or secondary hydroxyl groups on β carbon [4]. The hydroxyl groups can increase the water absorption, but on the other hand they also increase chemical resistance [8] and improve adhesion [9,10].

There are some challenges in this reaction route. Firstly, the cyclic carbonates are typically synthetized from epoxy functional polymers and carbon dioxide at high temperature and pressure in the presence of a catalyst [11]. Furthermore, cyclic carbonates have very high viscosity [8,12] or are even solid at room temperature [13]. This leads to elevated processing temperatures or the use of solvents [13]. Secondly, the reactivity of cyclic carbonate and amine is low at room temperature. A plateau in the reaction is often reached at around 60-80% of conversion due to diffusion problems [14]. Therefore elevated temperatures are used for full cure [15], but then risks of side reactions such as amide [16] or urea formation [4] start arising. Secondary amines need even higher temperatures depending on the sterical hindrance of the amine [15].

To increase the reactivity and performance of PHU, polyfunctional starting materials can be used for crosslinking [13]. For example, very high strength results were obtained with polyethyleneimine (PEI) based hyperbranched polyamines [5,17,18]. Also so called hybrid NIPUs (combining epoxy, polyurethane or acrylic chemistry with PHU) are used to increase the properties of the final polymer [4,19]. Cornille et al. [20] used cyclic carbonate or amine functionalised prepolymers and chain extended them with epoxy or acrylate at

room temperature. Annunziata et al. [21] made different prepolymers with cyclic carbonate ends from different polyols and cured them with polyether diamines reaching relatively high molecular weights. Ke et al.[12] used amine terminated PHU prepolymers and cured them with a common epoxy resin i.e. Bisphenol A diglycidyl ether at elevated temperatures reaching high tensile strength and elongation. Together, these reports give a toolbox for designing new NIPUs, although no single approach has been proven superior so far.

From an application point of view, it is important that the mechanical and adhesive properties match the required level. Adhesive properties of PHU's have been studied in the literature [9,10,19,22,23]. Leitsch et al. [19] made a PU/PHU hybrid material from toluene di-isocyanate (TDI) based prepolymer, glycerol carbonate and triethylenetetramine (TETA). The hybrid had good adhesive performance on polyimide, polyvinylchloride (PVC) and aluminum. However, the final tensile strength was low compared to the PU analogue. Cornille et al. [10] cured different cyclic carbonates with commercially available diamines at elevated temperature. When trifunctional carbonate was used, high gel content was measured indicating highly crosslinked structure. Also good strength properties as well as cohesive adhesion results on glass and wood were reported. The failure type on coated aluminum specimen was adhesive. Very recently Detrembleur's research group has published several articles on the adhesive behavior of thermoset PHUs on various materials including aluminum and stainless steel [9,22,23]. High lap shear and tensile strength results were reported and they even challenged the industrial PU analogues when cured at elevated temperature [22]. At room temperature the strength remained low [9]. Furthermore Vanbiervliet et al.[24] has studied commercially available amines (EDR-148 and Lupasol) with cyclodithiocarbonate for non-isocyanate thiourethane (NIPTU) synthesis at room temperature in an adhesive application. In contrast to the present work, these were further crosslinked with an oxidizing agent. In tensile test the materials were soft and brittle.

Although excellent results for the adhesive use of NIPUs have already been reported, the synthesis of PHU and its raw materials is still challenging and expensive. In this study, the aim was to find commercially available and low toxic raw materials that could react and reach a high strength level already at room temperature. As the cyclic carbonate synthesis is not straightforward, an alternative route based on isocyanate terminated polyurethane prepolymers was used. By producing PU/PHU hybrid materials, it was possible to avoid sensitizing the end-user to monomeric di-isocyanates in the final stage of the application. Typically in the final stage of application, the reaction is performed in environments that are not designed for reactive chemicals and there is a risk of being more exposed to free monomeric di-isocyanates. In addition, the production of glycerol carbonate terminated prepolymers could be carried out with the same equipment that was used for isocyanate terminated polyurethane prepolymer manufacture. When isocyanates are handled in factories designed to use them, the sensitizing risk to a user is minimized.

Herein, it was seen that prepolymers with different isocyanate chemistries i.e. TDI, hexamethylene di-isocyanate (HDI) and isophorone di-isocyanate (IPDI) can be terminated with cyclic carbonate when a catalyst is used.

The suitability of the synthetized PU/PHU hybrid materials for industrial bonding was evaluated. In order to find the best reaction partners, the reactivity of different cyclic carbonate terminated prepolymers with different commercially available di- and polyamines were tested. The combinations that were able to react at room temperature were further tested for their adhesive and strength properties i.e. the adhesive strength build up over time in the lap shear strength test on stainless steel and their cohesive mechanical properties. The main focus was to use multifunctional starting materials in order to achieve a crosslinked structure. Conversions were measured by Fourier transform infrared spectroscopy (FTIR). All these results were compared to the samples that were cured at elevated temperatures and compared to known industrial analogues from market.

2. Materials and Methods

2.1 Materials

Commercially available isocyanate terminated polyurethane prepolymers were used to synthetize cyclic carbonate terminated prepolymers. Selected prepolymers had low viscosity and low NCO content in order to optimize the viscosity of the synthetized prepolymers. Selected isocyanates were TDI, HDI and IPDI. The prepolymers mentioned in the Table 1 refer to the isocyanate containing polyurethane prepolymers used in the synthesis. They are labelled P-TDI, P-IPDI, P-HDI-L, P-HDI-S and the cyclic carbonate terminated prepolymer products are labelled CC-TDI, CC-IPDI, CC-HDI-L, CC-HDI-S, respectively. Glycerol carbonate from Huntsman was used as end functionalizing agent (M_w 118 g/mol, functionality 1). The bismuth catalyst was obtained from Sigma Aldrich. All chemicals were used without further purification.

Table 1. Used isocyanate terminated polyurethane prepolymers for cyclic carbonate synthesis.

Sample name	Commercial name	Isocyanate type in prepolymer	Free isocyanate content, %	Viscosity, mPas	Molar mass, g/mol	Functionality	Supplier
P-TDI	Desmodur E14	Toluene di-isocyanate (TDI)	3.3	6800	3175	2.5	Covestro
P-IPDI	Desmodur VPLS 2371	Isophorone di-isocyanate (IPDI)	3.7	9800	2200	2	Covestro
P-HDI-L	Desmodur XP 2599	Hexamethylene di-isocyante (HDI)	6.0	2500	2800	4	Covestro
P-HDI-S	Tolonate X FLO 100	Hexamethylene di-isocyante (HDI)	12.3	140	682	2	Vencorez

The studied amines A-PEI-1 to A-Ar (Table 2) were based on their proven reactivity, high crosslinking and good strength results in previous publications with cyclic carbonates [5,8,10,12,13,16–19,25,26] and their commercial availability. Toxic amines like ethylenediamine (EDA) were left out. The chemical structures of the studied amines are presented in Fig. 1.

Table 2. Tested poly- and diamines used in the PU/PHU synthesis.

Sample name	Commercial name	Chemical name	Molar mass, g/mol	Amount of primary amines	Supplier
A-PEI-1	LupasolFG	Polyethyleneimine (PEI)	800	8.1*	BASF
A-PEI-2	Lupasol G20	Polyethyleneimine, (PEI)	1300	12.2*	BASF
A-PEI-3	Lupasol PR 8515	Polyethyleneimine, (PEI)	2000	16.8*	BASF
A-DDA-1	Priamine 1071-LQ-(GD)	Dimerdiamine (DDA)	620	2.2**	Croda
A-DDA-2	Priamine 1073-LQ-(GD)	Dimerdiamine (DDA)	538.8	2.1**	Croda
A-DDA-3	Priamine 1074-LQ-(GD)	Dimerdiamine (DDA)	552	2**	Croda
A-PEA-1	Jeffamine® T-403	Polyetheramine (PEA)	403	3**	Huntsman
A-PEA-2	Jeffamine® D-230	Polyetheramine (PEA)	230	2**	Huntsman
A-PEA-3	Jeffamine EDR-148	Polyetheramine (PEA)	148	2**	Huntsman
A-IPDA	Baxxodur EC201	Isophoronediamine (IPDA)	170.3	2**	BASF
A-TETA	Triethylenetetramine	Triethylenetetramine (TETA)	146.23	2**	DOW
A-Ar	Ethacure 300	Aromatic amine	214	2**	Albemarle

* Molar mass from supplier data, functionality from previous publication [17] ** Information from supplier data

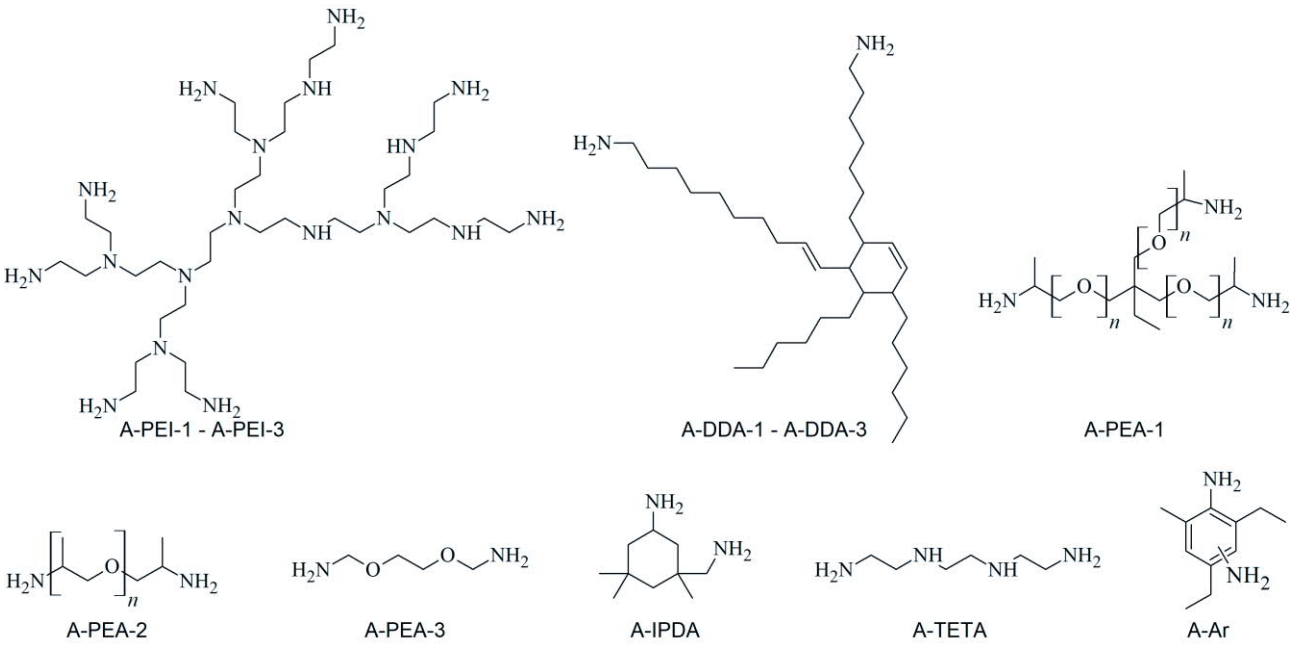


Fig.1. Chemical structures of the amines used (A-PEI-1 to A-Ar).

2.2 Synthesis of cyclic carbonate end functionalized prepolymers

All prepolymers were manufactured in the same way. First, 200 g of isocyanate terminated polyurethane prepolymer was weighed in a glass reactor. The bismuth based catalyst (0.1 wt %) was added for the reaction to complete. Glycerol carbonate was added in slight molar excess to ensure that all isocyanate (NCO) groups will react. The NCO/OH ratio was 0.93 in all the samples, similarly to a patent filed in this field [27], except for the CC-HDI-S prepolymer, in which case the NCO/OH ratio was 0.77.

The reaction mixture was heated to 80 °C during continuous stirring with 200 rpm. The reactor was kept at 80 °C and the reaction was followed with FTIR until no NCO absorption bands were detected and the cyclic carbonate absorption band for carbonyl group was detected. All the reaction products were used without further purification. The schematic presentations of possible chemical structures for each cyclic carbonate terminated prepolymer are shown in Fig. 2.

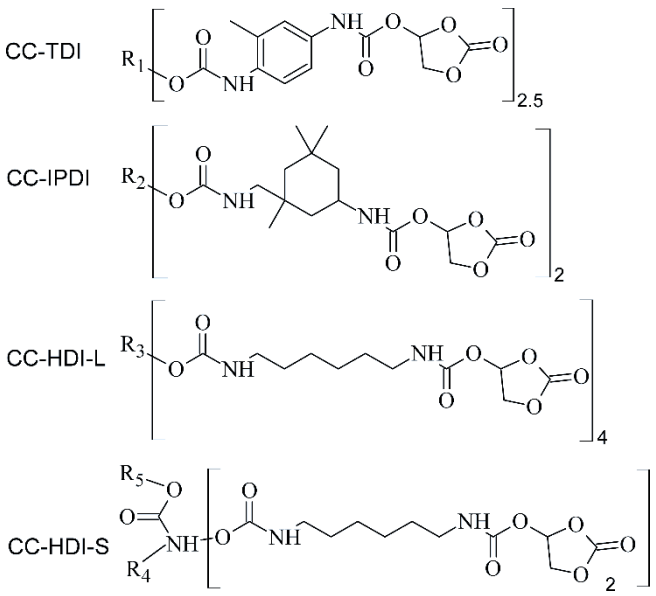


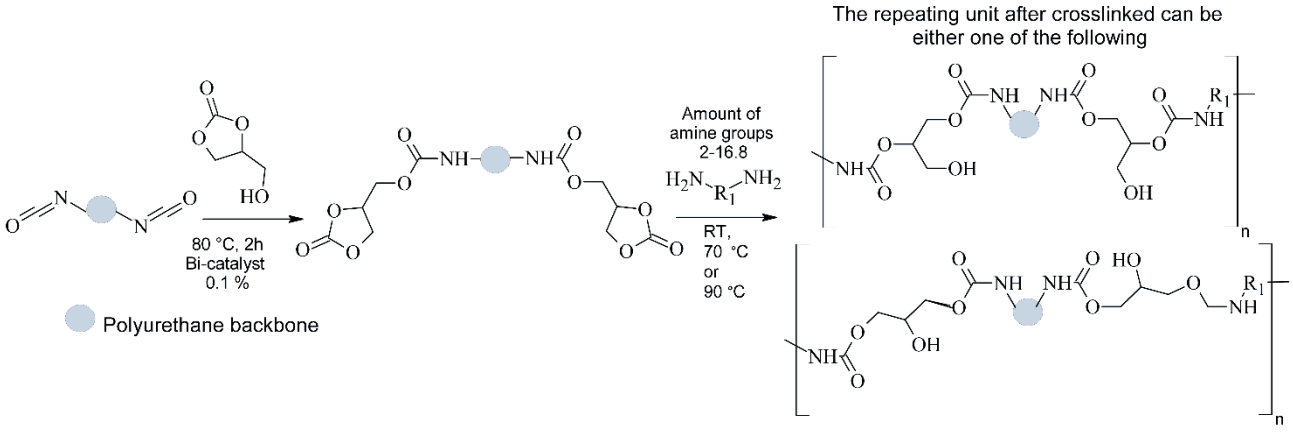
Fig. 2. Schematic presentation of the cyclic carbonate-end capped prepolymers. The $R_{1\text{-}5}$ on the figure refer to the original isocyanate terminated polyurethane prepolymer part of the molecule.

2.3 Evaluation of reactivity

The initial reaction tests were performed in a Petri dish. First, the cyclic carbonate terminated prepolymer was weighed and then a stoichiometric amount of amine was added. The mixture was stirred for a minimum of 2 minutes with a glass rod to ensure proper mixing. As in other literature reports [8,13,22], all reactions were performed with equimolar amounts. The equimolar amounts were calculated based on the

primary amine content in amine (secondary amines were not considered because of their low reactivity) and the added glycerol carbonate amount.

The reactivity was first estimated from the Petri dish by evaluating the hardness of the mixture manually with a glass rod and in more detail with FTIR. The reactivity was also evaluated at elevated temperatures 70 °C and 90 °C. An example of the reaction scheme from isocyanate terminated polyurethane prepolymer to cyclic carbonate terminated prepolymer and its reaction with di-or polyamine is shown in Scheme 1. This reaction scheme is simplified to highlight a possible outcome with primary or secondary hydroxyl groups depending on the ring opening mechanism (secondary OH-groups being favoured [4]). Furthermore, with multifunctional starting materials a complex thermoset network will be formed.



Scheme 1. Synthesis scheme for PU/PHU hybrid material showing two possible outcomes of the polyaddition reaction.

2.4 Characterization of materials

2.4.1. FTIR

FTIR measurements were performed with Perklin Elmer Frontier FT-IR spectrometer equipped with a Specac attenuated total reflectance (ATR) diamond module. Spectra were collected at over a range of 4000-550 cm^{-1} with a resolution of 0.4 cm^{-1} and with 8 scans per run. Spectra were analysed with the PerklinElmer Spectrum (version 10.4.2.279) software. For liquid samples, a small droplet was placed with a glass rod on the top of the ATR diamond. For solid samples, a press was used to ensure a close contact with the ATR diamond.

2.4.2 Viscosity measurements

Anton Paar V301 rheometer with Rheoplus software was used for the intrinsic viscosity analysis with the spindle PP 25. Temperature sweep from 20 °C to 50 °C was performed, after which the system was cooled back to 20°C. Five measurement points at one-minute intervals with a shear rate of 2 s^{-1} were recorded.

2.4.3 Lap shear strength on stainless steel

Lap shear strength testing was done according to EN 1465 using the Instron 3366 machine with a load cell of 10 kN. The analysis was performed with Bluehill software. Minimum of four parallel tests specimens were tested with a speed of 50 mm/min. Stainless steel (SS) plates were purchased from Ilmastointi Turppa. As a pre-treatment, the surface was cleaned with isopropanol.

2.4.4 Gel content

The gel content was measured similarly to Panchireddy et al.[23]. First, the material was immersed in tetrahydrofuran (THF) for 96 h and then the sample was dried in an oven at 70 °C for 24 hours. The gel content was calculated using the formula below.

$$\text{Gel content (\%)} = \frac{w(f)}{w(i)} \times 100$$

Here $w(f)$ is the weight of the dried sample after immersion and $w(i)$ is initial weight of the sample.

