

The crosslinking of epoxidated Jatropha oil with diamines

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Abstract

In 2010, 130 million tonnes of epoxy resins were produced worldwide, most of them were made of petroleum based chemicals. In this research epoxidated Jatropha oil (EJO) is investigated as a renewable monomer for epoxy chemistry, and crosslinked with hexamethylenediamine (HMD), triethylenetetramina (TETA) and para-xylenediamine (pXD). First, Jatropha oil was successfully epoxidated with performic acid, in situ formed from formic acid and peroxide in toluene with a yield of >92%. Tin(II) methyl hexanoate was tested as a catalyst in 5 and 10wt% for the reaction of bisphenol A diglycidylether with HMD and the reaction was followed by DSC. The 5wt% of catalyst had no influence on the reaction. The 10wt% of catalyst decreased the reaction temperature from 150°C to 70°C and increased the reaction speed. The crosslink reaction with HMD, TETA and pXD was performed at 150°C (based on DSC) without a catalyst in different mol ratios and characterized with FT-IR and ¹H-NMR spectroscopies. Beside aminolysis of the epoxy group, amidation of the ester group took place. When increasing the amount of amine, a rubbery solid could be formed with TETA and pXD. The tin based catalyst was also tested for the crosslinking of EJO and HMD, in which it increased the speed of the amide formation. Therefore, the catalyst was not investigated further. From the TETA 1:1.65 and the pXD 1:3.3 mol ratio a series of test specimens were pressed and tested by tensile stretching. The tensile stretching results showed that EJO with TETA resulted in a very flexible rubbery material, while the pXD crosslinked with EJO network was much more rigid and showed necking with large deformation before breaking. All final test specimens had a T_g below RT, with a slightly higher T_g for the TETA material. The mechanical properties were determined above the T_g of the material, leaving it in a rubbery state, the values will be different when measured below the T_g. Although only three diamines were tested in this research, the results indicate that the properties of the final network correlate with the structure of the diamine used for the crosslinking. Additionally, more amines should be investigated to further determine the structure-properties correlation for the final network after crosslinking with EJ-oil.

Contents

Abstract.....	2
Contents.....	3
1 Theory	5
1.1 Epoxy resins	5
1.2 Jatropha oil.....	6
1.3 Amines	8
1.4 Catalysts	10
1.5 Research strategy.....	10
2. Experimental	11
2.1 Epoxidation of Jatropha oil	11
2.2 Amines	12
2.2.1 Hexamethylene diamine	12
2.2.2 Triethylene tetramine	13
2.2.3 p-Xylylene diamine.....	14
2.3 Methyl Oleate	14
2.4 Press parameters and DSC (T_g).....	14
2.5 Tensile testing	15
3 Results and Discussion	16
3.1 Epoxidation of Jatropha oil	16
3.1.2 Characterization of Jatropha oil.....	16
3.2 Hexamethylenediamine	18
3.2.1 DSC of Bis A and hexamethylenediamine	18
3.2.2 Crosslinking of EJO and Hexamethylenediamine.....	20
3.2.3 Catalyst Influence.....	22

3.2.4	DSC	22
3.3	Methyl Oleate	23
3.4	Triethylene tetramine	24
3.4.1	¹ H-NMR	25
3.4.2	FT-IR	26
3.4.3	Pressparameters	26
3.5	p-Xylylenediamine.....	28
3.5.1	FT-IR	28
3.5.2	¹ H-NMR	28
3.5.3	Press Parameters	29
3.6	Mechanical Properties	30
4.	Conclusion.....	32
	References	34
	Apendix 1	35

1 Theory

1.1 Epoxy resins

A wide range of materials are called epoxy resins, both monomers with reactive epoxy groups as their resulting polymers. Epoxy resins have at least two reactive epoxy groups within their structure. In industrial materials based on diglycidyl ether of bisphenol A (Bis A) mixed with diamines are widely used. The epoxy group consist of two Carbon atoms and one Oxygen atom in a three atom ring. The ring is planar and contains a lot of ring strain. This high ring strain makes the epoxy ring more reactive, compared to linear ether groups, towards bases like amines. Because of the ring strain reaction with some amines is possible at room temperature. Reactions which involve either electrophilic attack on the oxygen atom or nucleophilic attack at one of the ring carbon atoms are important for the synthesis and cure of epoxy resins.^[1]

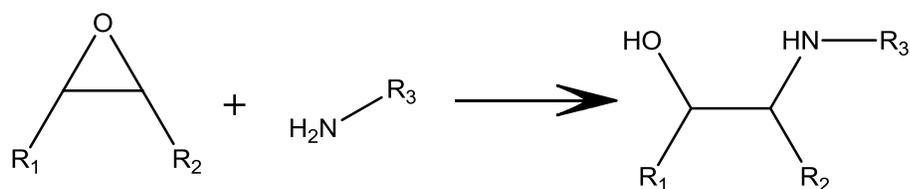


Figure 1. Schematic representation of a reaction between an epoxy ring and an amine.

Epoxy resins are worldwide used in high performance coatings, bonding, adhesives, composites, flooring and paving. In figure 2 a flow chart of the worldwide epoxy resin consumption in 2009 is shown. China is responsible for more than a third of the epoxy resin consumption followed by Europe and the United States of America. Industrialized nations are by far the largest producers and consumers of Epoxy resins.^[2] Further growth of the epoxy resin consumption is expected for the coming years.

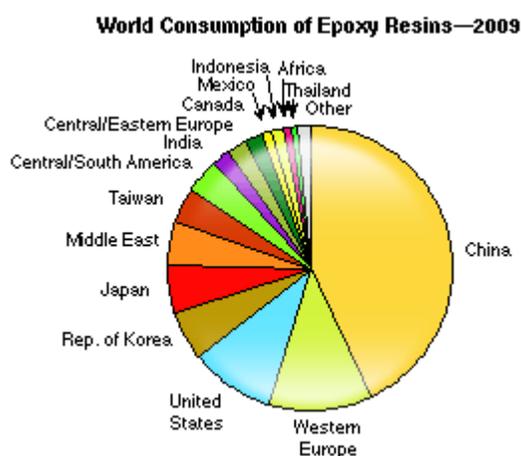


Figure 2. Flow chart of the worldwide epoxy resin consumption of 2009 adopted from reference^[2].

In 2010, 130 million tons of epoxy resins were produced worldwide,^[3] most of them were made from petroleum-based chemicals. In search for sustainable chemistry, with respect to the environmental issues, waste problems as well as the depletion of non-renewable resources, renewable resources for the synthesis of epoxy resins are important.^[4-6] These renewable resources should contain issues like

biodegradability, low costs and high availability. They should not compete with the food chain, cheap, ready to use and useful. “For non-food applications the most widely use renewable resources are polysaccharides (cellulose, starch), proteins and vegetable oils. They can be used as a raw material in its natural state or chemically modified, depending on the desired properties.”^[7]

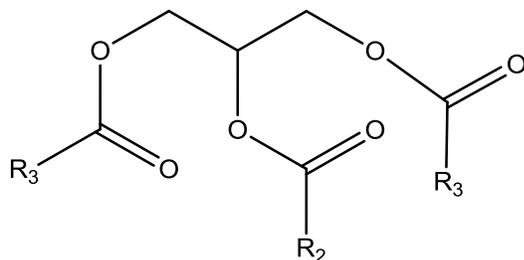


Figure 3. Schematic drawing of a triglyceride in which R can be any natural fatty acid, depending on the composition of the natural oil. In case of *Jatropha* oil, R will be mainly Palmitic -, Linoleic -, Oleic - and Stearic acid.

Vegetable oils like Sunflower oil, linseed oil, soybean oil and *Jatropha* oil are worldwide investigated as renewable resources for various applications. Vegetable oils contain mainly triglycerides (see fig. 3) together with di-, mono-glycerides, glycerol and free fatty acids. Each vegetable oil contains several different fatty acids with a specific ratio, which can vary under the growing conditions. Vegetable oils are classified by their relative iodine value or their unsaturated fatty acid content.^[5] The triglycerides can be used directly or be chemically modified and transformed into polymerizable monomers via epoxidation, methathesis of the double bonds, acrylation of epoxies, reaction with maleic anhydride or transesterification.^[5, 6, 8] Among these reactions the epoxidation is important because the epoxy ring has a high reactivity. The epoxy group can be easily transformed into desired functionalities by reactions with different molecules.^[5] Terminally epoxidated fatty acids are far more reactive than the epoxy groups within the chain.^[9]

1.2 *Jatropha* oil

The focus of this thesis will be on *Jatropha* oil (JO). JO is extracted from the *Jatropha curcas* L. This plant is a drought resistant tree that grows in Central and South America, south-east Asia, India and Africa. The tree can grow in marginal lands. The *Jatropha* tree is used for different applications as natural tooth paste and brush. The latex from the stem is used as natural pesticides and for wound healing while its the leaves are used as feed for silkworms.^[10, 11] During the Second World War JO was used as substitute for mineral diesel.^[12] JO is extracted from the seeds of the tree. The seeds contain 30-50 weight % of oil; the oil content of the kernel is higher (45-60 weight %).^[10, 12] The oil itself and the press cake are toxic for both human and animals.



Figure 4. Photograph of *Jatropha* seeds ^[13]

The overall composition of JO of five different provenances is shown in table 1. The specific ratios of fatty acids differ per different provenances of the *Jatropha curcas*. The JO used in this thesis comes from Cape Verde and is studied earlier by Kalpoe ^[14]. JO is rich in Oleic acid (C18:1), Linoleic acid (C18:2) and Palmitic acid (C16:0) in respectively 45.7%, 35.5% and 13% for the JO from Cape Verde.

Table 1. Fatty acid profiles of seed oils of different provenances of *Jatropha curcas* (area %)

Fatty acid Samples	1	2	3	4	5
Palmitic acid (C16:0)	11.4	12.3	13.0	10.5	13.0
Linoleic acid (C18:2)	40.3	36.7	34.6	44.4	35.5
Oleic acid (C18:1)	45	47.1	48.8	41.5	45.7
Stearic acid (C18:0)	2.27	2.80	2.53	2.45	5.8
Other	1.03	1.1	1.07	1.15	-

1. Castillo de Teayo, Ver.; 2. Puebla (Papantla, Ver.); 3. Coatzacoalcos, Ver.; 4. Yautepec, Mor.; 5. Cape Verde. The values were adopted from the references 11 and 14.

JO contain two different chemical groups; an ester and an unsaturated double bond, both groups can be a starting point for further modifications. In this thesis the double bonds of *Jatropha* oil will be transformed in an epoxy group with the use of performic acid (see fig. 5). Performic acid is formed by an *in situ* reaction of H₂O₂ and formic acid. ^[15, 16] Performic acid acts as an oxygen donor for the unsaturated bond. The formed epoxy group can be hydrolysed by water or opened by formic acid. To diminish the degradation of the epoxy ring toluene is added as inert solvent. The epoxidation is possible because formic acid and performic acid can move between the two immiscible phases. After epoxidation the EJO will be crosslinked with a reaction of a diamine with the epoxy group towards a secondary amine and an alcohol (see fig. 6).

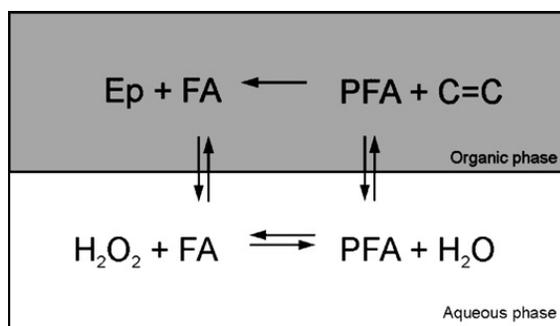


Figure 5. Schematic representation of the epoxidation reaction in the organic phase and the performic acid (PFA) formation in the aqueous phase. Performic acid (FA) and formic acid move between both phases. In this figure Ep represents an epoxy group and C=C an unsaturated bond.^[15]

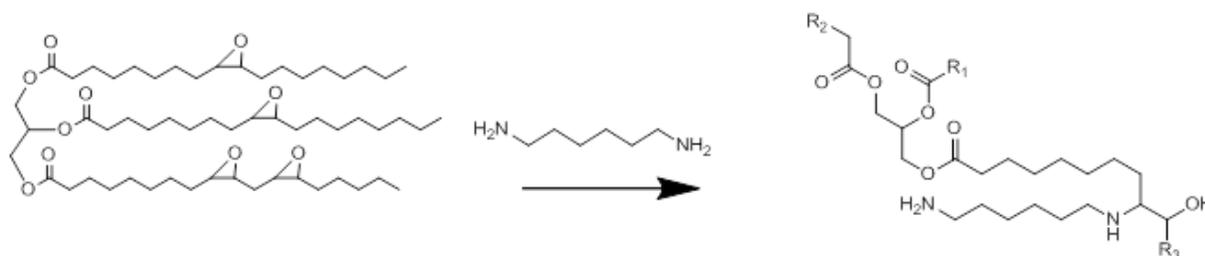


Figure 6. Schematic representation of the crosslink reaction between EJO and hexamethylene diamine, also known as an aminolysis reaction.

1.3 Amines

For the crosslink reaction with an epoxy group, the reactivity and structure of the amine is important. The amine takes the role of a nucleophile in this reaction and should be strong enough to open the epoxy ring.^[1] Primary alkyl amines are the most reactive, because the amine group is good accessible. Aromatic amines have a much lower reactivity caused by resonance stability.^[16] In case of 4,4'-diaminodiphenylmethane^[18] even a catalyst was necessary to open the epoxy ring. Besides their reactivity the structure of the amine is determinant for the flexibility of the final product and the rigidity of the resulting network. Ring structures especially aromatic ring structures are very rigid, introducing them to a network will enhance the stiffness of the network. Introduction of long aliphatic diamines will increase the flexibility of the network.^[19]

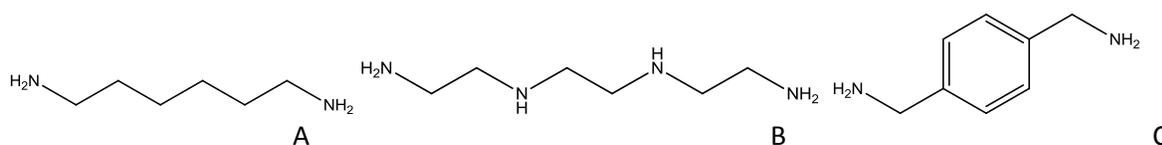


Figure 7. The structures of a) hexamethylenediamine, b) triethylenetetramine and c) p-Xylylene diamine.

In this thesis hexamethylenediamine (HMD), triethylenetetramine (TETA) and p-Xylylene diamine (pXD) were used as crosslinkers. The structures of these amines are shown in figure 7. HMD and TETA have the same amount of carbon atoms but differ in nitrogen content, TETA has two more nitrogen atoms. This higher amount of nitrogen results in more crosslink possibilities.^[19-21] After crosslinking, EJO crosslinked with TETA is expected to be less flexible than EJO crosslinked with HMD. pXD contains an aromatic benzene ring which makes this amine more rigid than the other two. The aromatic ring is separated

from the amine group by a methyl group. This way the amine group is unable to take part in the resonance of the benzene ring and the reactivity is not decreased. The presence of the benzene ring should result in a stiffer material after crosslinking with EJO than the other described amines.

In summary it is expected that all three amines have a similar reactivity, because they are all primary alkyl amines. Probably pXD has a slightly lower reactivity caused by of the bulky benzene ring. Looking at the properties of the three amines is expected that TETA results in the most flexible network and pXD in the most rigid network after crosslinking with EJO.

To the best of our knowledge no research is done on crosslinking of EJO with diamines beside a pilot project by Mevius.^[18] A lot of research has been done on aminolysis reactions of other epoxidated vegetable oils with amines.^[5, 23-26] K-W Lee et al.^[23] reacted epoxidated modified soybean oil (ESBO) with different alcohols and amines, to give ESBO better lubricant properties. The reactions of n-hexamethylene amine with ESBO progressed towards amidation (see fig. 8). instead of aminolysis (in 10h). They investigated this further with some additional research on HMD and ESBO. This reaction first progressed toward amidation with crosslinking over a longer time frame. Over time both the amidation and the aminolysis occurs, with a network as result, see figure 9.

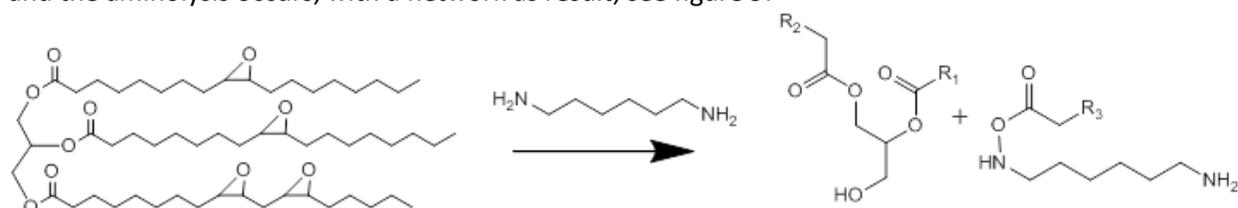


Figure 8. Schematic representation of the amidation reaction between EJO and hexamethylene diamine.

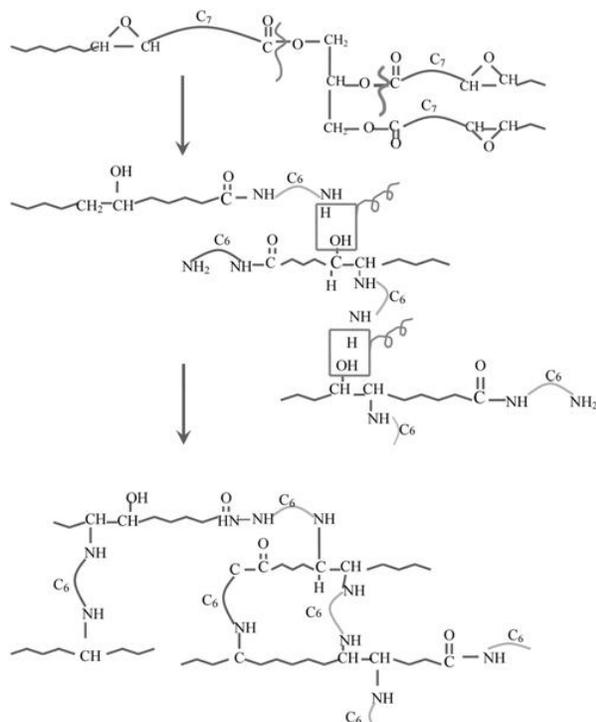


Figure 9. This schematic drawing is a representation of the network formed after the crosslink reaction of epoxidated soybean oil with hexamethylene diamine as proposed in reference [22].

1.4 Catalysts

There is a wide range of possible catalysts for the epoxy ring opening reaction, all the catalysts coordinate on the oxygen.^[24, 27-30] EJO contains ester groups beside epoxy groups, both containing oxygen, the found catalysts are not selective for the epoxy oxygen. According to Biswas et al.^[24] $Zn(Cl)_2$ is the best catalyst for aminolysis of ESBO with dimethylamine, without crosslinking and disruption of the ester linkage. The same catalyst is used by Lopéz Teléz et al.^[22] in a kinetic study on the curing of epoxidated linseed oil (ELO) with ethylenediamine, pXD and TETA.