2.4.5 Tensile strength and elongation

Tensile strength and elongation were measured according to EN 527-1 using Instron 3345 machine with a load cell of 1 kN and Instron extensiometer. The analysis was performed with Bluehill software. In order to avoid bubbles the resin was heated to 50 °C and the reaction mixture was first carefully stirred by hand followed by degassing in a speed mixer DAC 400 FVZ for 20 seconds. The reaction mixture was cast into a 1 mm thick film and cut into a dumb bell shaped specimen. Minimum of three parallel dumb bell specimens were tested with a speed of 50 mm/min. For all reported values, the samples broke within the narrow area of the dumb bell sample as required by the standard (Fig. ESI 1).

3. Results and discussion

3.1 Synthesis of cyclic carbonate terminated polyurethane prepolymers

A relatively easy synthesis method for cyclic carbonate terminated prepolymers is to use isocyanate terminated polyurethane prepolymers with glycerol carbonate by using the same equipment as for the

polyurethane prepolymer manufacturing. This kind of approach makes it possible to use polyurethane chemistry without the end user being sensitized to di-isocyanates. In other reports, the approach has been to synthetize a cyclic carbonate terminated prepolymer from TDI based prepolymer [19], but in the current study also IPDI as well as two different HDI based prepolymers were used. The reaction was followed with FTIR until no absorption band of NCO group-was seen at 2270 cm^{-1}. An example of the P-TDI spectra is shown in Fig. 3, others in supplementary data (Figs. ESI 2-4). From the spectra it can be seen that the absorption bands typical for polyurethane (NH at 3300 cm^{-1} and at 1530 cm^{-1} as well as C=O at 1718 cm^{-1}) have increased in intensity indicating that the NCO has reacted with the OH group in the glycerol carbonate. This is further proven by the fact that the carbonyl absorption band typical for cyclic carbonate 1800 cm^{-1} is visible. This reaction is expected as isocyanate readily reacts with the primary OH group of the glycerol carbonate. The properties of the manufactured cyclic carbonate terminated prepolymers are listed in Table 3. The synthesis of cyclic carbonate terminated prepolymer was successful with all of the prepolymers, although adding 0.1 wt % of catalyst was necessary as otherwise the reaction was not complete in two hours. The lower molar mass HDI (P-HDI-S) needed a longer reaction time (4 hours).

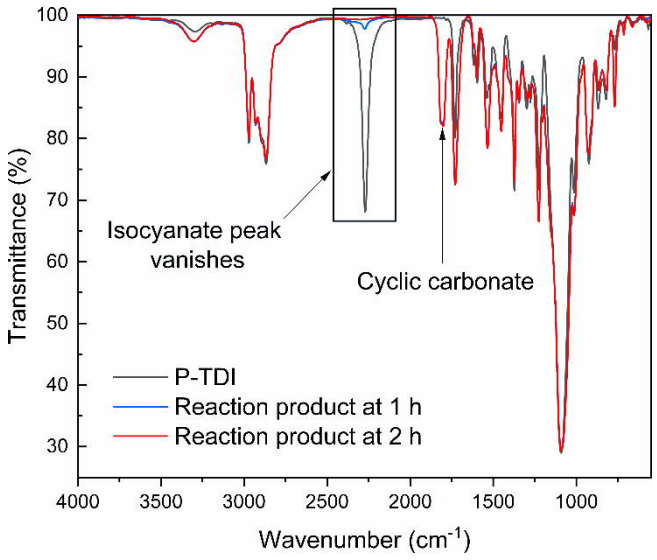


Fig. 3. FTIR spectra showing that the NCO absorption band vanishes as the reaction proceeds. The Isocyanate absorption band in PU prepolymer (P-TDI) gets smaller and finally disappears in the spectrum of the reaction product (CC-TDI).

Table 3. Properties of the manufactured cyclic carbonate terminated prepolymers.

Sample name	Isocyanate type	NCO/OH ratio	Viscosity 20°C, mPas	Viscosity 50°C, mPas
CC-TDI	TDI	0.93	445 000	31 600
CC-IPDI	IPDI	0.93	568 000	32 500
CC-HDI-L	HDI	0.93	414 000	29 300
CC-HDI-S	HDI	0.76	516 000	18 000

All cyclic carbonate terminated prepolymers were viscous liquids and had a honey-like sticky appearance. This kind of viscosity increase is typical and the reason is the additional hydrogen bonding caused by the cyclic carbonates [8,27]. By increasing the temperature, the viscosity was significantly decreased and the material became easier to handle. Typical viscosities for two component polyurethane industrial adhesives range from 15 000 to 30 000 mPas and similar viscosity levels were reached for all cyclic carbonate terminated prepolymers by increasing the temperature to 50 °C. Thus, the synthetized polymers have potential to be used in real industrial applications.

3.2 Reactivity of amines with different cyclic carbonate terminated prepolymers

In order to find which amines react already at room temperature, a screening test was performed with several commercial amines (Table 4). The used amines were selected based on positive results in previous publications [5,8,10,12,13,16–19,25,26]. The evaluation started by dividing the results of the amine/prepolymer pairs into 3 groups based on their reactivity as evaluated based on the physical properties of the product: 1) hard and solid ones, 2) the ones that reacted, but were still soft and sticky, and 3) the ones that had no apparent reaction. After the screening test, FTIR spectra were collected from the combinations that reacted to verify that the reaction took place with the cyclic carbonate and the amine. The typical absorption band for cyclic carbonate carbonyl group at 1800 cm^{-1} was followed to be decreased or disappeared. Furthermore, the typical polyurethane absorption bands (C=O at 1728 cm^{-1} and NH at 1535 cm^{-1} and a broad band at around 3300 cm^{-1}) were visible and the primary amine (NH) absorption band at 1581 cm^{-1} had disappeared. An example of the spectra is shown in Fig. 4. However, even though the reaction took place, in some of the spectra the cyclic carbonate absorption bands did not disappear completely (Figs. ESI 5-15). The incomplete reaction could be because of the reactivity, miscibility and diffusion issues arising from viscosity increase when polymerization advances. The miscibility challenges could result from the high difference in viscosity caused by the hydrogen bonding in the cyclic carbonate prepolymer. Furthermore, using equimolar amine/prepolymer amounts can lead to large differences in weight ratios and mixing small amount of amine into the honey-like prepolymer material can be challenging (Table ESI 1). The most promising material combinations i.e. all cyclic carbonates with

amines A-PEI-1, A-PEI-2, A-PEI-3 and A-TETA, were selected for further studies to understand the conversions better.

Table 4. Reactivity of different amine and cyclic carbonate terminated prepolymer pairs at different temperatures evaluated based on their apparent reactivity and physical appearance.

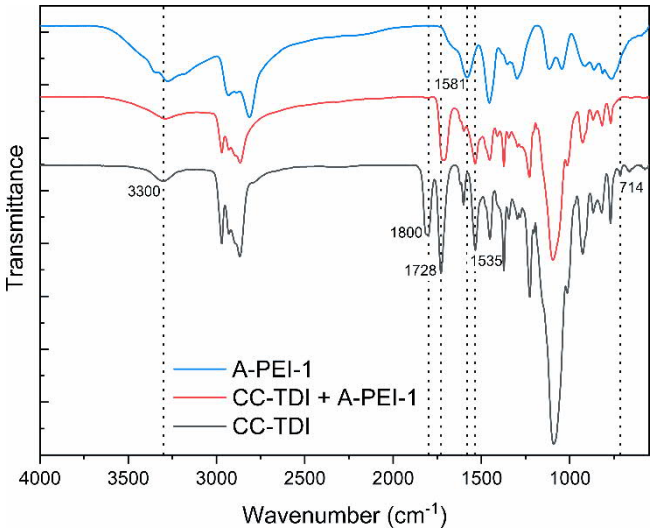


Fig.4. FTIR spectra for pure CC-TDI, the product of the CC-TDI/A-PEI-1 pair after the reaction, and pure A-PEI-1 amine. Relevant wavenumbers are highlighted with dashed lines.

All isocyanate terminated polyurethane prepolymers selected for the study had a low NCO content to make the cyclic carbonate prepolymer viscosity as low as possible (to avoid additional hydrogen bonding caused by cyclic carbonate groups). Typically, such low NCO content prepolymers have low strength and are flexible. In order to have high strength materials, crosslinking was necessary. Therefore, it was expected that the best results would be with amines that had the functionality higher than 2 resulting in thermoset

structure. Based on the preliminary screening this seemed to be true: A-PEI-1, A-PEI-2 and A-PEI-3 with high number of primary amines reacted very easily at room temperature with all cyclic carbonate terminated prepolymers and formed solid materials.

Another amine that was able to react at room temperature with all cyclic carbonate terminated prepolymers was A-TETA. But, although the reaction took place, the synthetized PU/PHU was soft and sticky, mainly because A-TETA had only dual functionality in primary amines. Increasing the temperature made the PU/PHU harder, indicating that secondary amines had then reacted as well. It was also noticed that the reaction had proceeded further at the bottom of the Petri dish than on the top (Fig. ESI 16). This could be explained by the separation of the lighter component; the viscosity difference of cyclic carbonate terminated prepolymers and A-TETA is big and the amount of TETA needed in grams for the equimolar reaction is small. Based on the findings, this material combination could have challenges in the industrial applications, even though the reaction was successful at room temperature.

At room temperature, the most reactive prepolymer was CC-HDI-L. It reacted also with the dimer diamines A-DDA-1, A-DDA-2 and A-DDA-3. However, these amines were not considered for further studies because the formed materials disintegrated easily with CC-HDI_L. When comparing the reactivity of different prepolymers in general, the HDI based cyclic carbonate prepolymers (CC-HDI-L and CC-HDI-S) were reactive, particularly CC-HDI-L had the best reactivity. The TDI based prepolymer CC-TDI was on a similar level. This is interesting, as typically aromatic isocyanates (present in CC-TDI) tend to react more readily than aliphatic, but in this case, the reason could be that the aromatic group was quite far away from the reactive centre. It could be that the reactivity is mainly influenced by the three dimensional structure of the cyclic carbonate terminated prepolymer. This is in line with the fact that CC-IPDI was the least reactive as it has IPDI in its backbone, which is known to have steric hindrance due to its asymmetric structure [28].

All the other amines required elevated temperature to react or they did not react at all. Some of the DDAs (A-DDA-1 and A-DDA-2) reacted at 70 °C, but the formed material stayed soft. From PEAs the least hindered A-PEA-3 reacted the easiest already at 70 °C, but again as expected due to the dual functional amine, the synthetized PU/PHU was very soft. When cured at 90 °C, A-IPDA formed very hard, brittle glass like material, similar to previous reports [16,23,29]. Aromatic amines (A-Ar) did not react in these temperatures at all, which is also in line with previous findings [4].

The screening results showed that having secondary amines in the chemical structure increased the reactivity towards cyclic carbonates at room temperature. The highest reactivity was seen with the PEI based amines, which have secondary and tertiary amines in their structure. Also having functionality higher than two helped to crosslink the PU/PHU hybrid and formed more rigid thermoset materials that could be suitable for industrial bonding. Based on the initial screening, all cyclic carbonate terminated prepolymers

with different isocyanate chemistry were able to react with amines to form PU/PHU hybrid materials. The materials that were able to react at room temperature with all cyclic carbonate terminated prepolymers were further used for the analysis of the mechanical properties.

3.3 Adhesion properties of PU/PHU

Lap shear strength is an essential property for industrial adhesives. Therefore, the initial lap shear strength results were measured from different cyclic carbonate terminated prepolymers with the amines that cured at room temperature (A-PEI-1-A-PEI-3 and A-TETA). The curing and sample storage was done at room temperature (23 °C, 50% RH) for one day. It is clearly seen from the Fig. 5 that the CC-HDI-S-based PU/PHUs outperformed other prepolymers and that PU/PHUs formed from CC-HDI-S with the PEI based amines A-PEI-1 to A-PEI-3 had higher strength (7.4-9.2 MPa) compared to A-TETA (4.6 MPa). All PEI amines resulted in similar strength levels within the standard deviation, however the highest value was seen with A-PEI-3. Typically, industrial polyurethane adhesives have lap shear strength levels of 7-13 MPa, so the PEI based amines were able to reach a similar level. The high lap shear strength values with CC-HDI-S can be explained by the highest amount of cyclic carbonate groups originating from the highest NCO content of P-HDI-S. This together with the short chain length in the prepolymer backbone resulted in a higher mass fraction of hard segments (PU and PHU groups) in the final polymer. Furthermore, the mass fraction of the amines in CC-HDI-S was the highest when equimolar amounts were used. High amount of NH groups can further increase the adhesion via hydrogen bonding. All the tested samples broke adhesively, which is typical when stainless steel is used only with surface cleaning. The numerical strength values are in supplementary data (Table ESI 2).

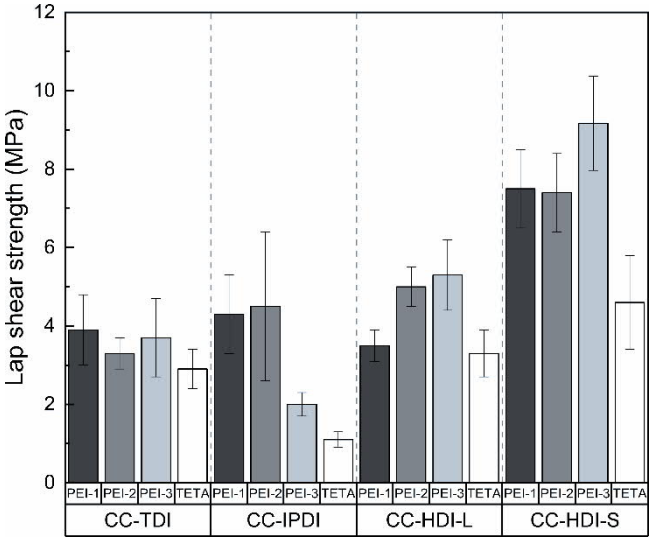


Fig. 5 Lap shear strength results on stainless steel with standard deviation, n=5.

It is known that the adhesion strength of polyurethane develops over time and that the final strength is achieved within 30 days from the reaction. It was studied if the same phenomena takes place with the synthetized PU/PHUs. To study this, the lap shear strength development over time was measured after 1, 7 and 30 days after the reaction (Fig. 6) and their conversions were measured (Table 5, Figs. ESI 17-28) based on the absorption band intensity change in carbonyl band from cyclic carbonate at 1800 cm^{-1}. According to the adhesion strength measurements, all cyclic carbonate terminated prepolymers had rather high strength already after one day from the beginning of the reaction. For CC-TDI-based PU/PHUs, the strength stayed the same within standard deviation from 1 to 30 days with all of the amines. The conversions of CC-TDI and the PEI amines was increasing over time and reached already 96% after 7 days from curing and finally 100% after 30 days from curing. More variation was observed in the lap shear strength with CC-IPDI and CC-HDI-L. When CC-IPDI reacted with A-PEI-2 or A-PEI-3 full conversion was reached after 30 days, but for some reason CC-IPDI with A-PEI-1 did not progress in conversion after the first day. Incomplete conversion with A-PEI-1 could lead to a plasticiser effect from the unreacted cyclic carbonate causing the reduced strength after 30 days from reaction. Interestingly, the strength levels of materials based on CC-HDI-L seemed to decrease over time even though the conversion reached 100% quite rapidly. This could be due to the four functional branch of the prepolymer, which can lead to very complex structures. High initial strength levels were observed with CC-HDI-S with A-PEI-1, A-PEI-2 and A-PEI-3. This is intriguing, as the initial conversions after one day had not yet reached 100%. The fastest amine to reach full conversion with CC-HDI-S was A-PEI-1, which is logical as it had the lowest molar mass from the PEI based amines and it was the easiest one to mix into the cyclic carbonate terminated prepolymer. Interestingly, the strength values did not markedly develop over time even though the conversion was increasing. The reason for this could be that even the conversion was not complete, the highly functional amines had already created a strong network.

Table 5. Conversion in percentage over time with PEI based amines at RT and after the cure cycle (70°C+100 °C).

	CC-TDI			CC-IPDI			CC-HDI-L			CC-HDI-S		
Time	A-PEI-1	A-PEI-2	A-PEI-3	A-PEI-1	A-PEI-2	A-PEI-3	A-PEI-1	A-PEI-2	A-PEI-3	A-PEI-1	A-PEI-2	A-PEI-3
1d	70	76	68	74	70	60	78	82	88	89	85	98
7d	96	96	96	75	73	97	92	100	100	100	93	92
30d	100	100	100	74	100	100	100	100	100	100	100	99
Cure cycle	100			100			100			100	100	100

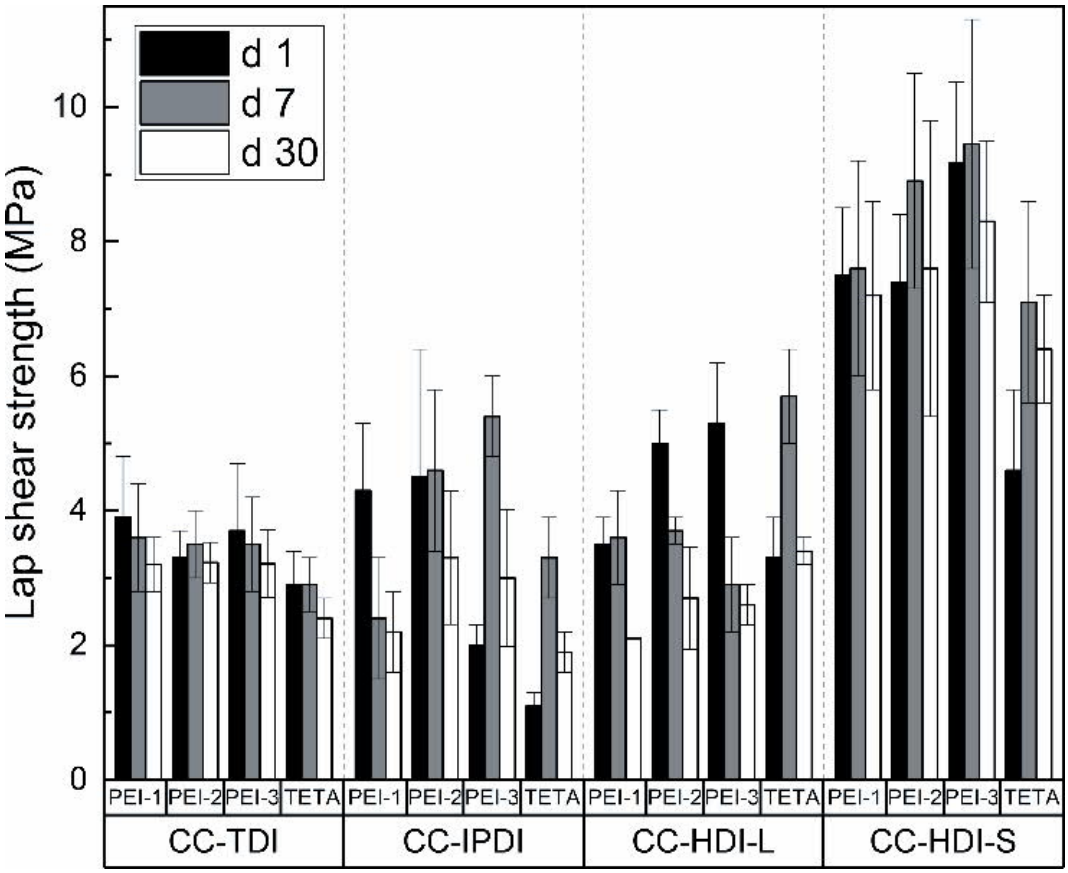


Fig. 6 Lap shear strength development over time on stainless steel with standard deviation, n=5.