Based on literature $ZnCl_2$ is the most promising catalyst, but this catalyst was not investigated in this thesis. The used catalyst, tin(II)methylhexanoate, is a liquid which makes it easy to mix homogeneous with the reaction mixture. Removing of the catalyst after the reaction is difficult and not done in this case. This tin based catalyst was chosen in order to continue the work done by Mevius.^[18] The influence of the catalyst on the crosslink reaction is not studied intensively in this thesis.

1.5 Research strategy

The objective of this work is to determine the structure property relationships of the crosslinked EJO and the used diamine. In other words, how much influence has the structure of the diamine on the properties of the final product? To answer this question the following research strategy was used: First JO will be epoxidated to EJO, followed by crosslinking reactions with HMD, TET and pXD. DSC will be used to determine the curing temperature. And finally the T_g and mechanical properties will be measured of the crosslinked EJO.

2. Experimental

Used chemicals

Chemicals: Toluene 99.5% (Aldrich), Hydrogen peroxide (H_2O_2) 30wt% pro analysis (Merck), formic acid 98-100% (Merck), Bisphenol A diglycidylether (Sigma), Tin(II)methylhexanoate 95% (Sigma), p-xylylene diamine 99% (Aldrich), triethylenetetramine $\geq 97.0\%$ (Aldrich), hexamethylenediamine 98% (Sigma), all used as received without further purifications. Jatropha-oil is pressed locally from seeds with as provenance Cape Verde.

Used equipment

Equipment: All ^1H -NMR spectra were recorded on a 400 MHz Varian AS400 spectrometer at ambient temperature, with CDCl_3 (Aldrich) as solvent.

The attenuated total reflection (ATR) infrared measurements were made on a Bruker IFS88 spectrometer, using a golden gate MCT-A detector with a resolution of 4 cm^{-1} and 50 scans per run.

Differential scanning calorimetry (DSC): The first series of DSC were measured on a TA instruments DSC 2920 modulated DSC, later measurements were performed at a Q1000 DSC, with a heating/cooling rate of $10^\circ\text{C}/\text{min}$.

For pressing a hot press Fontijne Holland was used at 150°C and 200kN.

The tensile testing was performed on an Instron 5565 at 20°C and 50% humidity.

Thermogravimetric analysis were done with a TGA 7 of Perkin-Elmer under N_2 and a heating rate of $10^\circ\text{C}/\text{min}$ up to 600°C

2.1 Epoxidation of Jatropha oil

In a three necked flask with cooler, stop and dropping funnel, 10g (11.2mmol) Jatropha oil is dissolved in 100 ml toluene. 6 ml formic acid is added and the reaction is stirred at 200rpm. Slowly 156 ml 30wt% H_2O_2 is added over 2 hours while stirring. The reaction mixture is stirred with 700 rpm at 40°C overnight. The water layer and toluene layer are separated and an ^1H -NMR spectrum (CDCl_3) is taken from the toluene layer. Two peaks at 2.90 and 3.30 ppm appear and none left at 5.4 ppm indicating the reaction has proceeded to completion. If not, the toluene layer is put back in the three necked flask and the procedure is repeated.

The toluene layer is washed twice with 150 ml 5wt% NaHCO_3 , with 200 ml water and twice with 150 ml 5wt% NaCl solution. The main part of the toluene is removed under reduced pressure (at 60°C and 130 mbar). The remaining toluene is removed in two steps: first with a Kugelrohr at room temperature (RT) and 1.3 mbar. Approximately 5% of the mixture is now toluene, this last part is removed in a vacuum oven at 30°C for 3 days. The amount of toluene in the final product is determined using TGA. The epoxidated Jatropha oil is dried longer in the vacuum oven, until no toluene or less than 0.5wt% could be detected by TGA. The yield of the epoxidation reaction is $>92\%$. The end product is characterized using ^1H -NMR and FT-IR. Over time the EJO will precipitate as a white solid. Using warm water the oil becomes liquid again. ^1H -NMR (CDCl_3): δ 0.88(br s, 9 H CH_3) 1.25-1.33 (br m, 4-7 and 12-17 CH_2) 1.49 (br s, 8*, 14* 8, 11 neighbor epoxy) 1.61 (br d, 6H ester(3) $\text{CH}_2\text{-C-C(O)-C}$) 1.72 (m, 2H 11,9) 2.31 (br t, 6H ester (2) $\text{C-CH}_2\text{-C(O)-C}$) 2.89-3.10 (three peaks epoxy) 4.16, 4.28 (d, 4H CH_2 triglyceride) 5.26 (s, 1H CH triglyceride) (The numbers are corresponding to the numbers in figure 10).

Later series of epoxidations reactions of Jatropha oil were done using a Jatropha oil: toluene ratio of 1:5. In a three necked flask with cooler, stop and dropping funnel, 20g (22.5mmol) Jatropha oil is dissolved in

100 ml toluene. Varying amounts of formic acid (9.5, 10 and 12.5 ml) were added and the reaction was stirred at 700rpm. 150 ml 30wt% H₂O₂ is added dropwise over the course of several hours. The reaction is stirred overnight at 40°C. The following day the water layer and toluene layer were separated. An ¹H-NMR is recorded from the toluene layer and confirmed that in all cases the reaction was completed .

The toluene layer is washed with batches of 150 ml 5wt% NaHCO₃ until all the remaining peroxide is removed. (determined with Quantofix peroxide 25 test sticks) Then the toluene layer is washed twice with 150 ml water and twice with 150 ml brine. The main part of the toluene is removed under reduced pressure (at 60°C and 130 mbar). The remaining toluene is removed with a Kügelrohr at room temperature and 1.3 mbar. Followed by 3 days in a vacuum oven at 30°C. TGA is used to determine the amount of toluene left in the final product. The end product is characterized using ¹H-NMR and FT-IR. A part of the EJO will precipitate as a white solid.

2.2 Amines

2.2.1 Hexamethylene diamine

2.2.1.1 DSC

All the described DSC measurements below were executed with a mass between 5 and 10mg of the mixture in a closed LVC DSC cups. First a mixture of BIS A and HMD (1:1 mol ratio) was made, by stirring the mixture at 45°C for 5 min. The first sample was measured in three cycles:

Cycle one: heating from 30°C to 300°C with 10°C/min

Cycle two: cooling from 300°C to 30°C with 10°C/min

Cycle three: heating from 30°C to 300°C with 10°C/min

This was followed by another measurement on the same sample with an extra heating cycle, this time the sample was heated from 10°C to 300°C with 2°C/min.

Another mixture, consisting of Bis A and HMD (1:1 mol ratio) with 5 wt% of Tin(II)methyloctanoate, was prepared by stirring at 45°C for 5 min. In order to find the reaction time different samples of the mixture were measured isothermal during 60 min, at 125, 135 and 150°C, followed by a heating cycle from 10 to 250°C with 2°C/min (according the following cycles:)

Cycle one: heating towards 125°C with 20°C/min, isothermal at 125°C for 60 min

Cycle two: cooling from 125°C to 10°C with 10°C/min

Cycle three: heating from 10°C to 300°C with 2°C/min

Later samples were measured with the same method, only there were two additional cycles of heating and cooling with 2°C/min over a temperature range from 10 to 250°C.

Samples of a mixture of Bis A and HMD (1:1 mol ratio) with 10wt% Tin(II)methylhexanoate, (prepared by stirring at 45 °C for 5 min) and pure Bis A were measured in 5 cycles:

Cycle one: heating from 10°C to 250 °C with 2°C/min

Cycle two: cooling from 250°C to 10°C with 2°C/min

Cycle three: heating from 10°C to 250°C with 2°C/min

Cycle four: cooling from 250°C to 10°C with 2°C/min

Cycle five: heating from 10°C to 250°C with 2°C/min

A mixture of EJO and HMD (1:1.8 mol ratio) was mixed at 30-38°C for 5 min. In order to find the reaction temperature a sample of the mixture was measured in 4 cycles:

- Cycle one: heating from 20°C to 260°C with 2°C/min
- Cycle two: cooling from 260°C to 10°C with 2°C/min
- Cycle three: heating from 10°C to 260°C with 2°C/min
- Cycle four: cooling from 260°C to 10°C with 2°C/min

In order to find the reaction time, other samples of the same mixture were measured isothermal during 10 and 30 min at 150°C, followed by a heating cycle from 10°C to 260°C with 2°C/min.

Finally a mixture of JO with HMD (1:1 mol ratio) was made at RT and measured in three cycles:

- Cycle one: heating from 10°C to 300°C with 2°C/min
- Cycle two: cooling from 300°C to 10°C with 2°C/min
- Cycle three: heating from 10°C to 300°C with 2°C/min

This measurement was not completed, the DSC cup exploded around 240°C in the first cycle.

2.2.1.2 Hot pressing and the analysis with FT-IR and ¹H-NMR

All pressing was done following the same procedure. A press-packet was made out of two glossy plates, two sheets of aluminum foil and the mold. The mold was put between two sheets of aluminum foil, which were put between two glossy plates. The press-packet was put in a preheated press of 150°C. The press was closed and immediately the pressure was increased to 50kN and held for 1min. The pressure was released for degassing and build up again to 100kN for 1 min. This was repeated by increasing the pressure each time with 50kN until 200kN was reached. The pressure was released one more time, after which the press was left at 200kN for several hours according to the pressing time. After the pressing time the press-packet was cooled with water under pressure and removed when the temperature was between 30-10°C, or the press-packet was directly removed from the press (at 150°C) and allowed to cool at the bench.