The adhesion strength level and its development over a longer period is important, but also the behaviour in the beginning of the cure is of interest in order the material to be industrially feasible. This is related to the required pressing time in the process. The reasonable strength level after the pressing time is considered to be 3 MPa and this kind of level can be reached with industrial polyurethane adhesives from 15 minutes to 7 hours depending on the adhesive speed. This kind of adhesion strength development was studied with the best combination (CC-HDI-S with A-PEI-3) and after 2 hours from the reaction, the reasonable strength level was reached. After that, the reaction slowed down and the full adhesion strength was reached after 24 hours. From a practical point of view, this is a very promising result.

Finally, the impact of curing temperature was studied as there are many publications where elevated temperatures have been used (e.g. refs.[9,10,19,22,23]). For a closer analysis, materials composed of CC-HDI-S with all the PEI amines (A-PEI-1, A-PEI-2 and A-PEI-3) were selected as they had the most promising strength results in previous tests. With CC-TDI, CC-IPDI and CC-HDI-L only one amine type (A-PEI-1) was used for evaluating the impact of the temperature. Two different elevated temperatures were tested; 70 °C for 12 hours, and a cure cycle of first 70 °C for 12 hours and 100 °C for 3 hours similar to Panchireddy et al. [22]. After the curing, the samples were left to stabilize at room temperature for one day. As can be seen from Fig. 7, increasing the temperature had neutral or positive impact on the lap shear strength results. It was also seen that heat cycle was more efficient compared to 70 °C. With most of the PU/PHUs, the lap shear strength was higher when cured at higher temperatures, the only difference was CC-HDI-S with A-PEI-3, which reached the same lap shear strength level already at room temperature. The conversions were measured after the cure cycle and all of them reached 100% (Table 5, Figs. ESI 29-32).

Since it was possible to see some improvement in the strength values at elevated temperature, gel contents were measured from the CC-HDI-S based PU/PHUs. Gel content indicates the crosslinking degree. Gel contents from the room temperature cured polymers were high, more than 94% for A-PEI-1, A-PEI-2 and A-PEI-3 (Table 6). This was expected as PEI amines have a high number of primary amines resulting in highly crosslinked thermoset material. The amount of primary amines in A-PEI-1, A-PEI-2 and A-PEI-3 (i.e. 8.1, 12.1 and 16.8, respectively) did not have an impact on the gel content. The gel contents from the samples cured with the cure cycle at elevated temperature (70 °C + 100 °C) were slightly higher between 95-99%, but the increase was not significant. The reason for the small improvement in gel content could be the better diffusion and organisation of the polymer network at elevated temperatures.

Table 6. Gel content after room temperature curing and after the cure cycle used with CC-HDI-S.

Used amine	RT Gel Content	70 °C + 100 °C Gel Content
A-PEI-1	94.9	98.4
A-PEI-2	94.0	97.8
A-PEI-3	94.9	95.4

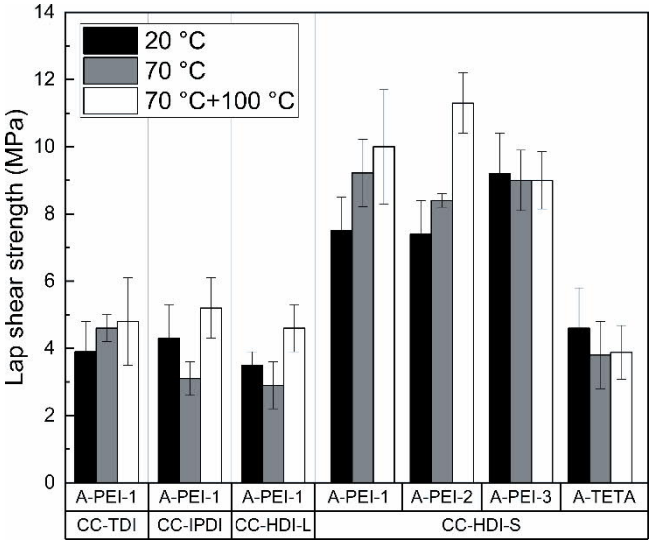


Fig. 7 Lap shear strength of samples cured at different temperatures on stainless steel with standard deviation, n=5.

3.4 Mechanical properties of PU/PHUs

Tensile strength and elongation at break indicate the cohesive strength of the polymer. In this study, tensile strength and elongation at break were measured after 30 days from the reaction. Samples were stored at room temperature. For reference, another set of samples was prepared with the cure cycle of 12 h at 70 °C and 3 h at 100 °C followed by one day stabilization at room temperature. The tensile strength specimens were difficult to produce due to the high viscosity of the starting materials and their tendency to separate after film application (see Fig. ESI 33). This was particularly the case with CC-IPDI with all the PEI amines and with CC-TDI with A-PEI-2 and A-PEI-3 amines. With A-TETA, the films were so flexible that cutting was not possible. Only the well-mixed films were cut and tested. The well-mixed samples formed transparent and colourless materials (see Fig. ESI 1). When evaluating the results in Fig. 8, the samples cured at elevated temperature had better or similar results, with the strength improvement from varying between ca. 10% and 57% (Table ESI 4). The highest tensile strength was reached with CC-HDI-S with A-PEI-3. Surprisingly, also the elongation was slightly higher for the higher temperature cured samples, although in some cases the high standard deviation can mislead the conclusions. Typically, when the strength is increased, the elongation will decrease. Improved elongation and the better results in general at elevated temperatures could be because of better diffusion and orientation of polymer chains. When compared to industrial analogues, which range from 5-12 MPa in tensile strength, the PU/PHUs did not quite reach the same levels. There is room for improvement in the cohesive strength of the material e.g. by fillers.

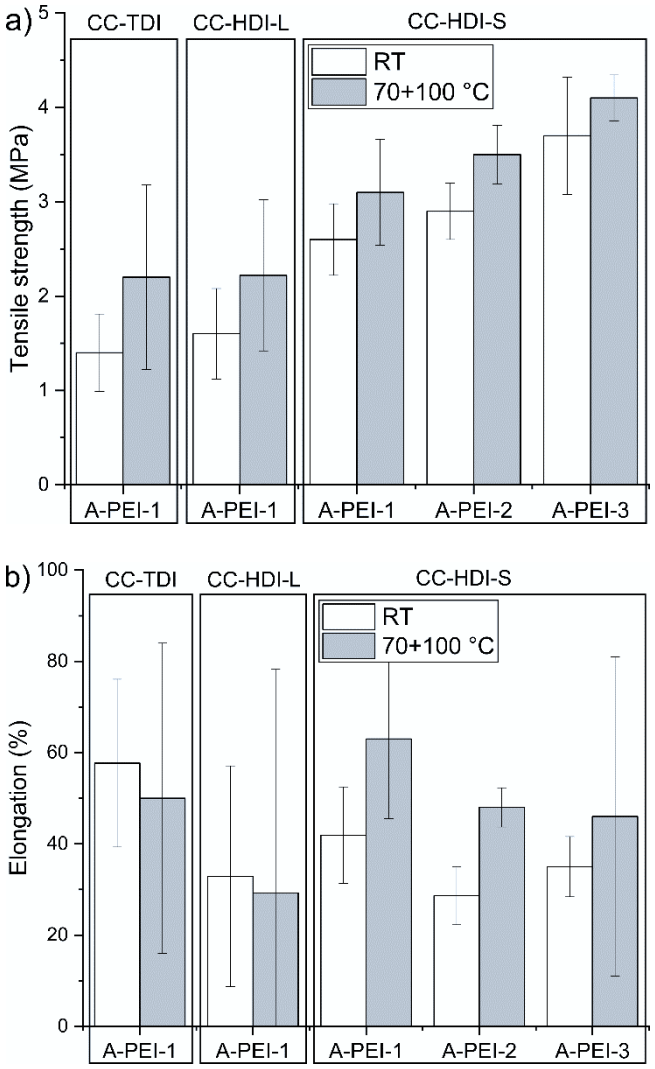


Fig. 8 Tensile strength (a) and elongation at break (b) of different prepolymers at room temperature and at elevated temperature, n = 3-5.

4. Conclusions

The aim of the study was to find alternative PU/PHU hybrids where the cyclic carbonate terminated prepolymer could be manufactured in mild conditions and the resulting PU/PHU would have high strength level when cured at room temperature. Based on the findings, it was possible to synthetize cyclic carbonate terminated prepolymers from different commercially available isocyanate based prepolymers (TDI, IPDI and HDI) with glycerol carbonate in the presence of catalyst. From the initial screening tests with different commercially available amines, only PEI amines and TETA reacted at room temperature with cyclic carbonate terminated prepolymers. These amines had secondary amines, which catalysed the reaction. Adhesive and mechanical properties were evaluated for the successful prepolymer/amine pairs. The

highest lap shear strength results were obtained with a cyclic carbonate terminated prepolymer made from lower molar mass HDI prepolymer with PEI amine. The reason for the superior performance could be the high initial NCO content, short backbone and high amount of hydrogen bonding from PU, PHU and NH groups. Furthermore, PEI amines are polyfunctional enabling the structure to be highly crosslinked and this was further proven by the high gel content. The synthetized PU/PHUs reached high lap shear strength level already after one day from reaction and in most cases, the strength stayed approximately the same over time. When comparing the tensile strength and lap shear strength results to the typical industrial adhesives, the lap shear strengths were on similar level, but the tensile strength was lower. This implies that the adhesion properties of the PU/PHU materials seem to be very good (due to additional hydrogen bonding from PHU and NH), but the cohesive strength of the material could be improved. In both lap shear and tensile strength measurements, increasing the curing temperature had a positive impact. Therefore, the optimization of the reaction at room temperature would be interesting to study further via improving the miscibility of the components or by using a catalyst. Better miscibility could improve the reliability of the reactions minimising the deviations.

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Appendix A. Supplementary material

Supplementary data is available.

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Figure Captions

Fig.1. Chemical structures of the amines used (A-PEI-1 to A-Ar).

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Supplementary data for the article

Feasibility of polyamines and cyclic carbonate terminated prepolymers in polyurethane/polyhydroxyurethane synthesis

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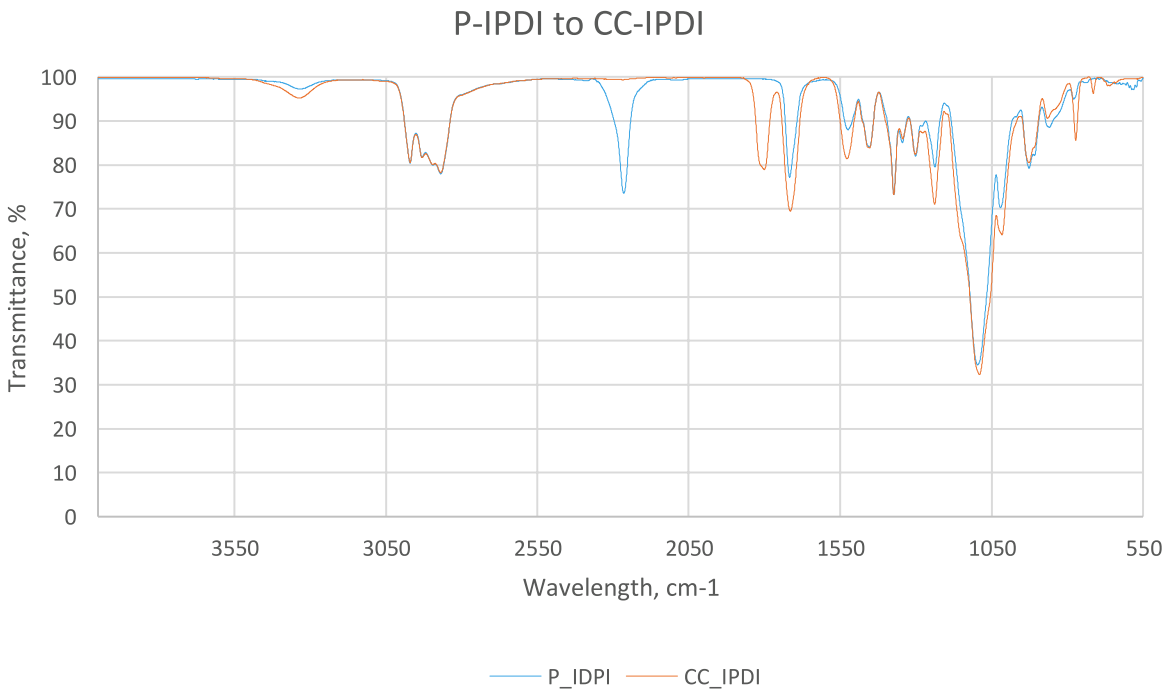

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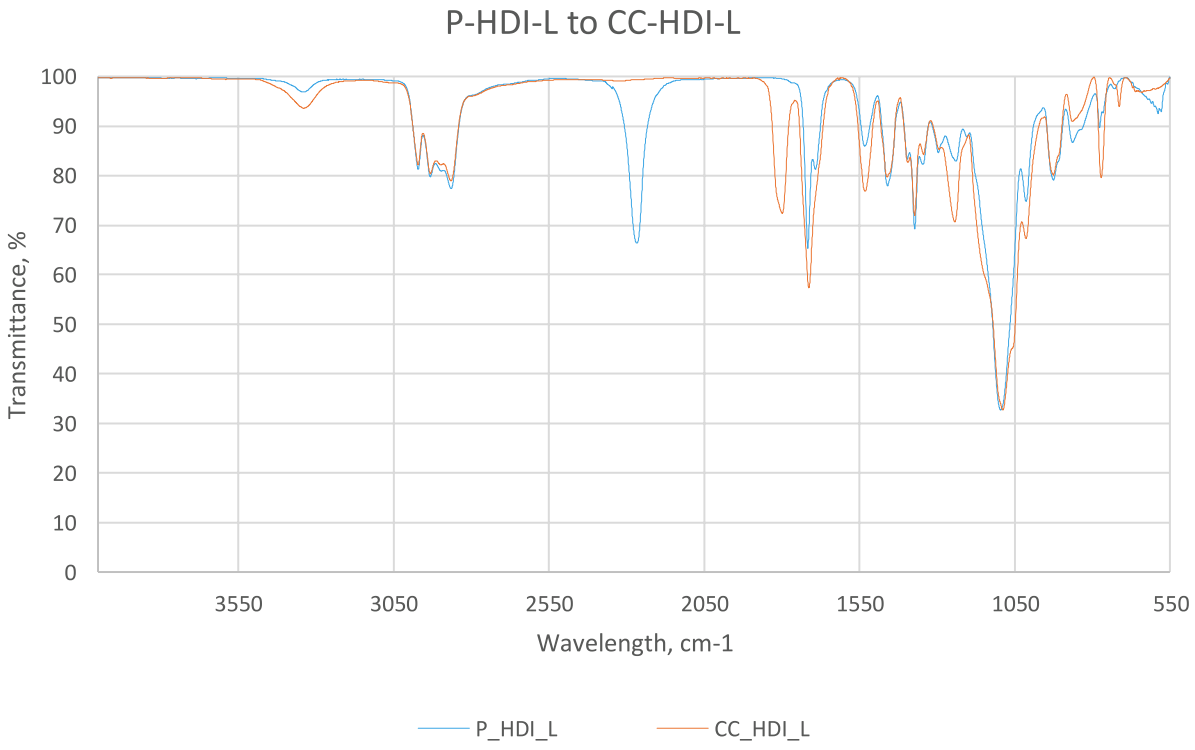

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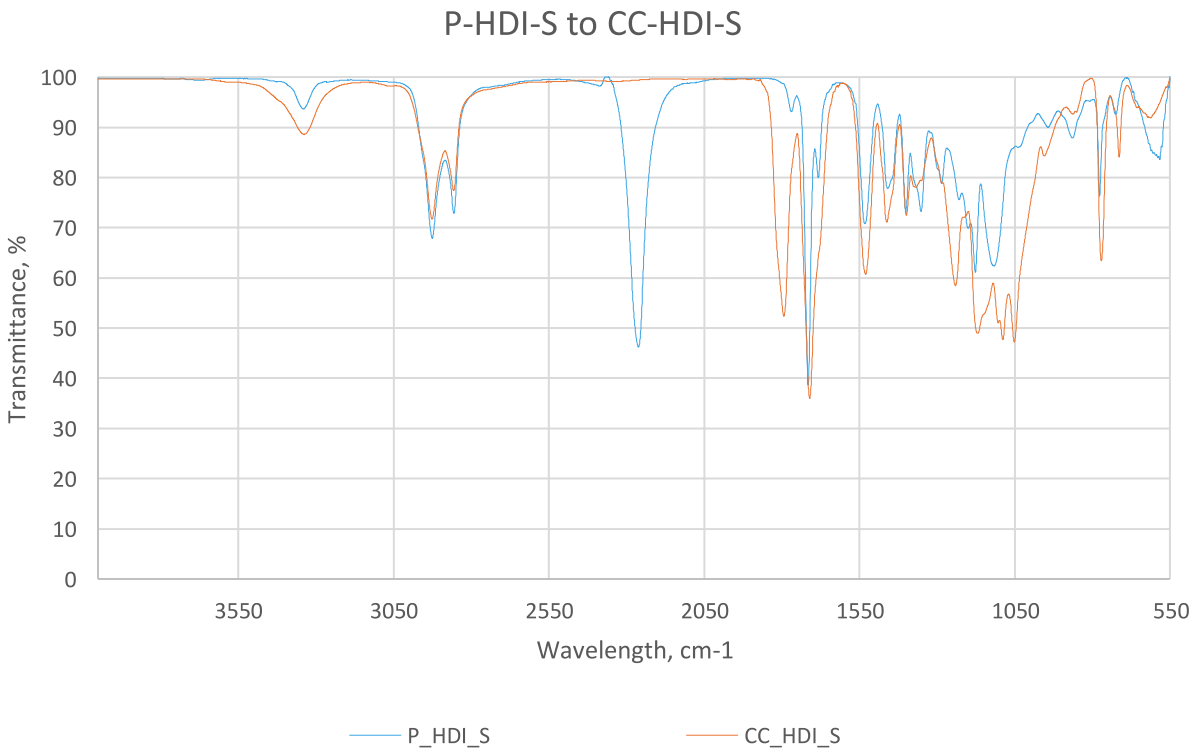

Fig. ESI 4. P-HDI-S synthesis to CC-HDI-S after four hours (NCO absorption band at 1800 cm^{-1} disappeared).

1.2 ***Initial screening results***

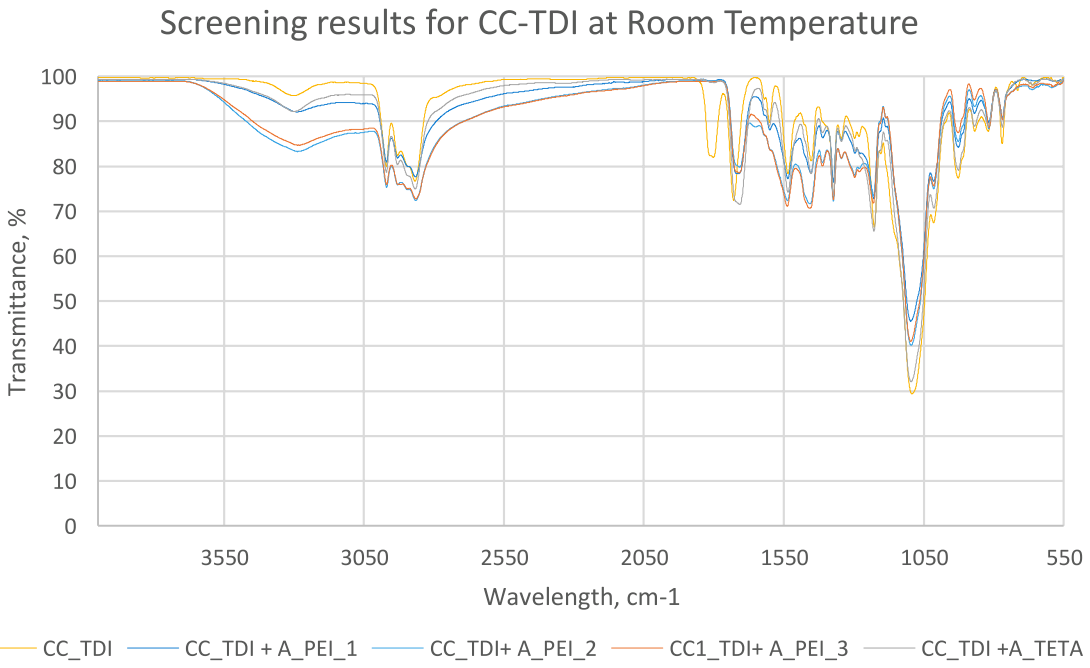

Fig. ESI 5. Initial screening results for CC-TDI and A-PEI-1, A-PEI-2, A-PEI-3 and A-TETA at room temperature.

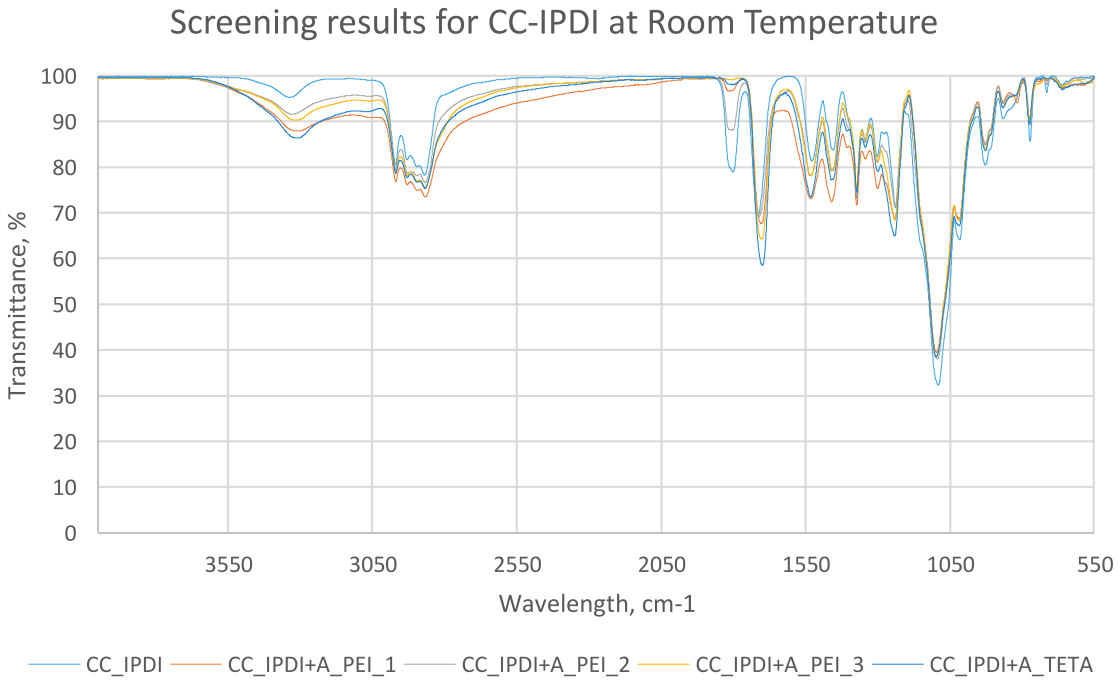

Fig. ESI 6. Initial screening results for CC-IPDI and A-PEI-1, A-PEI-2, A-PEI-3 and A-TETA at room temperature.

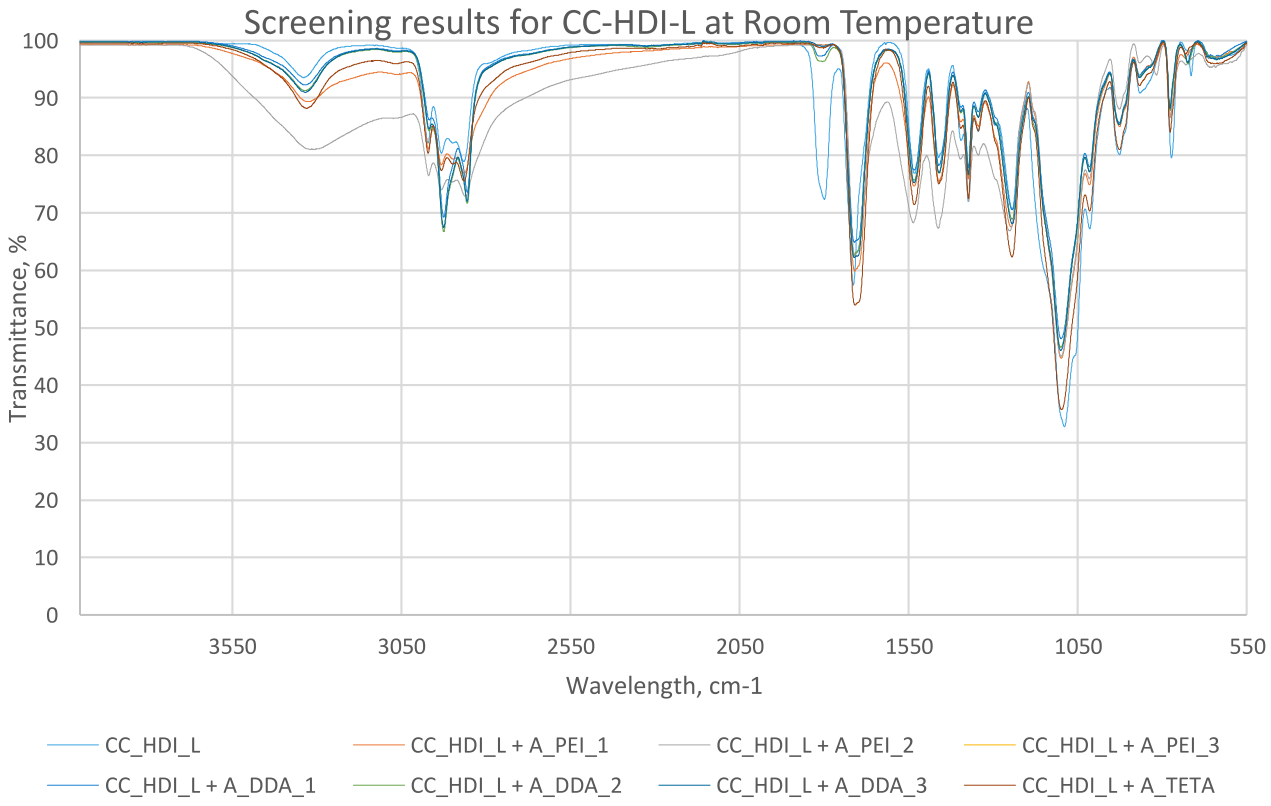

Fig. ESI 7. Initial screening results for CC-HDI-L and A-PEI-1, A-PEI-2, A-PEI-3, A-DDA-1, A-DDA-2, A-DDA-3 and A-TETA at room temperature.

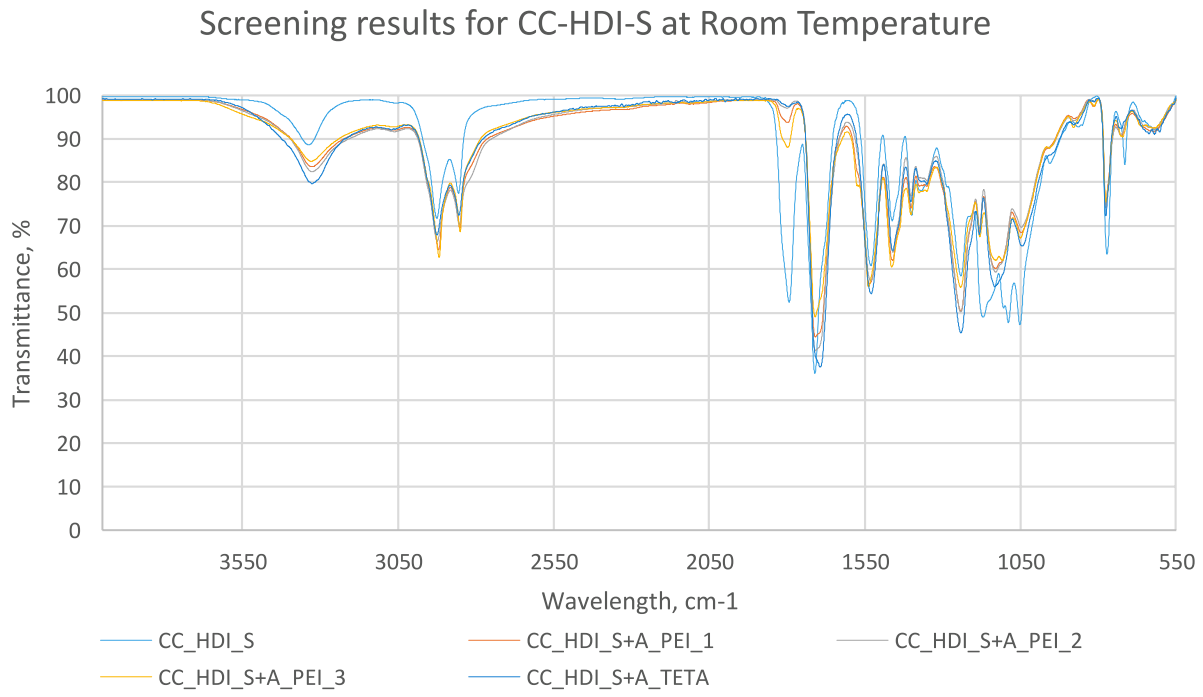

Fig. ESI 8. Initial screening results for CC-HDI-S and A-PEI-1, A-PEI-2, A-PEI-3 and A-TETA at room temperature.

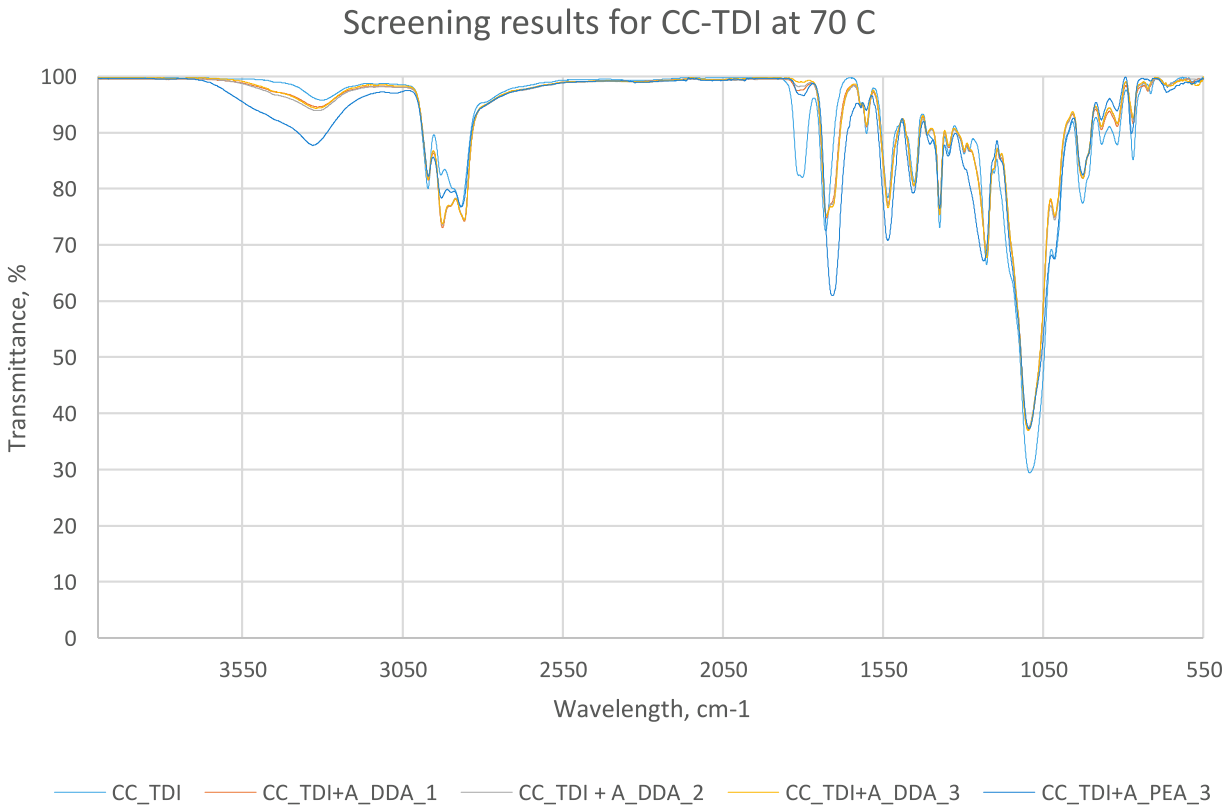

Fig ESI 9. Initial screening results for CC-TDI and A-DDA-1, A-DDA-2, A-DDA-3 and A-PEA-3 at 70 °C.

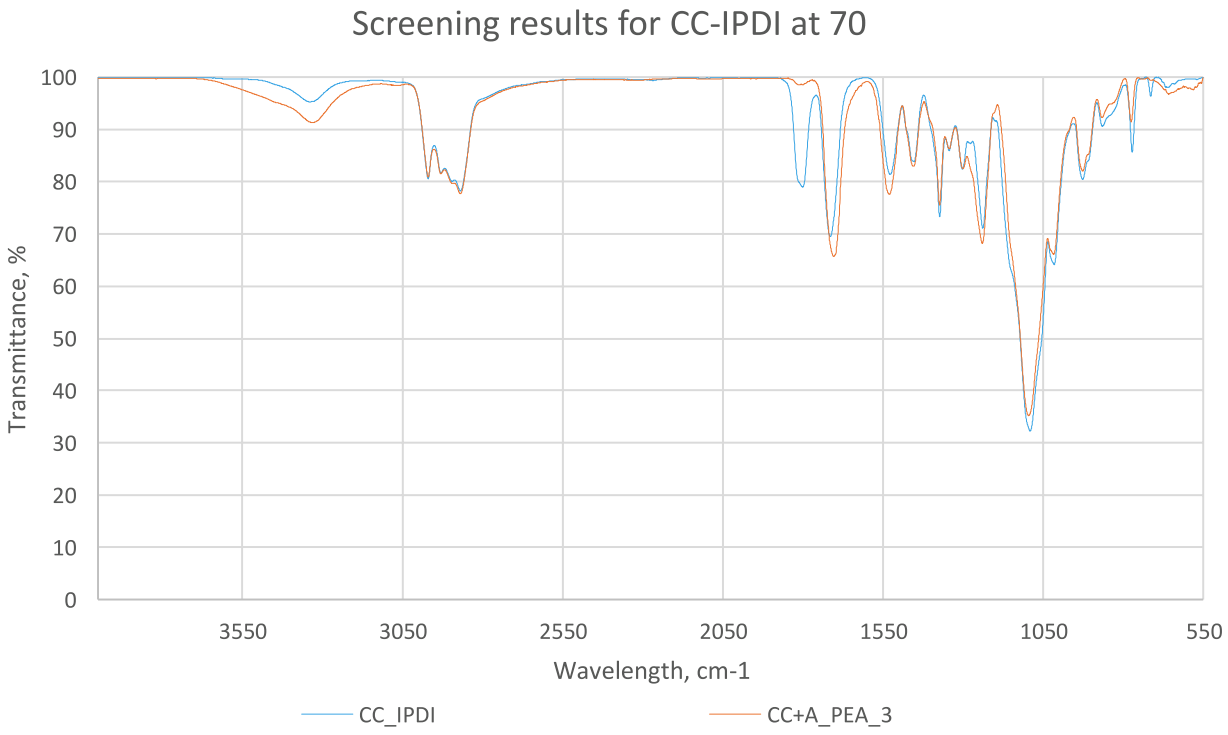

Fig. ESI 10. Initial screening results for CC-IPDI and A-PEA-3 at 70 °C.