A metal mold was filled with the liquid 1:1.8 mol ratio mixture of EJO and HMD. The mold was pressed in a pressing packet at 150°C and 200 kN for 30 min. The result was a white butter-like substance that was characterized with FT-IR and ¹H-NMR.

The pressing residue and a sample of the 1:1.8 mol ratio mixture of EJO and HMD was put in an oven at 150°C for 24h. Both batches turned dark brown in the oven and became a sticky substance. The results of the 1:1.8 mixture after 24h was characterized with FT-IR and ¹H-NMR.

2.2.1.3 Catalyst influence

A mixture of 1:1.8 mol ratio of EJO and HMD with 10wt% of Tin(II)methylhexanoate was made. The mixture was heated for 3h at 150°C (220rpm). An FT-IR and ¹H-NMR sample were taken after 45 min and 3h. The mixture was reheated to 150°C (220rpm) for an additional 24h. The final product was characterized using FT-IR and ¹H-NMR.

2.2.2 Triethylene tetramine

Two different mol ratios of EJO and TETA (1:1.65 and 1:0.825) were made. Each mixture was heated for 24h at 150°C (200rpm). After 3, 6, 20 and 24h a ¹H-NMR sample was taken. The final products were characterized with FT-IR and ¹H-NMR. During the reaction the viscosity of the mixtures increased and the color changed from clear to slightly yellow after 3h to deep yellow to orange after 24h. Of each mixture a duplo was performed with similar results.

2.2.3 p-Xylylene diamine

Three different mol ratios of EJO and pXD (1:1.65, 1:3.3, 1:6.6) were tested by heating them for several hours at 150°C (220rpm). The mixture consisting of EJO and pXD in 1:1.65 mol ratio was heated for a total of 30h, with an FT-IR and ¹H-NMR samples taken every 3h. The color of the mixture changed from yellow to orange brown. The viscosity of the mixture increased over time, with a gom-like end product. The 1:6.6 mol ratio was only tested for 6h, with an ¹H-NMR sample after 3h. After 6h it was realized that this ratio could not result in a crosslinked product (due to a high amount of N) and was stopped. The 1:3.3 was heated for 28.5h with every 3h a sample for FT-IR and ¹H-NMR. This mol ratio resulted in a bright yellow solid. All end products were characterized with FT-IR and ¹H-NMR, (pXD did not dissolve completely in CDCl₃, but no other ¹H-NMR solvents were tested).

2.3 Methyl Oleate

A mixture of methyl oleate and HMD with a 1:1 mol ratio was made. The mixture was heated for 3h at 150°C (220rpm) After 3h the mixture was allowed to cool down to RT, a FT-IR and ¹H-NMR were made of the mixture. Both methods showed no reaction had occurred. Therefore the reaction was heated again at 150°C (220rpm). After 24 hours again a FT-IR and ¹H-NMR of the mixture was made. These showed amide formation.

2.4 Press parameters and DSC (T_g)

In order to find the best preheating and pressing time two mixtures were made. One of 1:1.65 mol ratio EJO:TETA and one of 1:3.3 mol ratio EJO:pXD. The mixtures were heated for several hours varying from 0.5 to 3.5h, after which a mold with square holes of 10x10x1mm was filled with the mixture. All the squares were pressed at 150°C and 200kN (following the in section 2.2.1.2 described procedure) for several hours varying from 8 to 88h. See table 2 for an overview of all the samples. Of each press result a DSC measurement was taken. To this end a DSC cup was filled with 5 to 10 mg of the pressed square and tested in three cycles:

Cycle one: heating from -20°C to 200°C with 10°C/min

Cycle two: cooling from 200°C to -20°C with 10°C/min

Cycle three: heating from -20°C to 200°C with 10°C/min

Of each sample the T_g is determined using the second heating cycle of the heat flow curve.

Table 2. An overview of the tested preheating and pressing times for each amine.

triethylene tetramine			p-Xylylenediamine		
mol ratio	preheating (h)	press time (h)	mol ratio	preheating (h)	press time (h)
1:1.65	1	8	1:3.3	1	24
1:1.65	1	24	1:3.3	1	88
1:1.65	2	8	1:3.3	2.5	8
1:1.65	2	16	1:3.3	2.5	16
1:1.65	2	20	1:3.3	2.5	24
1:1.65	2.5	16	1:3.3	2.5	88
1:1.65	3	16	1:3.3	3.5	24
1:1.65	24	0	1:3.3	28.5	0
1:1.65	24	24	1:1.65	30	24
1:0.825	24	24	-	-	-

2.5 Tensile testing

In order to measure the mechanical properties two mixtures were made: one of TETA with EJO and one of pXD with EJO. Samples were made with a 0.5mm tick mold for 8 T-bones, according to the ASTM D638 standard for micro tensile stretching. Analysis were performed with an Instron 5565 instrument with a pulling speed of 12 mm/ min and a clamp distance of 22mm at 20°C and 50% humidity. Each mixture was tested with a minimum of 6 halters.

DSC was used to determine the T_g of each test series as described in section 2.4.

pXD was dried overnight at 30°C in a vacuum oven. A mixture of 2.86 g pXD and 5.72 gr EJO (mol ratio 1:3.3) was stirred for 2.5h at 150°C. A white damp and solid is formed above the mixture as a side product. The mold was filled with the hot mixture, covered with Al-foil and a glossy plate. The resulting pressing packet was pressed under 200kN at 150°C for 24h. The press-packet was cooled to 6°C before opening. The halters were removed at room temperature. The mold was filled again with the cold mixture and pressed at 150°C and 200kN for 8h. After 8h the press-packet was cooled in the fridge (6°C) before opening. The halters were removed at RT. Both series gave a yellow material, that looked identical.

For the TETA test serie a mixture of 3.61g EJO and 0.99g TETA (1:1.65 mol ratio) is stirred at 150°C for 2h. The mold is filled with the hot mixture and pressed at 150°C and 200kN for 24h. Before opening, the press-packet is cooled in the fridge. The test specimens are removed at RT. The final product is slightly yellow and transparent.

3 Results and Discussion

3.1 Epoxidation of *Jatropha* oil

During the project several changes in the epoxidation conditions, adopted from A. Campanella et al.^[15] and Mevius,^[18] were made. The first change was the solvent, benzene was substituted by toluene for health issues. Based on the ¹H-NMR spectra it appears that 24h of reaction time and one addition of formic acid and peroxide is enough, instead of 4 days of reaction time, with each day a fresh amount of formic acid (FA) and H₂O₂ added. The third change was the JO-toluene ratio, which was changed from 1:10 to 1:5 to get a greater amount of EJO per synthesis. For the new ratio the same amounts of formic acid (10ml) and peroxide (150ml) were enough to complete the reaction. This reduces the amount of chemicals needed for the epoxidation reaction to 1/8 of the original and reduces the reaction time by three days (compared to Mevius approach).

Further optimization of the epoxidation conditions is possible, but was not performed. Knigge^[7] performed the epoxidation reaction in benzene with the following ratio 1:1:10:5 C=C:FA:H₂O₂:benzene. For 10g EJO (11.2 mmol) this results in: 1.53 ml FA, 11.5 ml H₂O₂ 30wt% solution and 6.02 ml benzene. This ratio reduces the use of chemicals substantial and should be tested with toluene as solvent for further optimalization.

Performic acid was made *in situ* from H₂O₂ and formic acid. Optimal reaction conditions for the *in situ* formation of performic acid were created by dropwise addition of the peroxide over several hours. Probably the conversion of the double bond is already complete after addition of all the peroxide, but this was not tested.

It is important to wash the toluene layer with a 5wt% NaHCO₃ solution in water until all the peroxide is removed. The excess of peroxide can be destroyed by carefully adding small amounts of the 5wt% NaHCO₃ solution over a long time frame. During the addition of the 5wt% NaHCO₃ solution a lot of bubbles and even a foam layer appear.

3.1.2 Characterization of *Jatropha* oil

3.1.2.1 ¹H-NMR

JO is a natural triglyceride oil containing mainly oleic, linoleic and palmitic acid. As natural oil it also contains mono and diglycerides combined with some free fatty acids. For all calculations JO is approached as a pure triglyceride oil. In the ¹H-NMR spectra of EJO (fig.10) the ratio is 9:1 protons for the 0.9 and 5.3 ppm signals, representing the 9 protons of the three terminal CH₃ and the proton of the middle carbon of the triglyceride (glycerol).

In the ¹H-NMR spectra of JO and EJO (fig. 10) the different signals from oleate and linoleate content of the triglyceride are visible. The chain of the oleate contains one double bond and give a signal for the double bond at 5.4 ppm. The protons of the neighboring carbon gave a signal at 2 ppm. After the epoxidation these signals shift, the 5.4 to 2.89 and the 2 to 1.49 ppm. Linoleate contains two double bonds in the fatty acid chain, separated by one carbon atom. The protons of this middle carbon atom gave a different signal. Before epoxidation they are visible at 2.7 ppm, after epoxidation they shift to 1.72 ppm. The other neighboring carbon atoms of the double bond were visible at 5.4 ppm before the epoxidation and they shift to 2.8-3.2 ppm after epoxidation

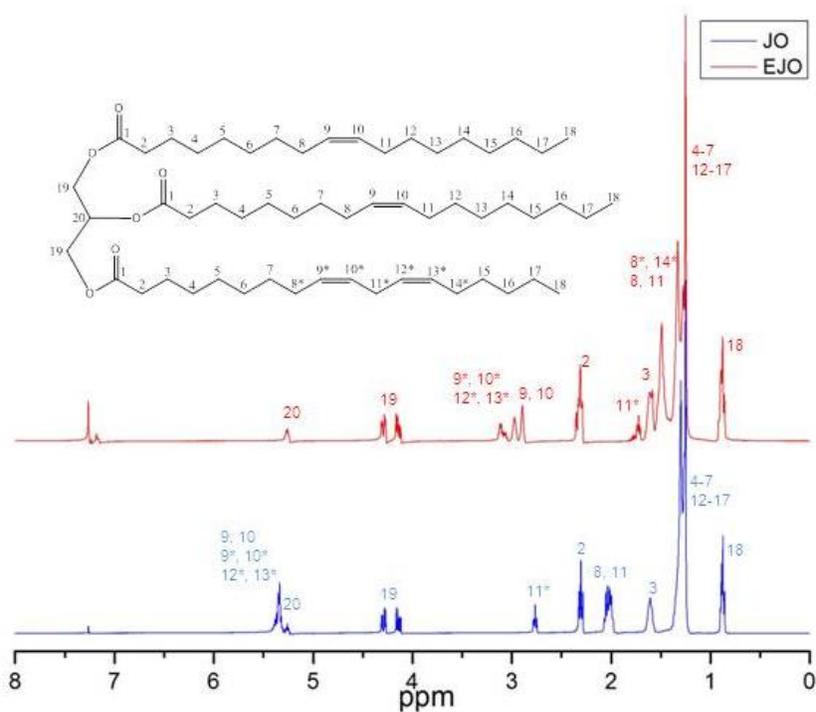


Figure 10. $^1\text{H-NMR}$ (CDCl_3) spectra of JO and EJO shown together with a schematic drawing of JO. The carbons in the schematic picture were numbered to label the proton signals.

JO contains on average 1.2 double bonds from oleate per molecule and 2.3 double bonds from linoleate. This gives a total of 3.5 double bonds per triglyceride (based on $^1\text{H-NMR}$ peak areas of NH1_02_12), this is in accordance with the work of Kalpoe.^[14] Besides triglycerides there are diglycerides, monoglycerides and even free fatty acids present in *Jatropha* oil. All calculations were done with the assumption that only triglycerides with an unsaturation of 3.6 were present.

3.1.2.2 FT-IR

In the two FT-IR spectra of JO and EJO the epoxidation is clearly visible (see fig. 11). In the JO spectra the C=C vibration is visible at 3008cm^{-1} . After epoxidation the absorption at C=C bond disappeared and the epoxy signals are visible at 821 , 840 and 1140cm^{-1} .

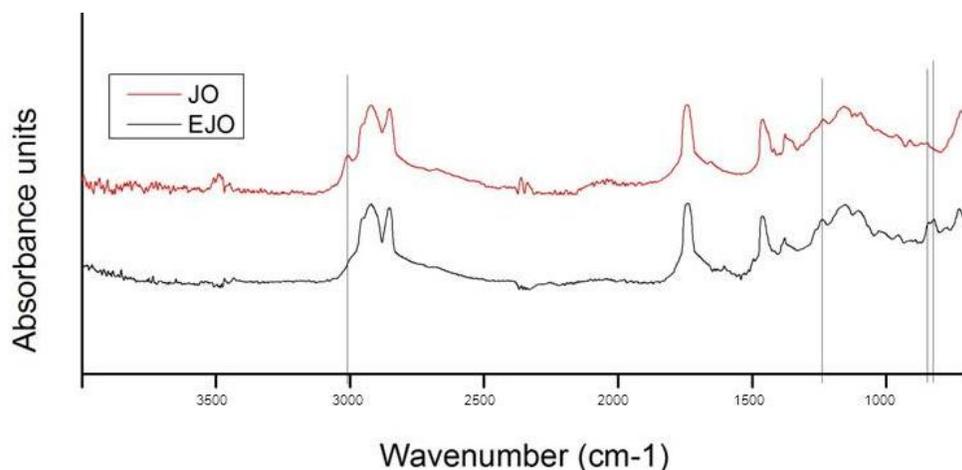


Figure 11. FT-IR spectra of JO and EJO, the lines in the graph are placed on the wavenumbers of the C=C vibration and the three epoxy group vibrations.

3.2 Hexamethylenediamine

3.2.1 DSC of Bis A and hexamethylenediamine

The ring opening reaction of the epoxy ring with different amines can be followed with DSC according to López Téllez et al.^[22] The ring opening reaction is exothermic and therefore visible in the heat flow curve (DSC thermogram).

The first experiments were done with a mixture of Bis A and HMD. Bis A was chosen because it is widely used in the industry for epoxy resins. HMD is a highly reactive primary linear amine and is therefore a good nucleophile. Several measurements were done with a mixture of Bis A and HMD, in all recorded heat flow curves two exothermic broad transitions were visible (see fig. 12 and 13). Based on the isothermal measurements at 125 , 135 and 150 °C it is clear that within 60 minutes the ring opening reaction is completed. The first exothermic transition disappeared after 60 minutes isothermal reaction time. The second exothermic transition (around 200 °C) is caused by an internal reaction of Bis A and is still visible.

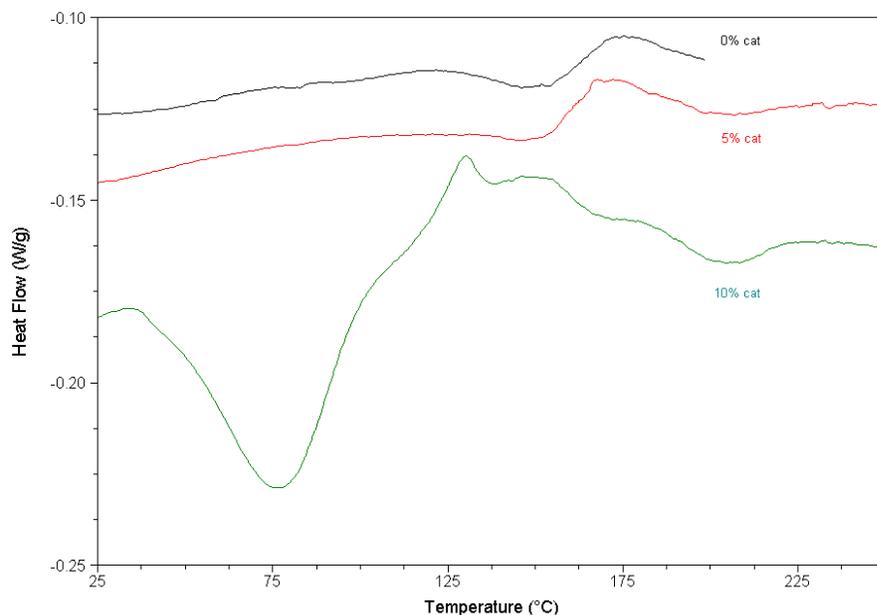


Figure 12. Thermogram of the first heating cycles of Bis A with 0, 5 and 10wt% of Tin(II)methylhexanoate.

The reaction temperature for the ring opening is 150°C with and without 5wt% of catalyst (fig. 12). When the amount of catalyst is increased to 10wt% the reaction temperature decreases to 70°C. The addition of 5wt% catalyst has no effect on the reaction temperature and reaction speed. Probably the catalyst is toxicated by the small amount of H₂O present in the diamine and a minimum of 10wt% catalyst is necessary to overcome this side reaction. In figure 10 the second heating curve of the reaction with HMD and Bis A is visible, showing some transitions that were not identified.

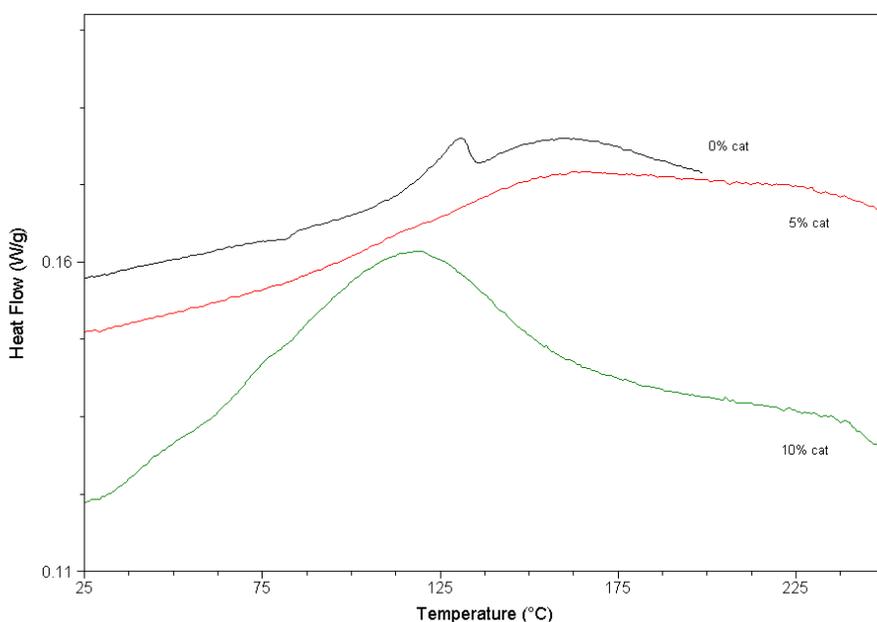


Figure 13. Thermogram of the second heating cycle of Bis A with HMD with 0, 5 or 10wt% Tin(II)methylhexanoate as catalyst.