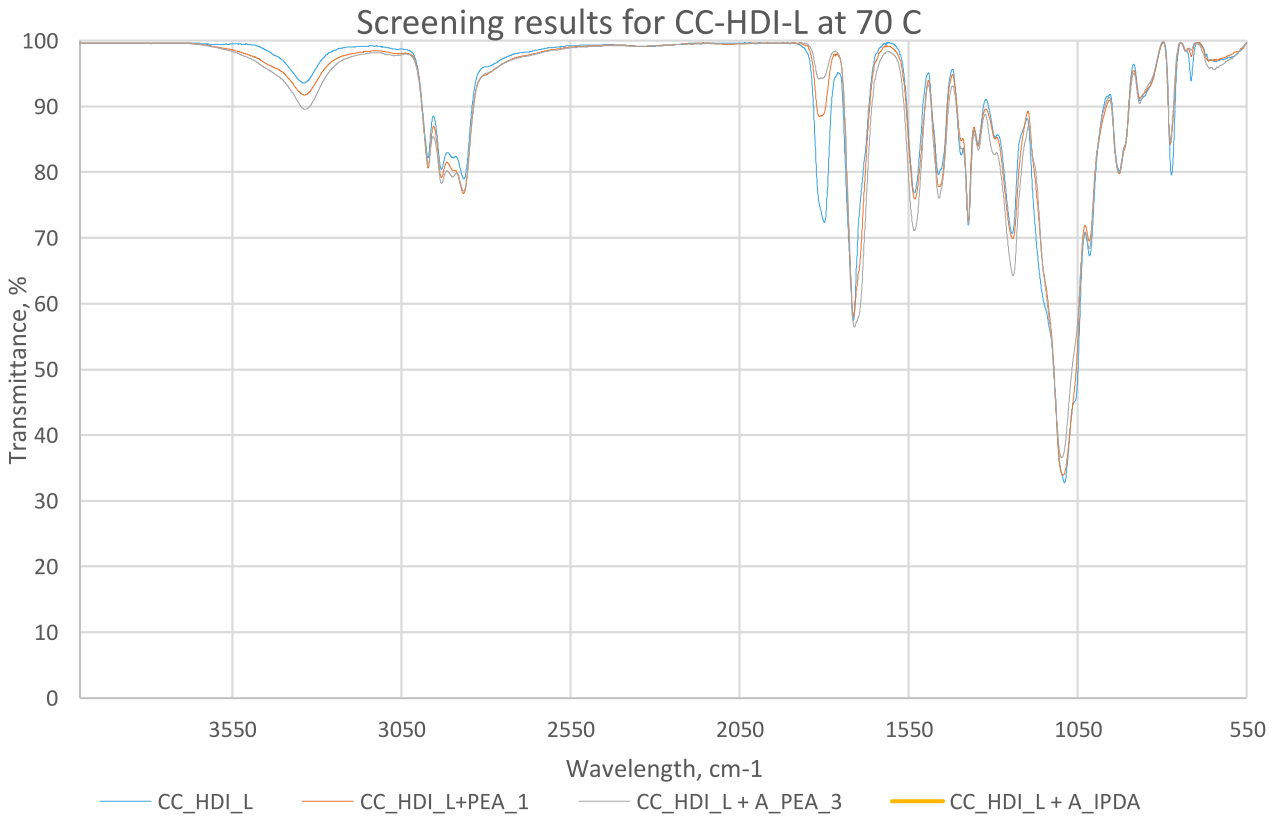

Fig. ESI 11. Initial screening results for CC-HDI-L and A-PEA-1, A-PEA-3 and A-IPDA at 70 °C.

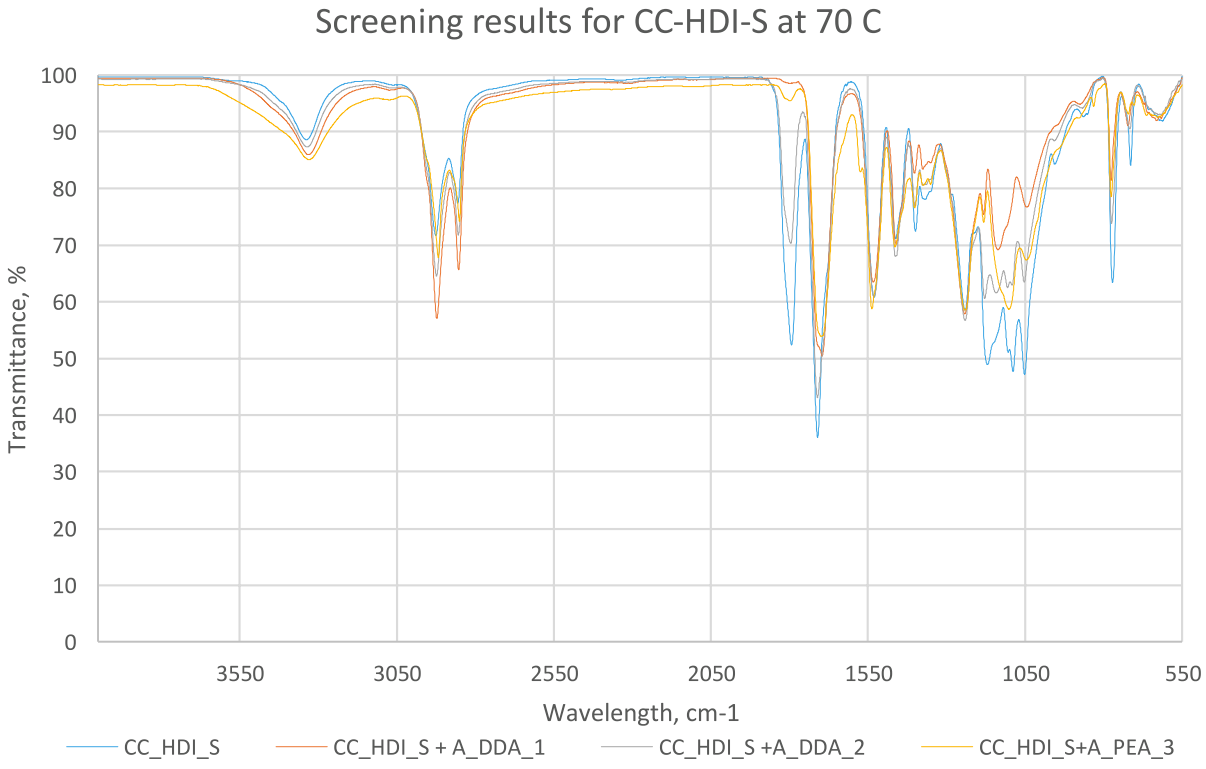

Fig. ESI 12. Initial screening results for CC-HDI-S and A-DDA-1, A-DDA-2 and A-PEA-3 at 70 °C.

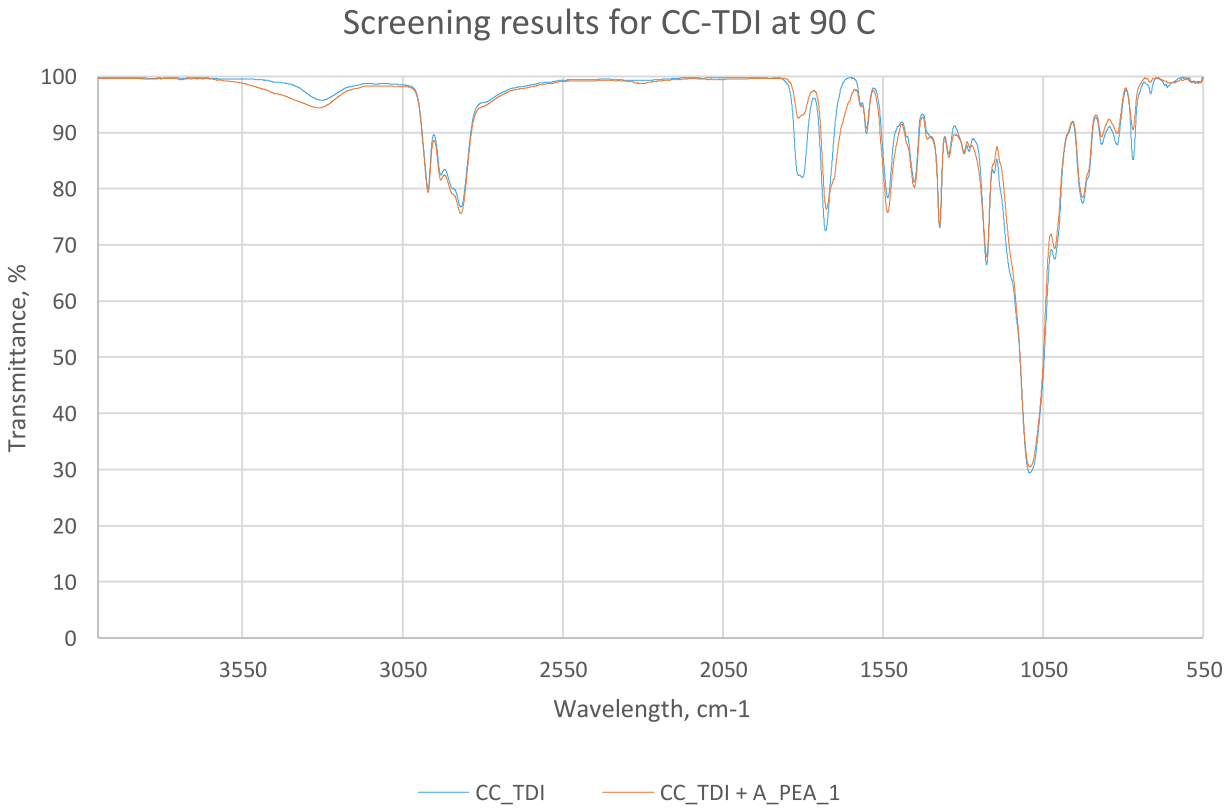

Fig. ESI 13. Initial screening results for CC-TDI and A-PEA-1 at 90 °C.

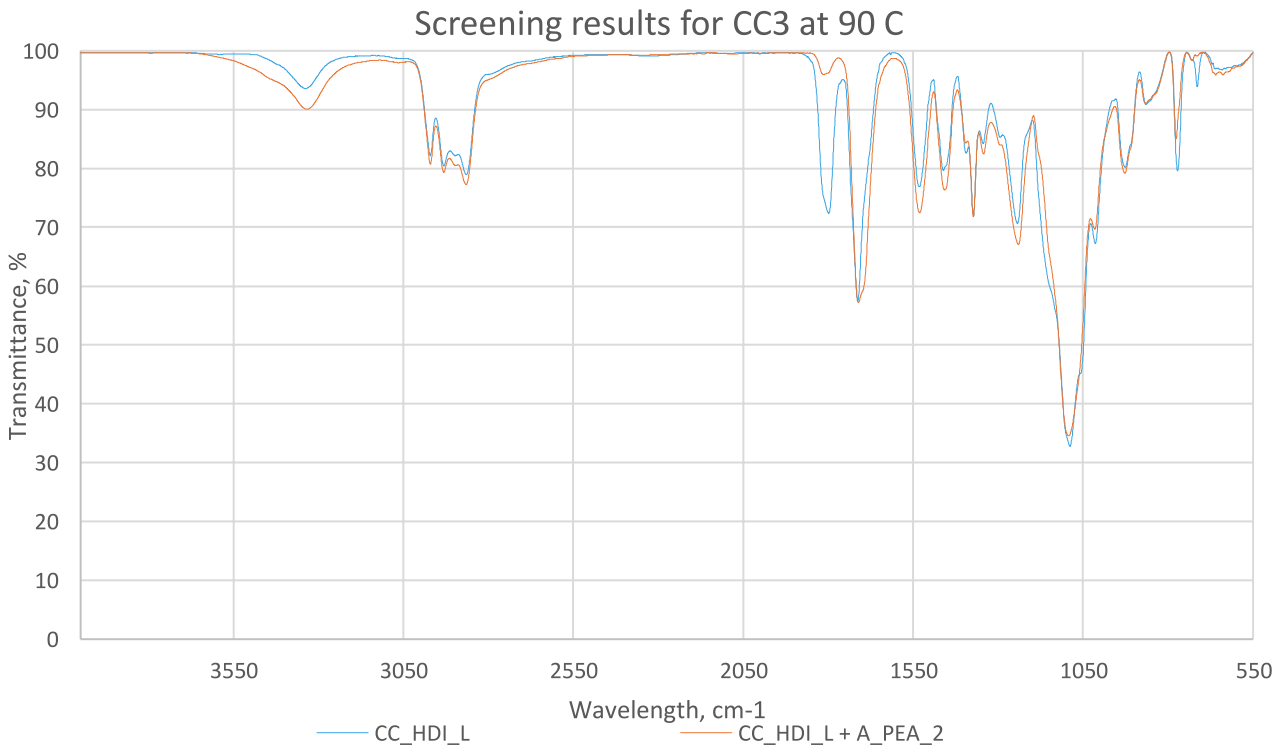

Fig. ESI 14. Initial screening results for CC-HDI-L and A-PEA-2 at 90 °C.

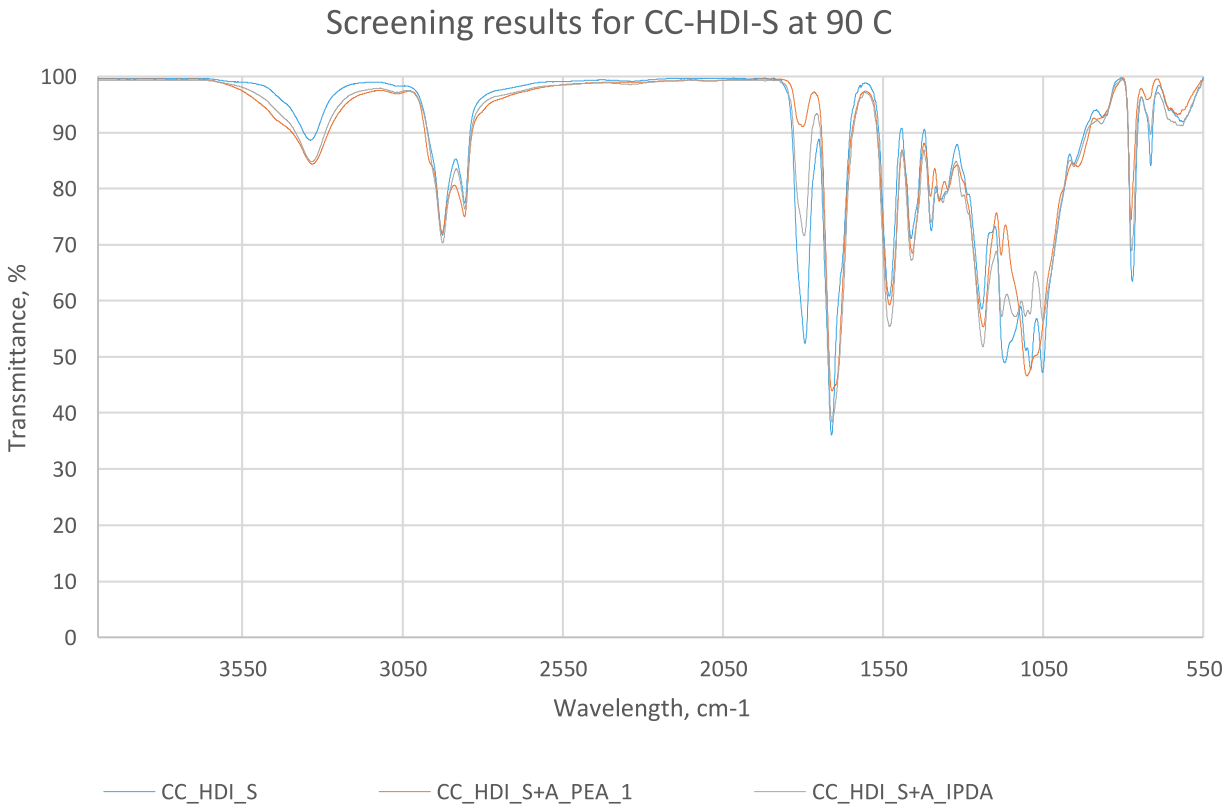

Fig. ESI 15. Initial screening results for CC-HDI-S and A-PEA-1 and A-IPDA at 90 °C.

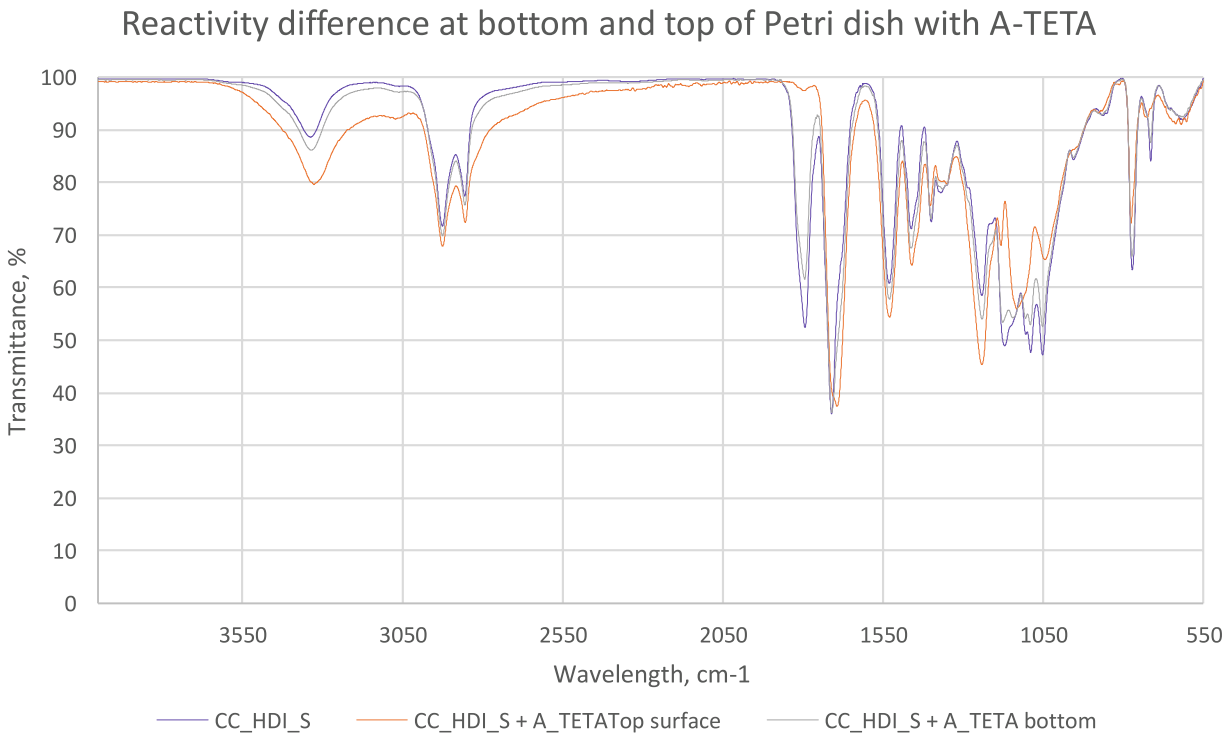

Fig. ESI 16. Reactivity difference at top and bottom of the Petri dish with CC-HDI-S and A-TETA.

1.3 ***Curing over time***

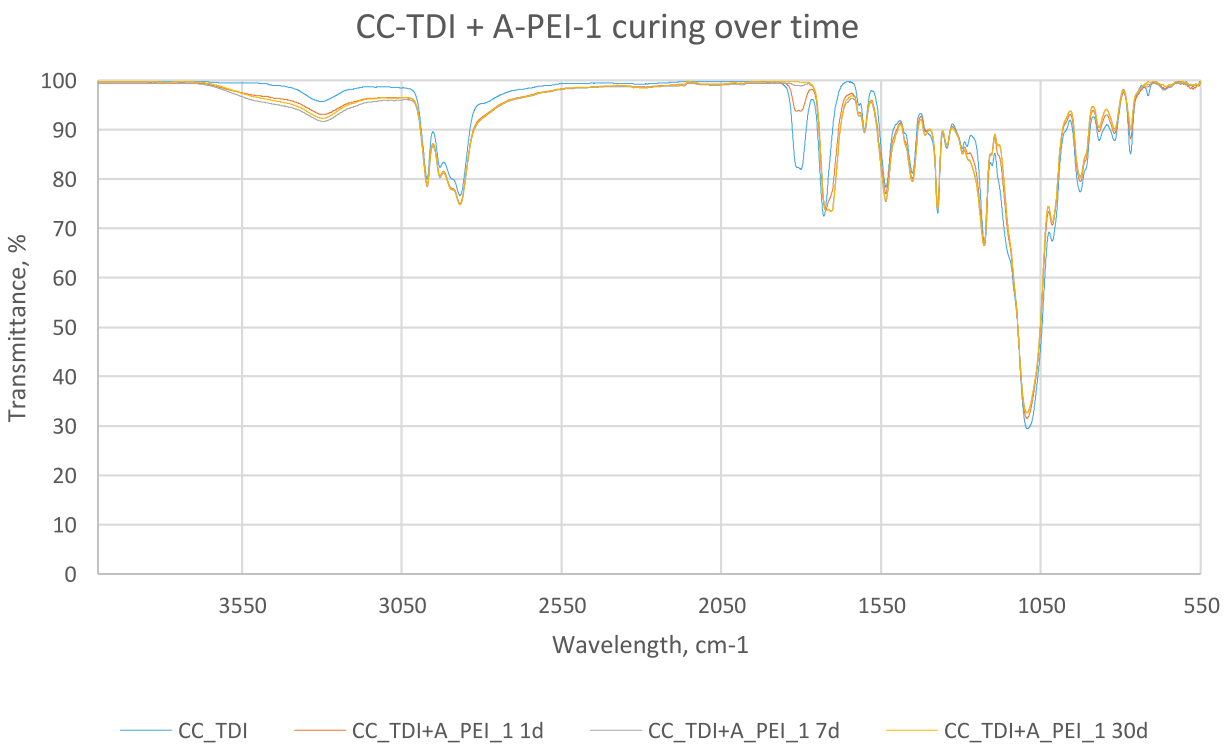

Fig. ESI 17. Curing over time with CC-TDI and A-PEI-1.

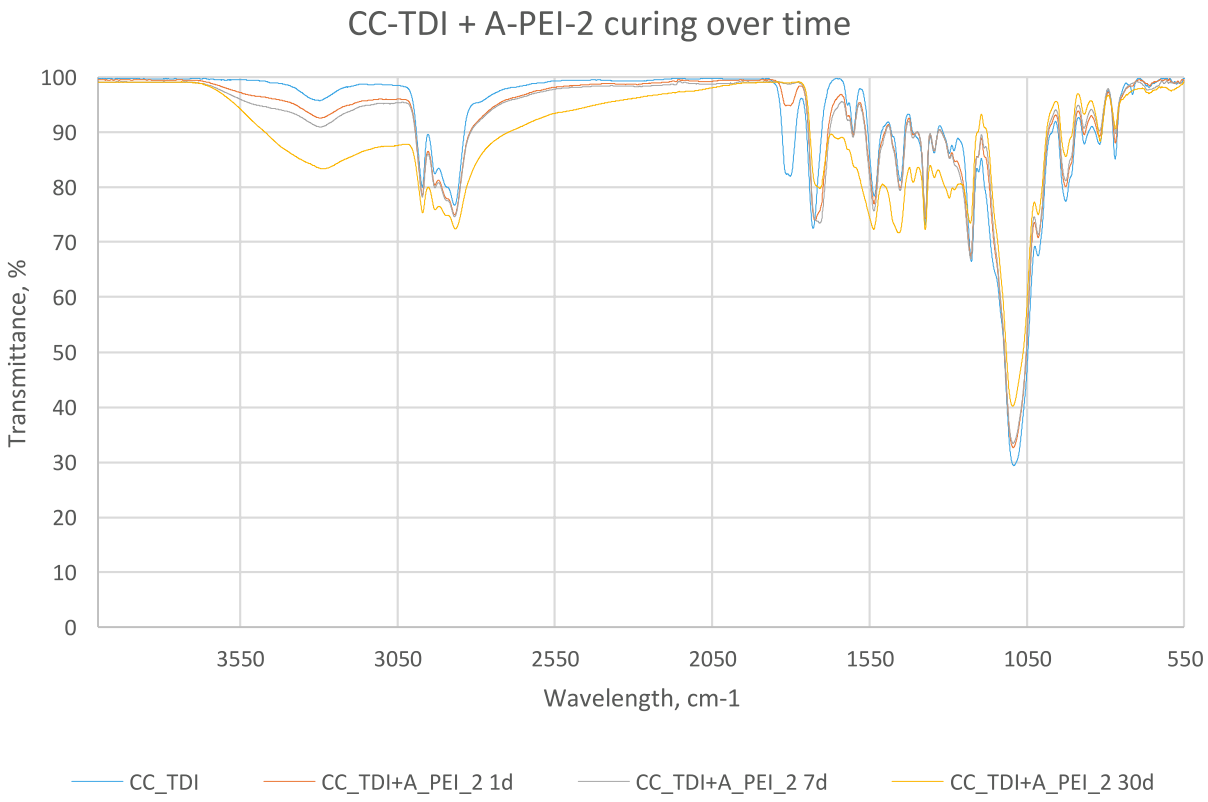

Fig. ESI 18. Curing over time with CC-HDI-S and A-PEI-2.

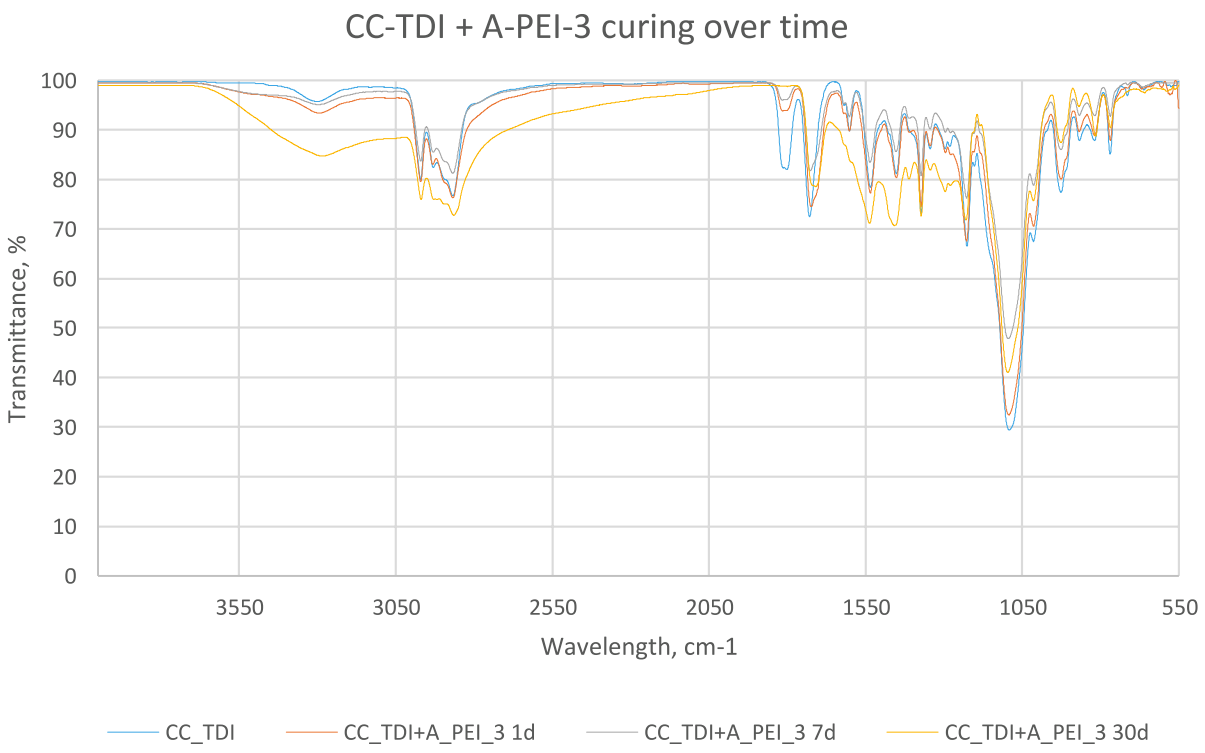

Fig. ESI 19. Curing over time with CC-TDI and A-PEI-3.

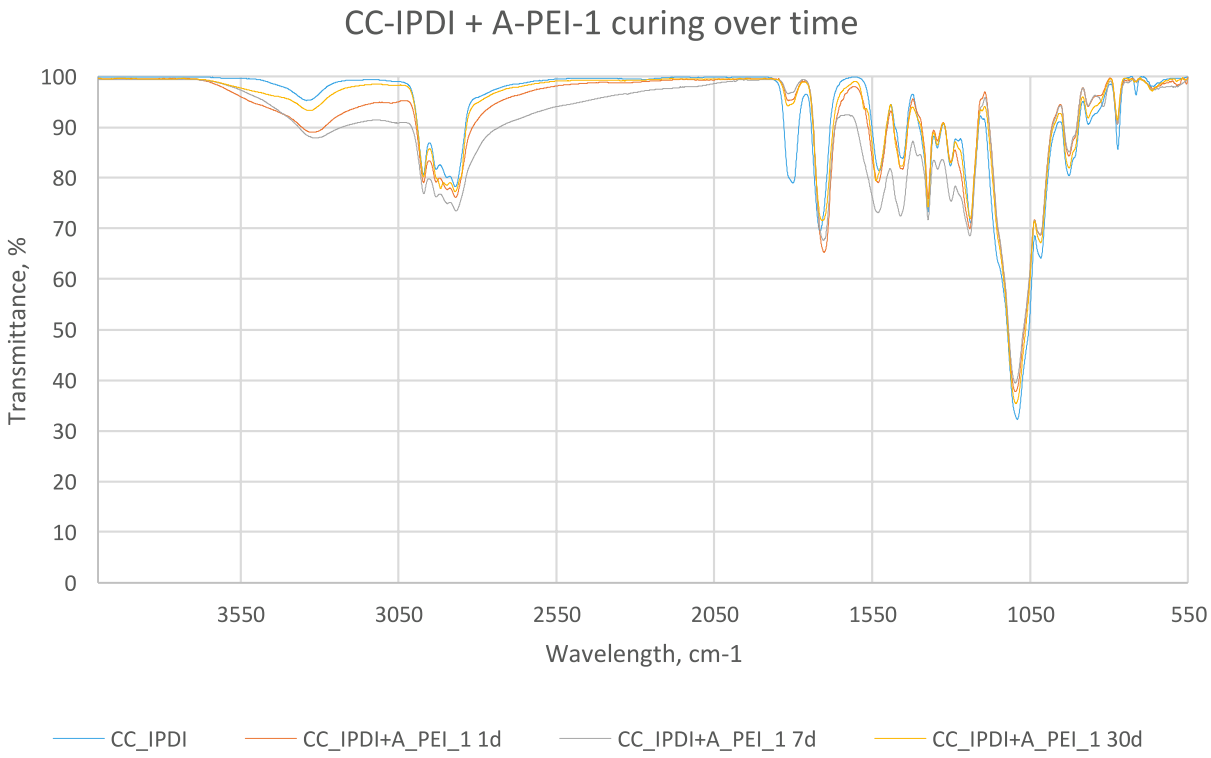

Fig ESI 20. Curing over time with CC-IPDI and A-PEI-1.

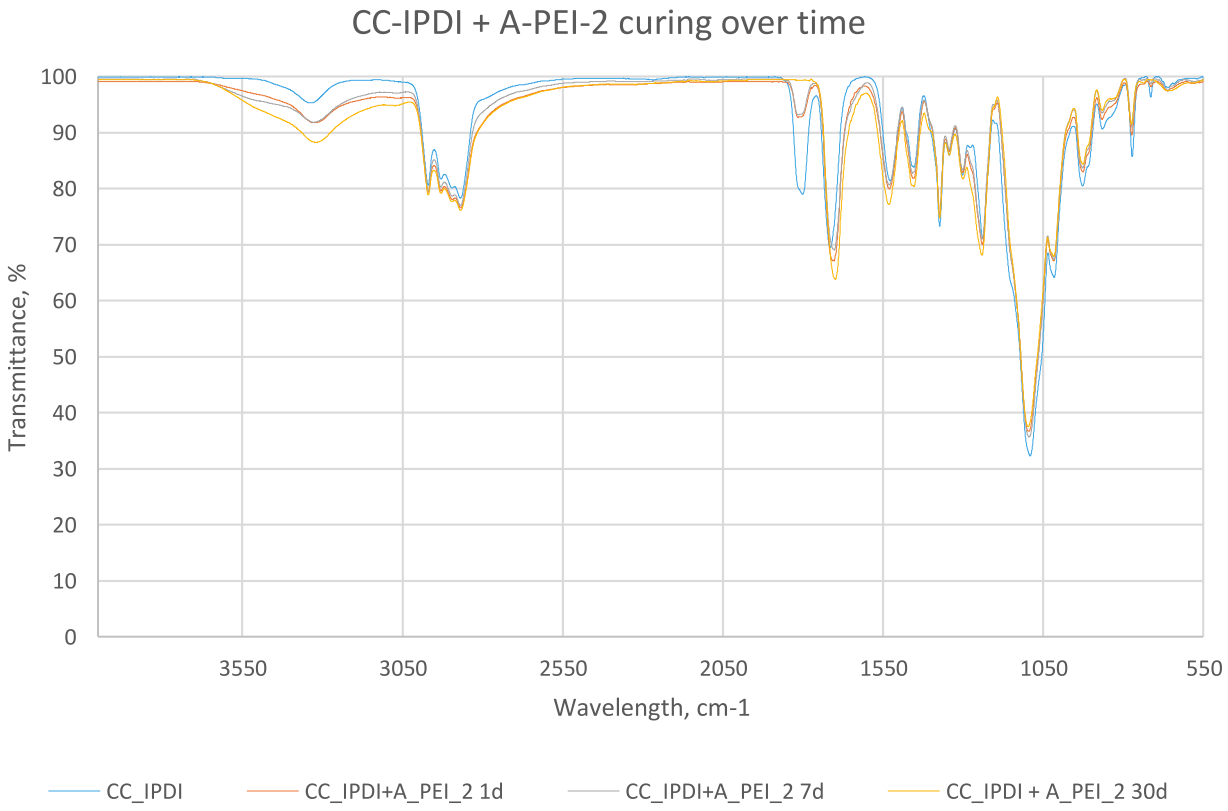

Fig. ESI 21. Curing over time with CC-IPDI and A-PEI-2.

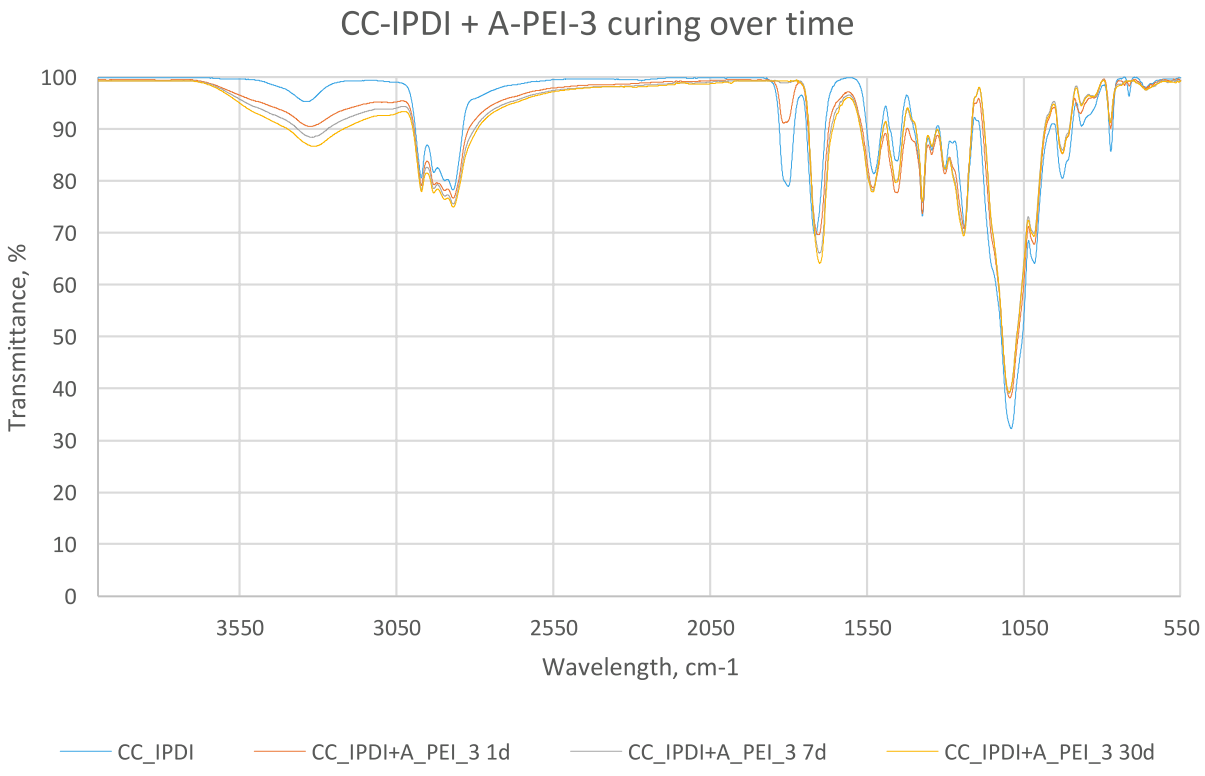

Fig. ESI 22. Curing over time with CC-IPDI and A-PEI-3.