3.2.2 Crosslinking of EJO and Hexamethylenediamine

A small part of the EJO and HMD mixture was pressed in the hot press at 200kN and 150°C for 30 min. The press result was a butter-like material that easily dissolves in CDCl_3 . The $^1\text{H-NMR}$ spectrum (fig. 14) of the material shows a shift of the triglyceride protons from 5.3 and 4.2 ppm to lower ppm values. And a part of the protons beside the ester group of the fatty acid backbone shifted from 2.35 to 2.14 ppm. These shifts indicate amide formation at the ester group of the triglyceride, instead of aminolysis of the epoxy ring. The protons of the epoxy ring are still visible at 2.89ppm

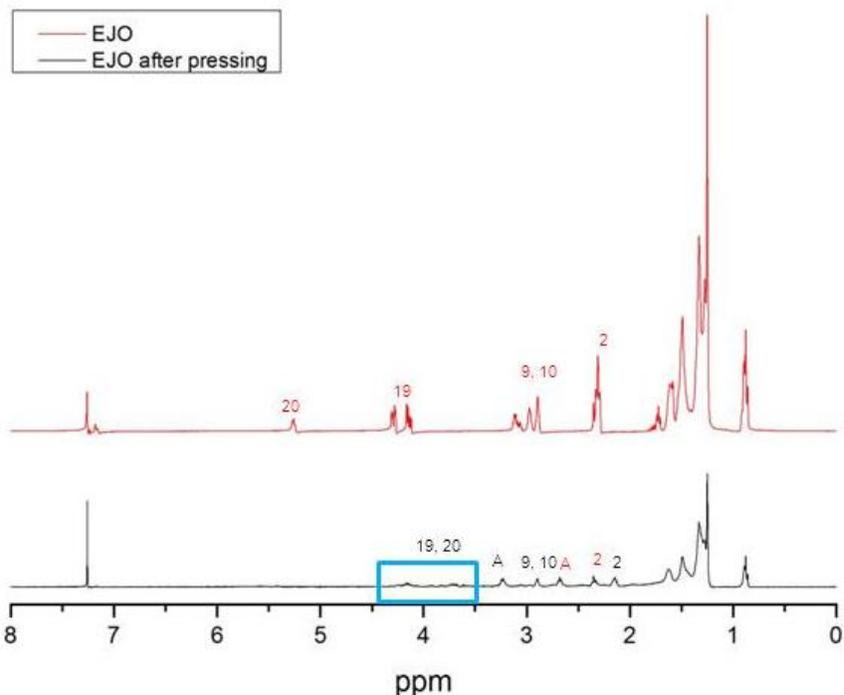


Figure 14. $^1\text{H-NMR}$ (CDCl_3) spectra of EJO mixed with HMD after 30 min of pressing together with the spectrum of EJO.

The FT-IR spectra of the pressed samples show that (fig. 15) the C=O vibration band at 1733 cm^{-1} decreases while two amide vibration bands at 1633 cm^{-1} (C=O) and 1559 cm^{-1} (N-H) appear. To confirm the amide formation a strong sharp band at 3341 cm^{-1} of the free N-H vibration is visible. The epoxy vibrations bands are visible at 821 , 840 and 1140 cm^{-1} .

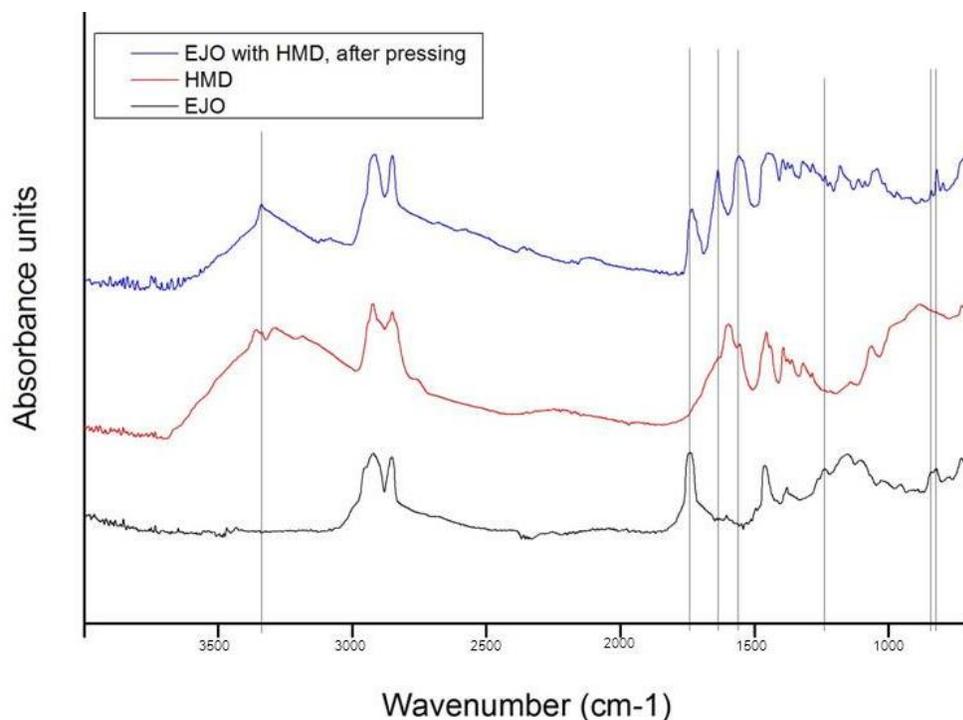


Figure 15. FTIR spectra of EJO mixed with HMD after 30 min of pressing together with the spectrum of EJO.

Based on the $^1\text{H-NMR}$ and FT-IR spectra, it is concluded that amidation instead of aminolysis took place. This is in accordance with the work of K-W Lee^[23]. Other authors who investigated reactions of epoxidated oils and amines got similar results^[24-26]. However not everyone reports the amidation, but a closer look at their FT-IR and $^1\text{H-NMR}$ data showed that beside aminolysis also amidation occurs.

To overcome the amidation the amount of HMD was increased from 1:1.8 to 1:3.3. On average EJO has 3.6 epoxy groups and 3 ester groups per molecule. To get a network it is necessary to crosslink the epoxy groups, but this will not happen if all or a part of the amine groups react with the ester groups. By increasing the amount of amine groups the reaction with the ester groups is taken into account and enough amine should be present to react with both the epoxy- and the ester groups. To check this a new batch with 1:3.3 mol ratio of EJO and HMD was made and reacted for 30h at 150°C. Over time the reaction mixture got dark brown and the viscosity increased a little bit, but no solid was formed. After 30hours a dark brown highly viscose sticky product was formed. The brown color indicates amide formation, which was confirmed by FT-IR and $^1\text{H-NMR}$. In the $^1\text{H-NMR}$ spectra the epoxy signal at 2.89 decreases after 24h, thus beside amidation aminolysis took place. After 24h beside amidation some aminolysis took place based on the decrease of epoxy signal at 2.89 ppm in the $^1\text{H-NMR}$.

In FT-IR and $^1\text{H-NMR}$ the presence of H_2O is visible. HMD was not dried before use and this could influence the reaction. Maybe the reaction is more efficient when the amine is dried before use. Or HMD is a too good nucleophile and therefore too reactive towards the ester group. The final product was not a promising material for this project and was not further investigated.

3.2.3 Catalyst Influence

The influence of the catalyst on the aminolysis was tested by a 24h reaction of EJO and HMD (1:1.8 mol ratio) with 10wt% of Tin(II) catalyst. The final product was dark brown and sticky. An FT-IR spectra was recorded after 6 and 24h. After 6h there was a decreased ester vibration visible at 1733 cm^{-1} and the amide was visible at 1642 and 1542 cm^{-1} . After 24h, the ester signal was no longer visible. In both FT-IR spectra the epoxy peaks were not visible but due to their relative low intensity it is not certain if they reacted or that the vibration is overlapped by other signals. During the reaction two $^1\text{H-NMR}$ spectra were recorded after 45 min and 6h. Both spectra indicate amidation with the signals of the amide protons at 2.15 and 3.2 ppm. In both cases the proton signals of the epoxy group were still visible at 2.89 ppm. Based on the FT-IR and $^1\text{H-NMR}$ spectra it can be concluded that the catalyst increases the speed of the amide formation, without a significant increase of the aminolysis reaction. The Tin(II)methylhexanoate catalyst is not specific for catalyzing the reaction at the epoxy ring and seems to increase the rate of the amidation. Therefore in this project the catalyst was not investigated further, but creates opportunities for other research.

3.2.4 DSC

In the heating curves of EJO with HMD a peak is visible caused by the melting of HMD and an broad exothermic transition (fig. 16). This transition is also visible in the heat flow curve of JO with HMD, this means that the amidation is also an exothermic reaction. With DSC it is not possible to distinguish between the amidation and the desired ring opening reaction.

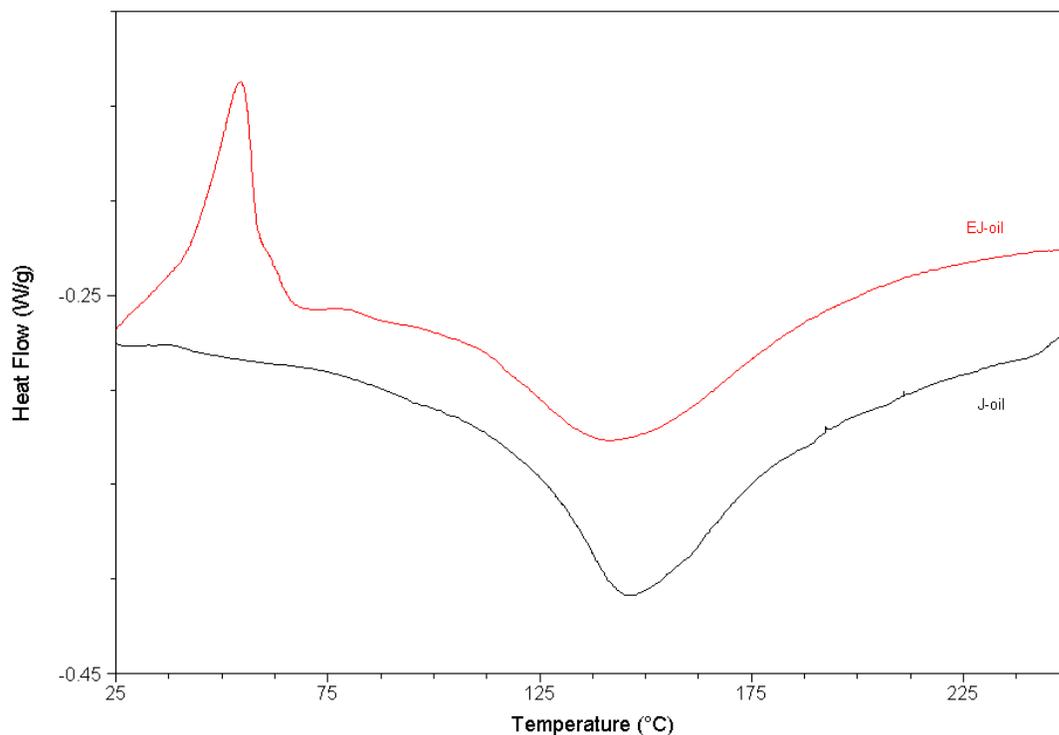


Figure 16. Thermogram of the first heating cycles of EJO and JO mixed with HMD.

3.3 Methyl Oleate

Methyl Oleate (MeO) was studied as model compound for the aminolysis reaction with HMD. In figure 17 are the $^1\text{H-NMR}$ spectra of MeO and MeO with HMD after 27h of reaction shown. Together with a schematic representation of the molecules. To identify the $^1\text{H-NMR}$ spectrum the carbons of the methyloleate are numbered. MeO is a methyl ester and instead of the three peaks of the triglyceride, one peak at 3.66 ppm is found, representing the methyl protons of the methylester. The protons of the double bond gave a signals at 5.34 ppm. The methyl protons at the end of the fatty acid chain are found at 0.87 ppm, corresponding with the proton signals of JO. All the other proton signals are corresponding with those of JO.

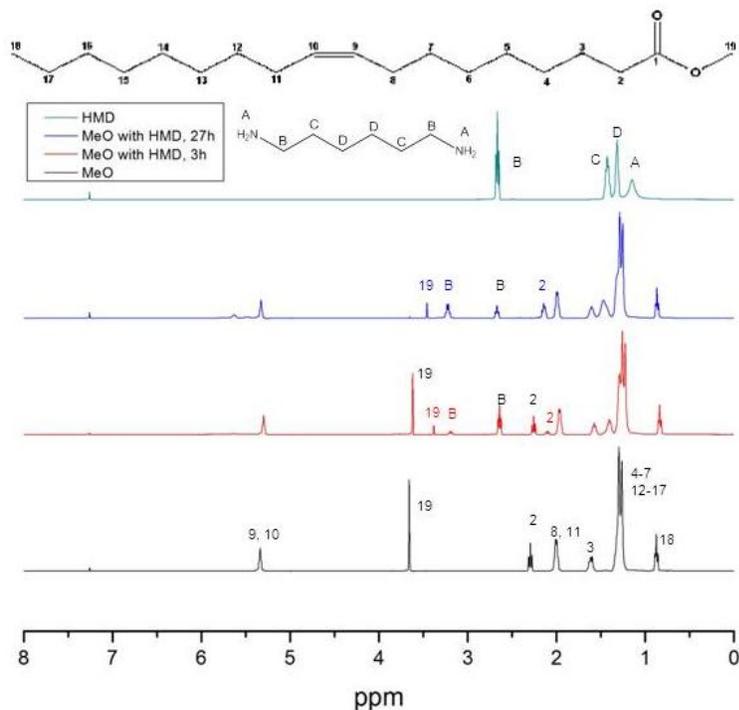


Figure 17. $^1\text{H-NMR}$ (CDCl_3) spectra of MEO, HMD and during the reaction of MeO and HMD after 3 and 27h, together with a schematic representation of MeO.

To prove the amidation, a mixture of HMD and MeO (mol ratio 1:1) was heated and stirred at 150°C . After 3 hours no reaction has taken place, according to $^1\text{H-NMR}$ and FT-IR. After 27 hours the ester signal in the $^1\text{H-NMR}$ spectrum (fig. 17 and table 3) at 2.26 ppm is gone, while the double bond at 5.34 ppm is still there. The ester signal shifts from 2.26 to 2.10 ppm after the reaction with HMD. The protons of the methyl peak (19) shift from 3.66 to 3.38 ppm, together with an OH peak at 5.63 ppm. The surface area of 3.38 ppm peak is small because the reaction temperature is above the boiling point of MeOH. After the reaction of MeO with HMD the ester protons of the carbon directly beside the ester group shift from 2.26 ppm to 2.1 ppm caused by the amide formation. The protons of the carbon beside the amine group of HMD shift from 2.64 to 3.2 after the amide formation. These proton shifts of 3.2 and 2.1 ppm are also found in literature,^[23] the proton signal at 3.20 ppm is addressed to an amide and the proton signal at 2.10 ppm is not attributed. Based on our measurements and work done by others in our group it is possible to address the proton signal at 2.10 ppm to the amide. More in detail to the proton attached at the carbon directly beside the original ester group (nr.2 in figure 17) $\text{R-CH}_2\text{-C(O)-NH-CH}_2\text{-R}'$.

Table 3. The proton shifts before and after the amidation of MeO. The carbon numbers correspond with the drawing of MeO in fig. 17.

Carbon atom	Before reaction (ppm)	After reaction (ppm)
2	2,26	2,10
19	3,66	3,38 with OH at 5,48 en 5,63
9,10 and 8, 11	5,34 and 2,01	5,34 and 2,01
B, Carbon atom beside amine	2,64	3,46

FT-IR confirmed the amide formation found in the $^1\text{H-NMR}$ spectra, see figure 18. In the FT-IR spectrum of MeO and HMD after 27h the C=C vibration is visible at 3005 cm^{-1} together with amide peaks at 1633 , 1540 and 3298 cm^{-1} . These amide vibrations were not visible in the FT-IR spectrum of MeO.

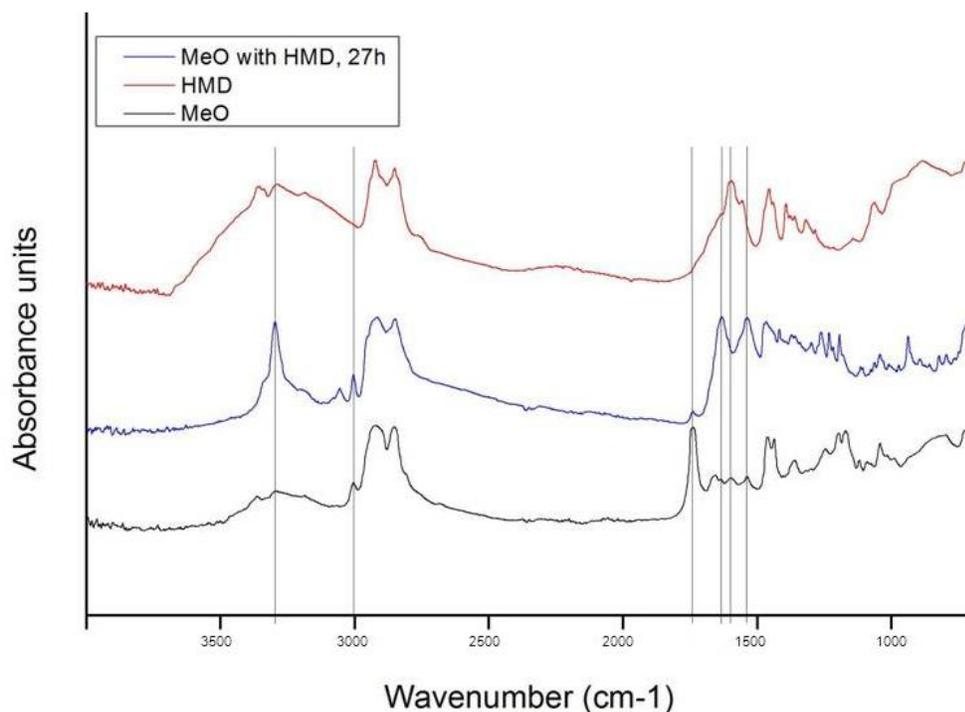


Figure 18. FT-IR spectra of MeO, HMD and their reaction product after 27h.

The reaction of MeO and HMD was performed to get a better understanding of the amide formation. The high reaction temperature makes direct comparison with the EJO and HMD reaction not possible. When the reaction is an equilibrium reaction the high reaction temperature (150°C) which is above the bp of MeOH, can drive the reaction in one side of the equilibrium. Therefore the performed reaction did not give a realistic picture of the reaction between MeO and HMD. In order to get a better comparison, the reaction temperature should be lower or JO instead of MeO should be used. Never the less, the reaction product with corresponding $^1\text{H-NMR}$ was of great value for the interpretation of the $^1\text{H-NMR}$ spectra in this thesis.

3.4 Triethylene tetramine

Different mol ratios of TETA were tested (1:0.825, 1:1.65 and 1:3.3) by stirring the solution for several hours at 150°C . The end product of the 1:0.825 mol ratio gave a slightly brown color, over time a white

solid appears at the surface. The final product of the 1:1.65 ratio had a nice yellow transparent color with some rubbery properties (elastic). Both ratios (0.825 and 1.65) gave a solid material after 24h of heating and stirring. The final product of the 1:1.65 mol ratio had a Tg of -0.9°C, after 24 h of pressing the Tg increased to 5.2°C The third ratio (1:3.3) was made and tested by accident. This ratio did not result in a solid material. This is as expected as there is a great excess of TETA present.