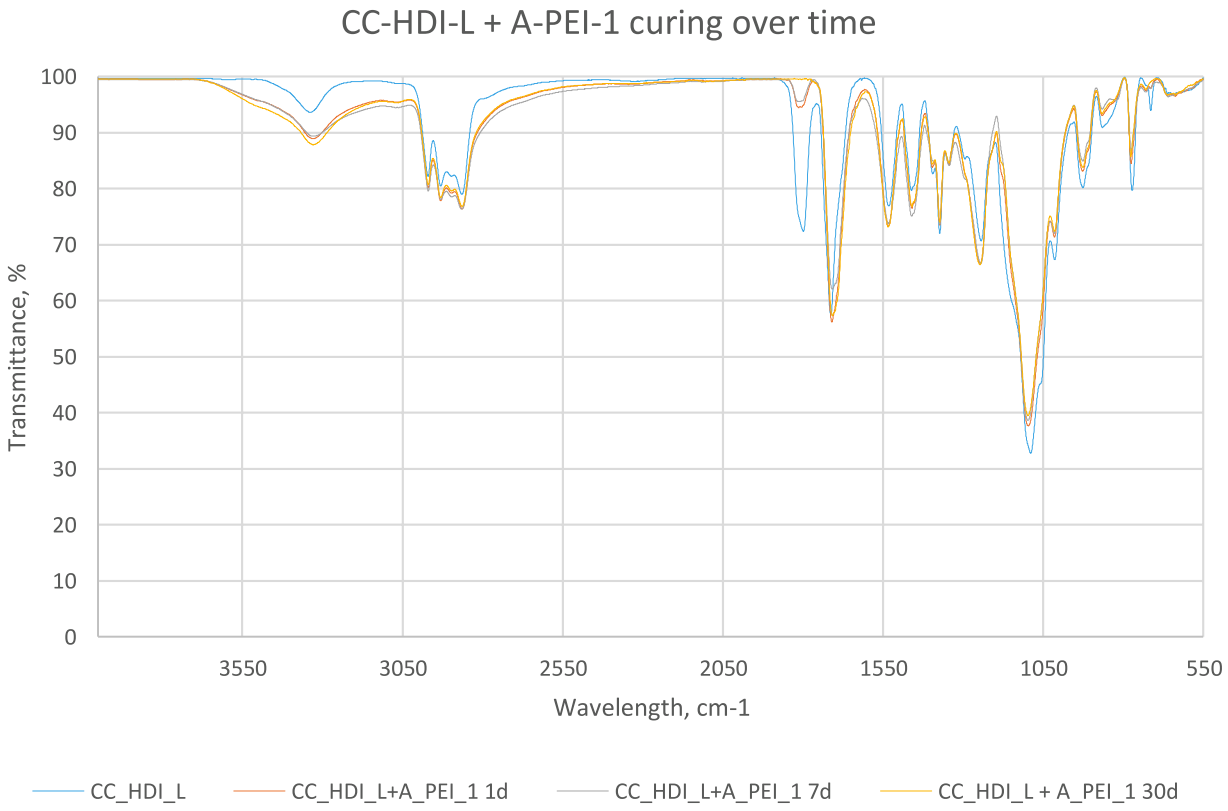

Fig. ESI 23. Curing over time with CC-HDI-L and A-PEI-1.

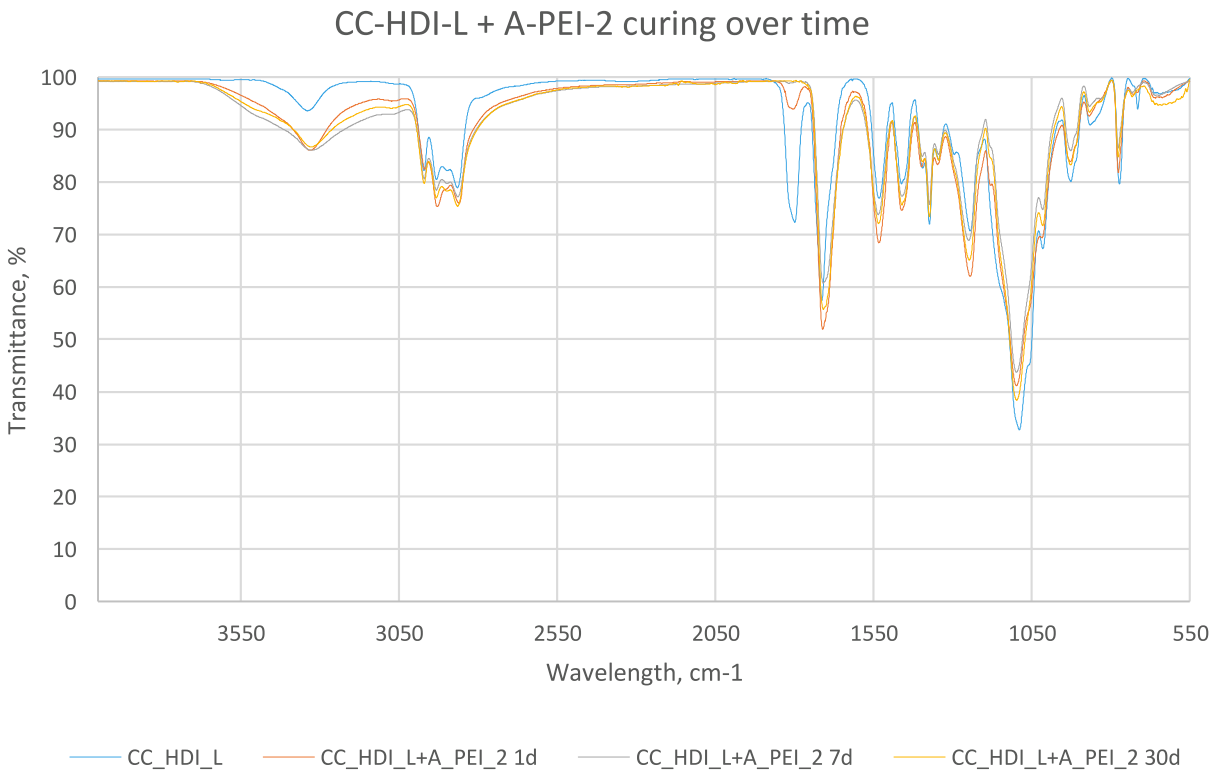

Fig. ESI 24. Curing over time with CC-HDI-L and A-PEI-2.

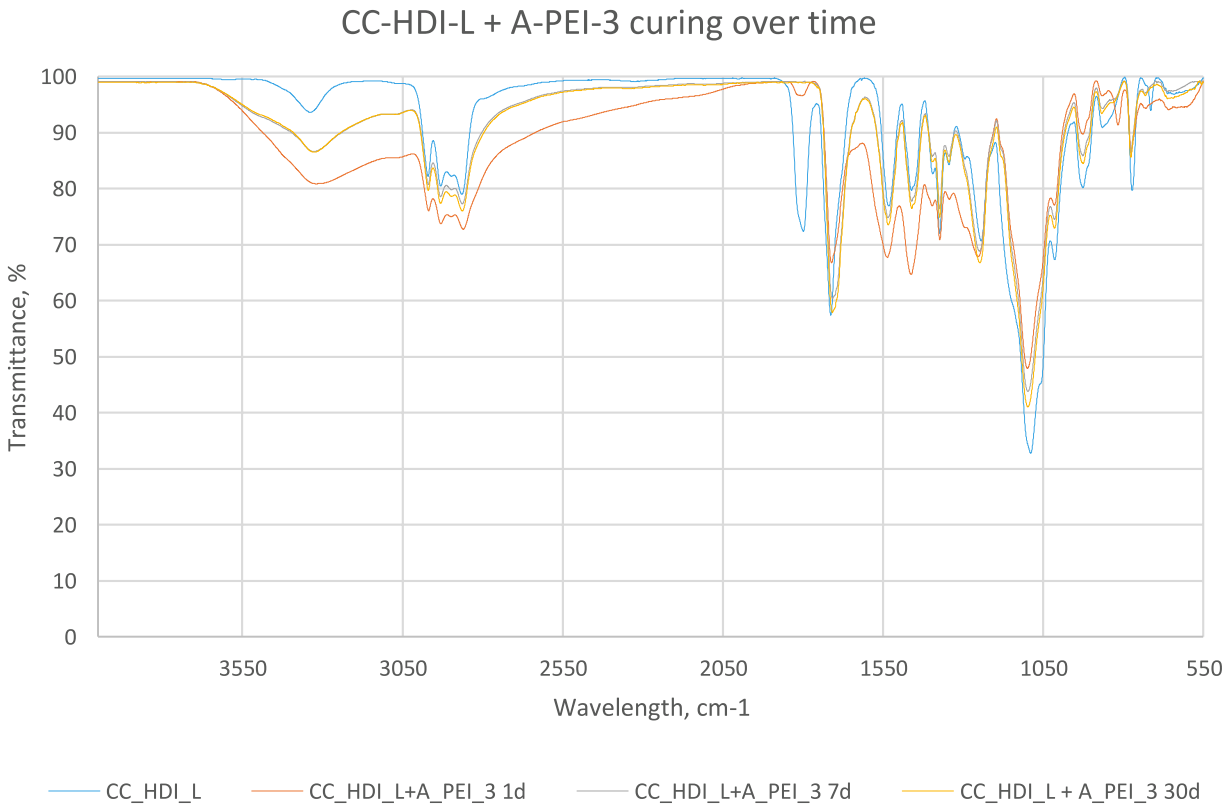

Fig. ESI 25. Curing over time with CC-HDI-L and A-PEI-3.

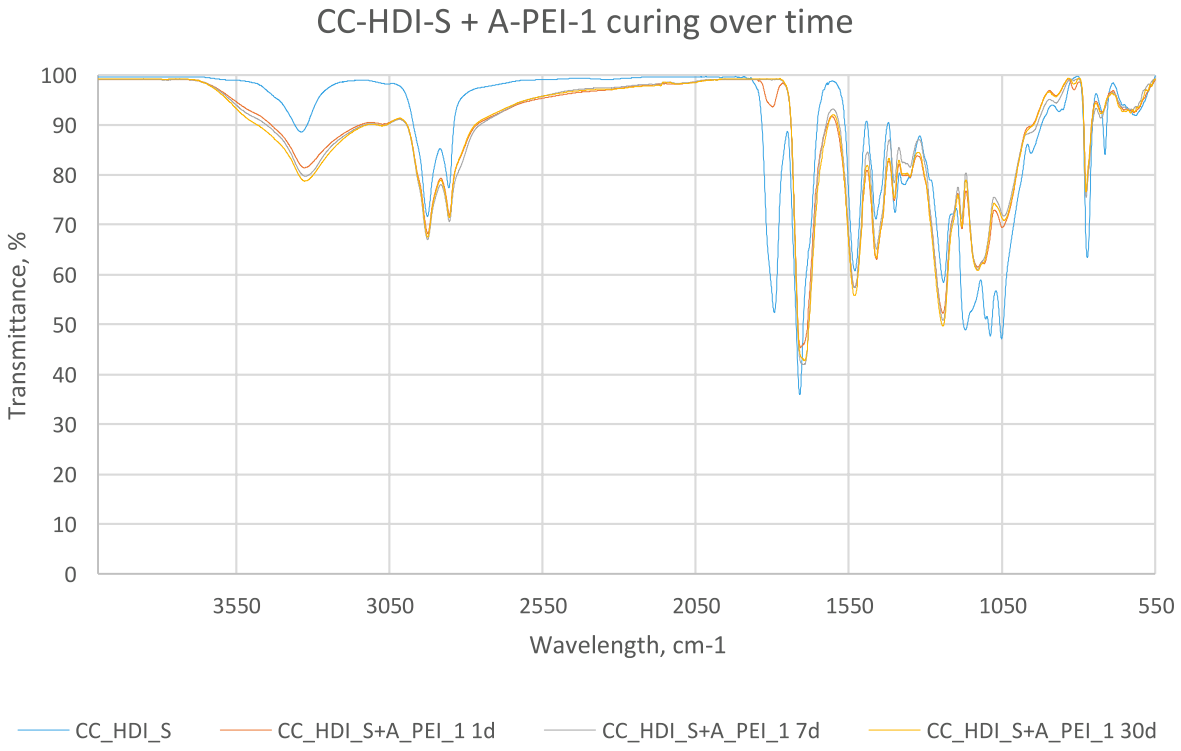

Fig. ESI 26. Curing over time with CC-HDI-S and A-PEI-1.

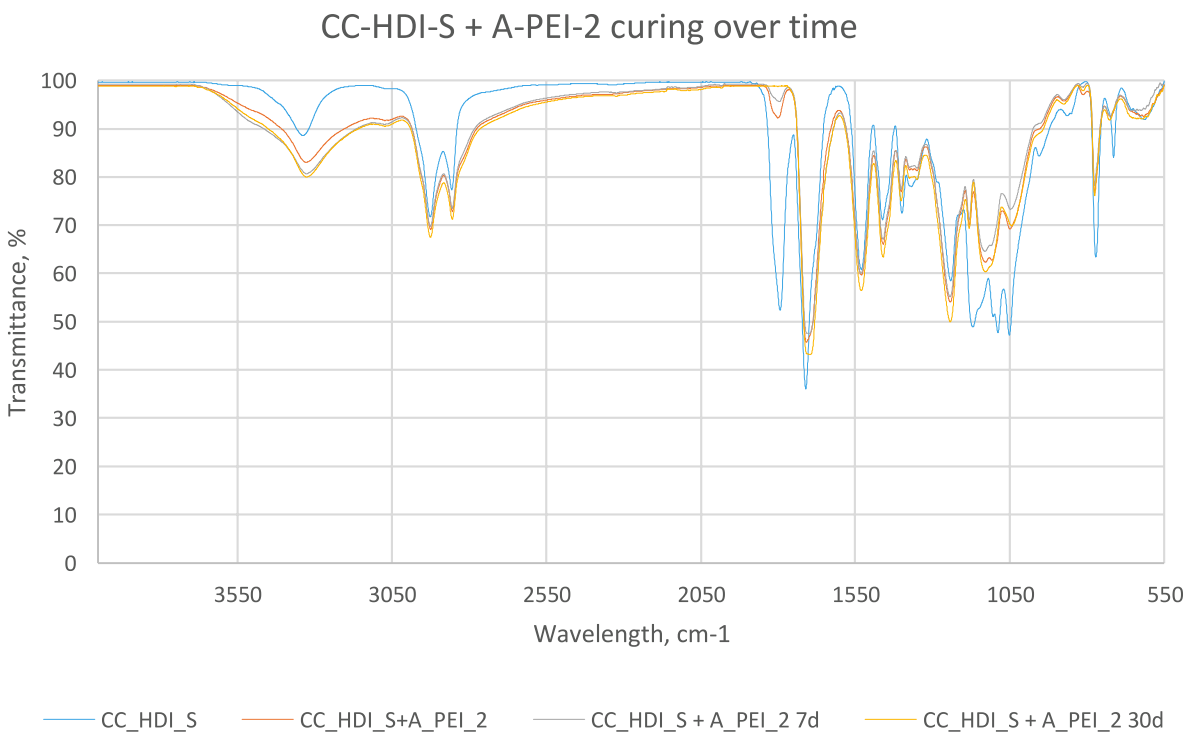

Fig. ESI 27. Curing over time with CC-HDI-S and A-PEI-2.

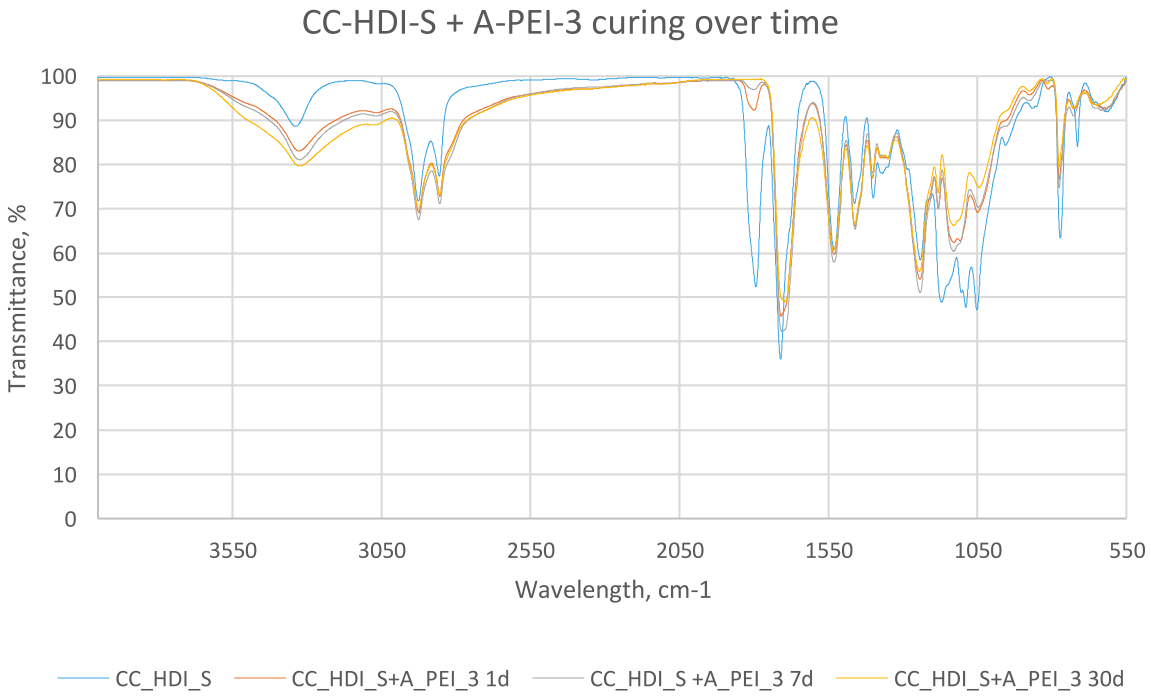

Fig. ESI 28. Curing over time with CC-HDI-S and A-PEI-3.

1.4 ***Impact of cure cycle***

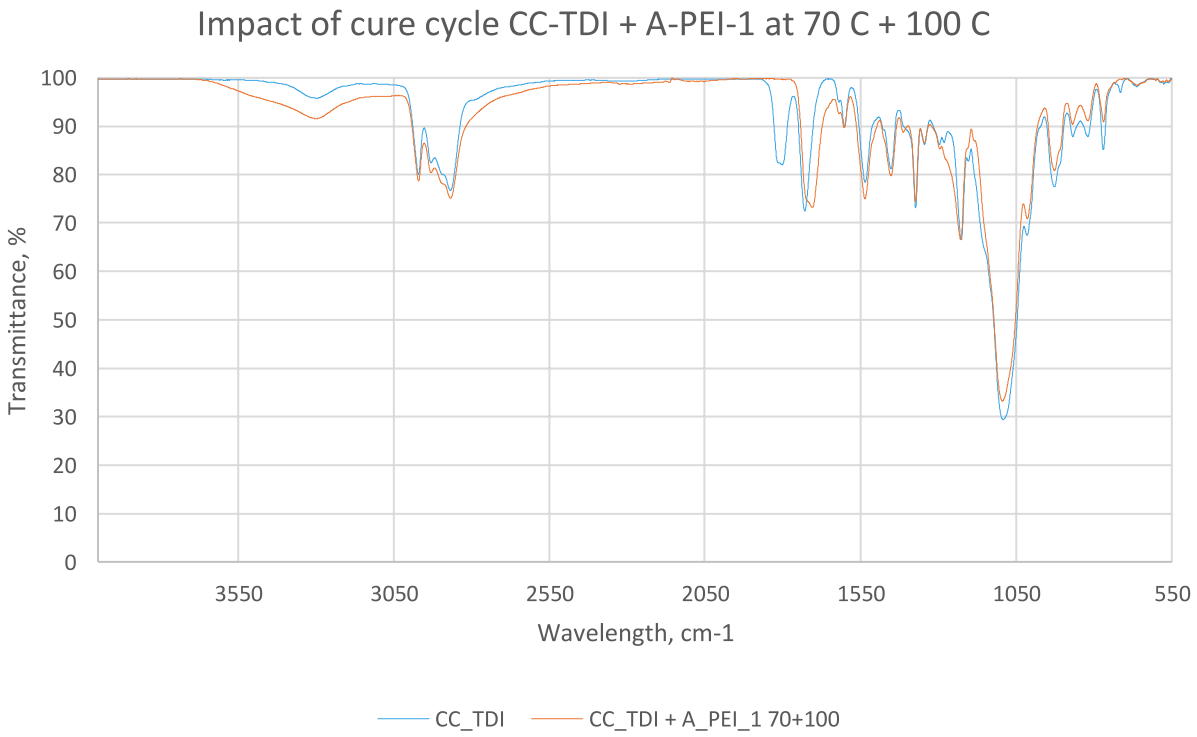

Fig. ESI 29. Impact of cure cycle to CC-TDI and A-PEI-1 (70 °C + 100 °C).

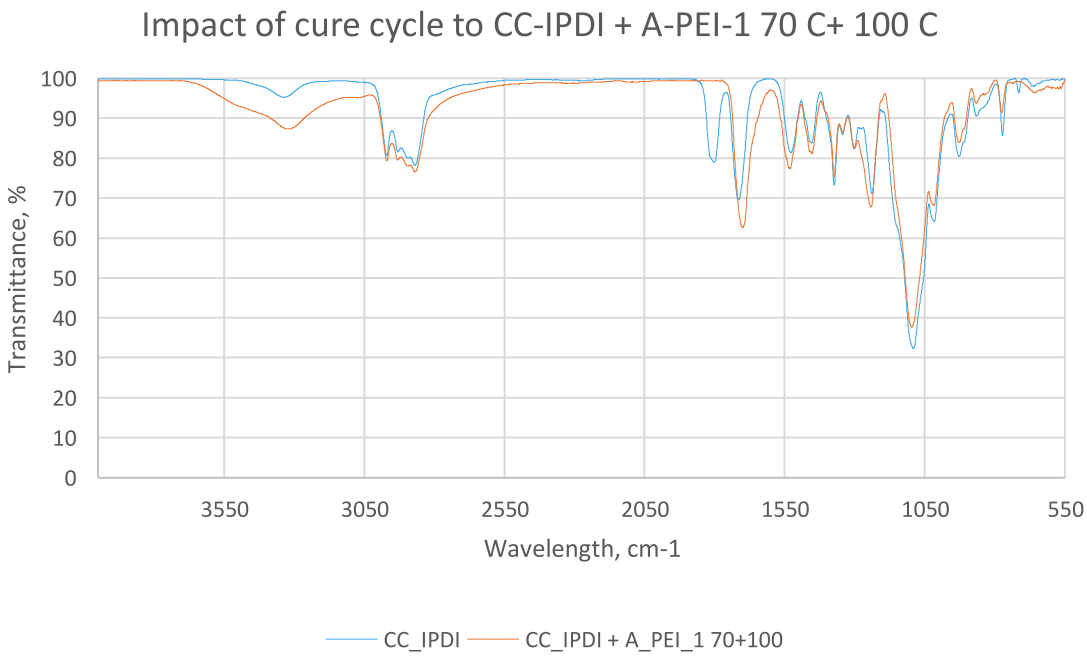

Fig. ESI 30. Impact of cure cycle to CC-IPDI and A-PEI-1 (70 °C + 100 °C).

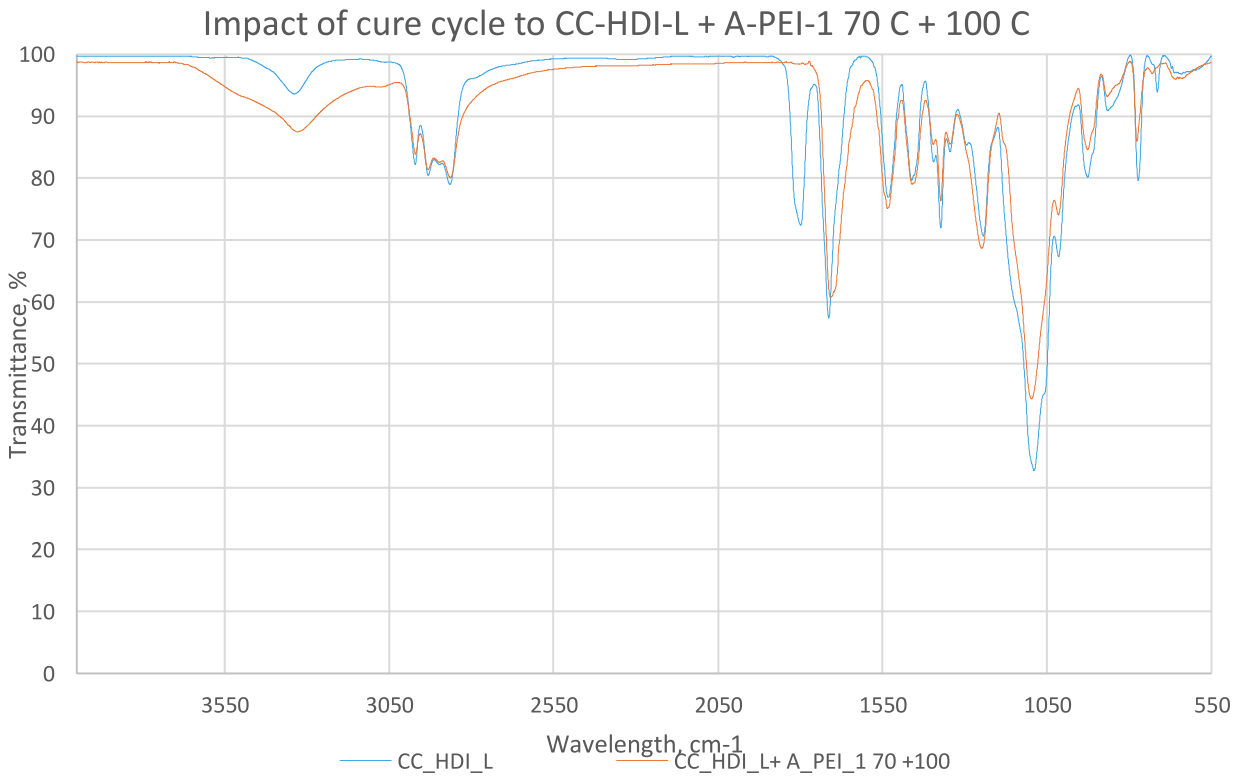

Fig. ESI 31. Impact of cure cycle to CC-HDI-L and A-PEI-1 (70 °C + 100 °C).

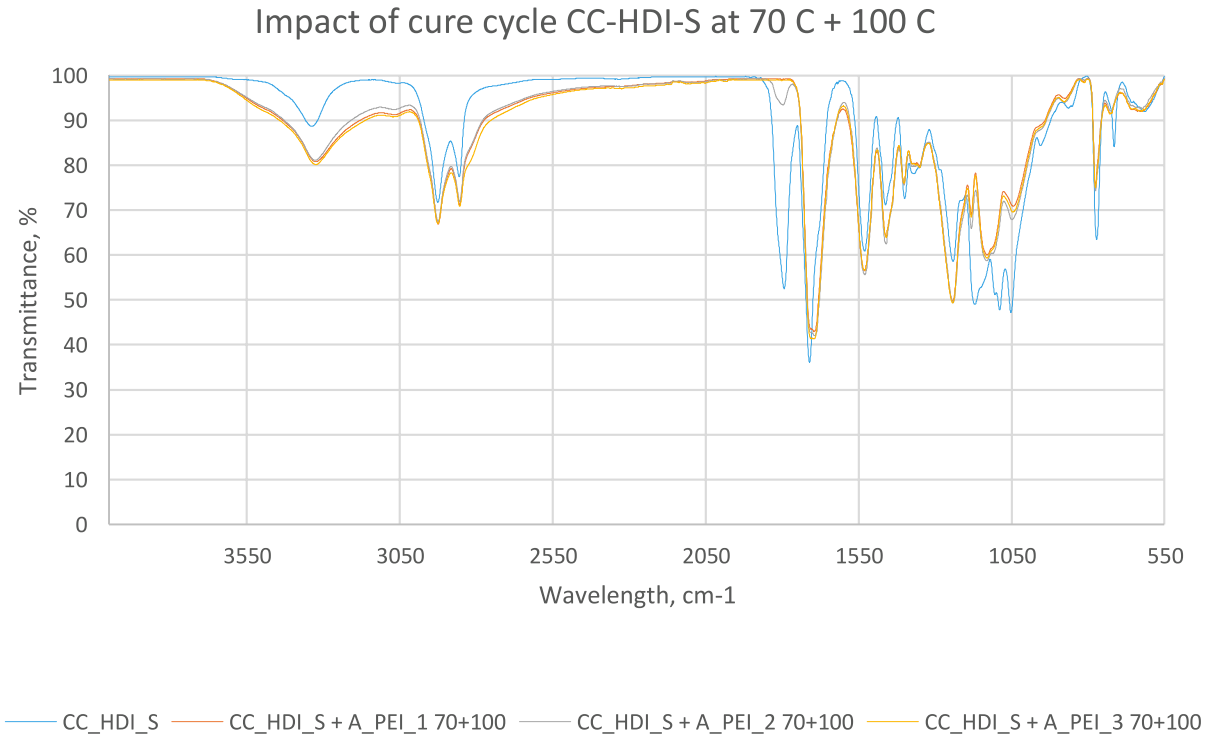

Fig. ESI 32. Impact of cure cycle to CC-HDI-S and A-PEI-1, A-PEI-2 and A-PEI-3 (70 °C + 100 °C).

1.5 ***Other figures***

Fig. ESI 33. Separated and well mixed film (CC-HDI-S+A-PEI-1 and CC-TDI+A-PEI-2).

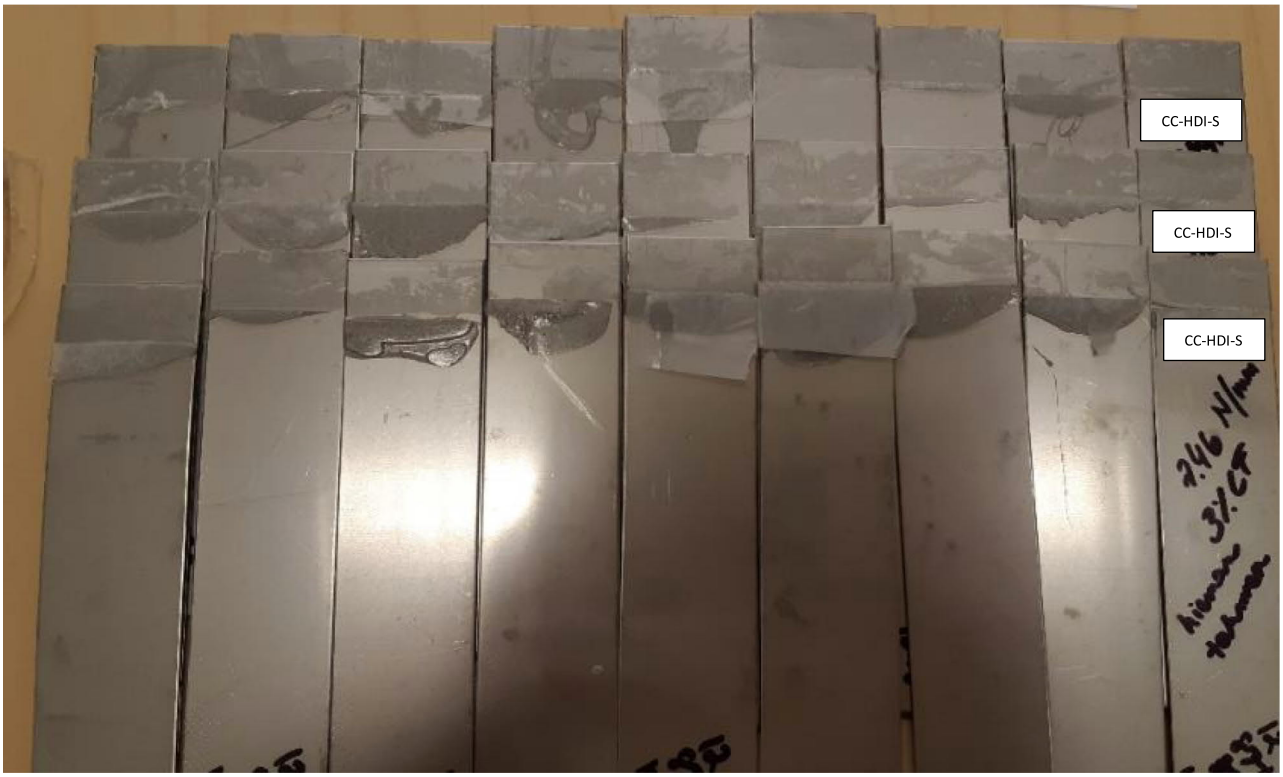

Fig. ESI 3. Lap shear strength specimen on stainless steel, failure type adhesive (CC-HDI-S+ A-PEI-1, A-PEI-2 and A-PEI-3).

2. Tables

Table 1. Added equimolar amounts (g) per 10g of cyclic carbonate terminated prepolymer.

Amine	CC-TDI	CC-IPDI	CC-HDI-L	CC-HDI-S
A-PEI-1	0.76	0.93	1.28	2.62
A-PEI-2	0.82	1.00	1.38	2.82
A-PEI-3	0.92	1.12	1.55	3.15
A-DDA-1	2.17	2.65	3.66	7.47
A-DDA-2	2.14	2.62	3.61	7.37
A-DDA-3	2.13	2.60	3.58	7.31
A-PEA-1	1.03	1.26	1.74	3.56
A-PEA-2	0.89	1.08	1.49	3.05
A-PEA-3	0.57	0.70	0.96	1.96
A-IPDA	0.66	0.80	1.11	2.26
A-TETA	0.56	0.69	0.95	1.94
A-Ar	0.82	1.01	1.39	2.84

Table 2. Lap Shear strength values in MPa with STD deviation as a function of time and at different temperatures.

	CC-TDI								CC-IPDI							
Result	A-PEI-1	STD	A-PEI-2	STD	A-PEI-3	STD	A-TETA	STD	A-PEI-1	STD	A-PEI-2	STD	A-PEI-3	STD	A-TETA	STD
1d	3.9	0.9	3.3	0.4	3.7	1.0	2.9	0.5	4.3	1.0	4.5	1.9	2.0	0.3	1.1	0.2
7d	3.6	0.8	3.5	0.5	3.5	0.7	2.9	0.4	2.4	0.9	4.6	1.2	5.4	0.6	3.3	0.6
30d	3.2	0.4	3.2	0.3	3.2	0.5	2.4	0.3	2.2	0.6	3.3	1.0	3.0	1.0	1.9	0.3
70 °C	4.6	0.4							3.1	0.5						
70 °C +100 °C	4.8	1.3							5.2	0.9						
	CC-HDI-L								CC-HDI-S							
Result	A-PEI-1	STD	A-PEI-2	STD	A-PEI-3	STD	A-TETA	STD	A-PEI-1	STD	A-PEI-2	STD	A-PEI-3	STD	A-TETA	STD
1d	3.5	0.4	5.0	0.5	5.3	0.9	3.3	0.6	7.5	1.0	7.4	1.0	9.2	1.2	4.6	1.2
7d	3.6	0.7	3.7	0.2	2.9	0.7	5.7	0.7	7.6	1.6	8.9	1.6	9.5	1.9	7.1	1.5
30d	2.1	0.0	2.7	0.8	2.6	0.3	3.4	0.2	7.2	1.4	7.6	2.2	8.3	1.2	6.4	0.8
70 °C	2.9	0.7							9.2	1.0	8.4	0.2	9.0	0.9	3.8	1.0
70 °C +100 °C	4.6	0.7							10.0	1.7	11.3	0.9	9.0	0.9	3.9	0.8

Table 3. Gel content of CC-HDI-S in % with A-PEI-1-A-PEI-3 for samples cured at room temperature and at elevated temperature.

Sample	RT GC	70 °C + 100 °C GC
CC-HDI-S + A-PEI-1	94.9	98.4
CC-HDI-S + A-PEI-2	94.0	97.8
CC-HDI-S + A-PEI-3	94.9	95.4

Table 4. Tensile strength in MPa and elongation in %.

	Cured at room temperature					Cure cycle at 70 °C and 100 °C				
Sample	Mpa	STD	%	STD	n	MPa	STD	%	STD	n
CC-TDI + A-PEI-1	1.4	0.4	57.7	18.0	4	2.2	1.0	50.0	34.0	4
CC-HDI-L + A-PEI-1	1.6	0.5	32.9	24.0	5	2.2	0.8	29.3	49.0	3
CC-HDI-S + A-PEI-1	2.6	0.4	41.9	11.0	5	3.1	0.6	63.0	17.5	5
CC-HDI-S + A-PEI-2	2.9	0.3	28.7	6.4	4	3.5	0.3	48.0	4.3	5
CC-HDI-S + A-PEI-3	3.7	0.6	35.0	6.6	5	4.1	0.2	46.0	35.0	5