3.4.1 ¹H-NMR

During the reaction of EJO and TETA ¹H-NMR samples were taken after 3, 6 and 21h. Figure 19 shows the ¹H-NMR spectra of TETA and EJO after 3 and 6h. The reaction products of the amidation and aminolysis are visible. The amidation gave peaks at 3.73 (glycerol), 3.34 and 2.17 both amide. The aminolysis results in a decrease of the peaks at 2.89 (epoxy) and 1.49 ppm (atoms 8, 11), together with the formation of T at 2.71 and atom 2 at 2 ppm. The peak at 2.71 ppm is from the original TETA backbone and of the TETA reacted with the epoxy group, because the reaction with the epoxy does not lead to a significant shift. (2.71 carbon beside sec. amine.)

After 21h the epoxy signal at 2.89 ppm is still visible, but the surface under the peak of the signal at 1.49 ppm (8, 11) decreases indicating that aminolysis took place. Not all the proton signals of the ¹H-NMR spectra could be identified because glycerol, mono- and diglycerides were formed during the amidation reaction. From the ¹H-NMR spectra could be concluded that total amidation and partly aminolysis took place.

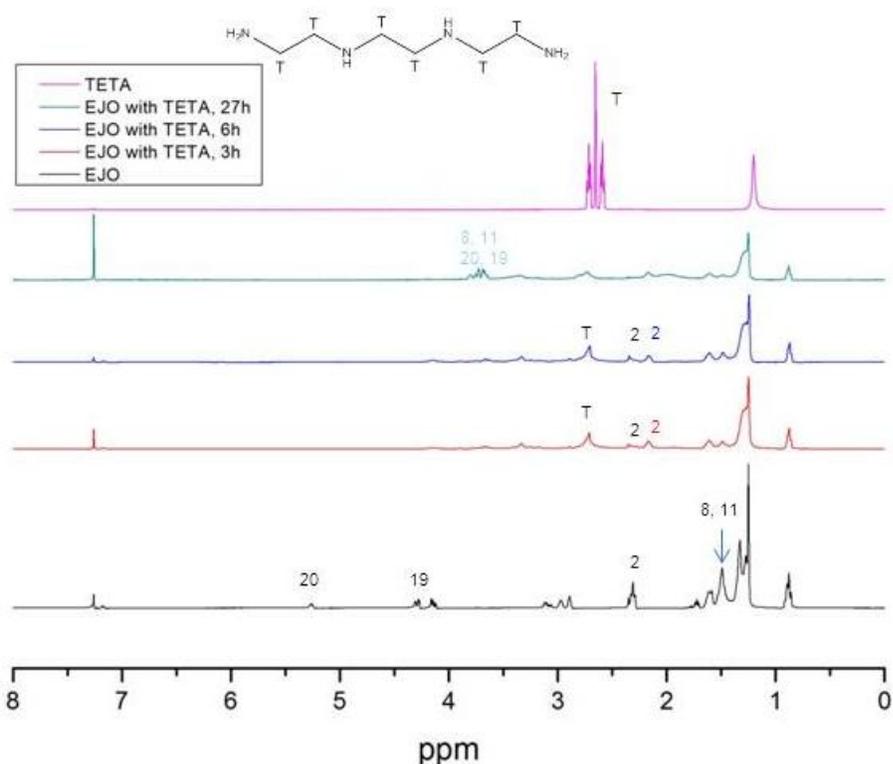


Figure 19. ¹H-NMR (CDCl₃) spectra of EJO, TETA and their reaction products after 3, 6 and 21h.

3.4.2 FT-IR

FT-IR spectra were recorded after 30 min, 3.5, 5.5 and 24h, see fig. 20. In all spectra the amide vibrations are visible at 1642 and 1554 cm^{-1} . The ester signal at 1733 cm^{-1} is visible in all spectra but decreasing in signal over the reaction time. The epoxy vibrations at 818, 841 and 1249 cm^{-1} are visible in the spectrum of 30 min. In the FT-IR spectrum of 3.5h only the 1249 cm^{-1} vibration is visible. After 5.5h the epoxy vibrations are no longer visible in the FT-IR spectra. FT-IR showed a decreasing of the ester peaks and an appearance of the amide peaks.

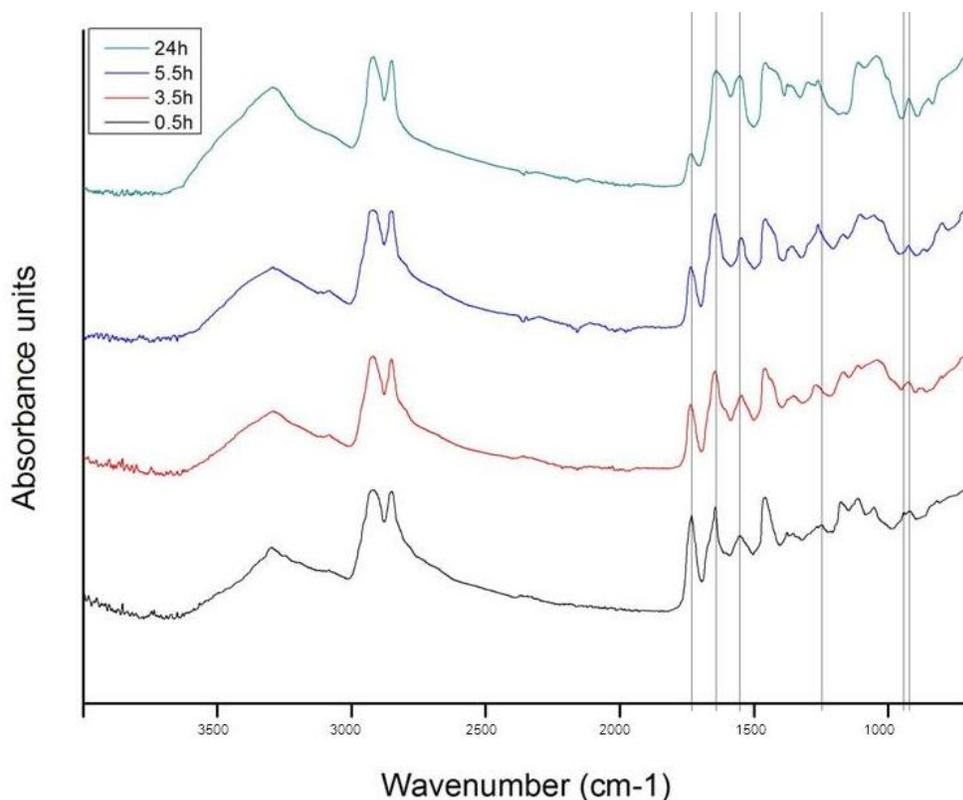


Figure 20. FT-IR spectra of TETA and EJO reaction mixture after, 0.5, 3.5, 5.5 and 24h.

Based on the FT-IR and $^1\text{H-NMR}$ spectra it can be concluded that both amidation and aminolysis took place in the reaction mixture.

In the FT-IR and $^1\text{H-NMR}$ spectra the presence of water is visible. This water can be a result of the formation of tertiary amines, or is already present in the amine. When the amine contains water, it may influence the reaction and the reaction should be repeated with a dried amine.

3.4.3 Pressparameters

In order to find the press parameters a 1:1.65 mol ratio mixture of EJO and TETA was made. The mixture was preheated at 150°C for 1-3 hours under stirring before filling the mold. (It is possible to make a square without air bubbles from the hot liquid and the more viscous cold mixture.) The mold was pressed at 150°C and 200 kN for 4, 16 or 20h, but most of them for 16 hours (overnight).

The time of preheating and pressing differs per sample in order to find the 'ideal' combination. Each press result was analyzed with DSC in order to determine the T_g , the T_g 's are shown in table 4. All the

pressed products were a slightly yellow transparent material, which is flexible and a little bit rubbery. With increasing pressing time the material become stiffer and slightly more yellow.

Table 4. The press results of the TETA series, in case of more samples the average T_g is given.

mol ratio	preheating (h)	press time (h)	T_g (°C)
1:1.65	1	8	5.78
1:1.65	1	24	8.27
1:1.65	2	8	0.88
1:1.65	2	16	5.32
1:1.65	2	20	8.66
1:1.65	2.5	16	6.67
1:1.65	3	16	6.42
1:1.65	24	0	-0.94
1:1.65	24	24	6.96
1:0.825	24	24	4.51

After pressing the material was tested with DSC in three cycles: heating, cooling and heating. Most samples showed no big difference between the first and second heating cycle, indicating that the reaction is completed. The second heating cycle was used to determine the T_g of the material. In table 3 and figure 21 the preheating and pressing times are shown together with the T_g of the resulting material. The trend is that longer pressing time leads towards a higher T_g . The preheating time had influence on the T_g till some extend. With the one hour of preheating series the T_g starts at 6°C after 8h of pressing and a T_g of 8°C after 24h. The 2h of preheating series gave a lower curve with a steeper slope, starting with a T_g of 1°C after 8h and ending with a T_g of 10°C after 24h of pressing time. With repeating of the experiment slightly different T_g 's were found (within 2 degrees), this is probably caused by a slightly different fatty acid content per EJO sample. The total difference found in de T_g values of the 1:1.65 EJO and TETA are within 10 degrees. Therefore, it was decided to do the mechanical testing with only one of the 2h of preheating samples combined with 24h of pressing time.

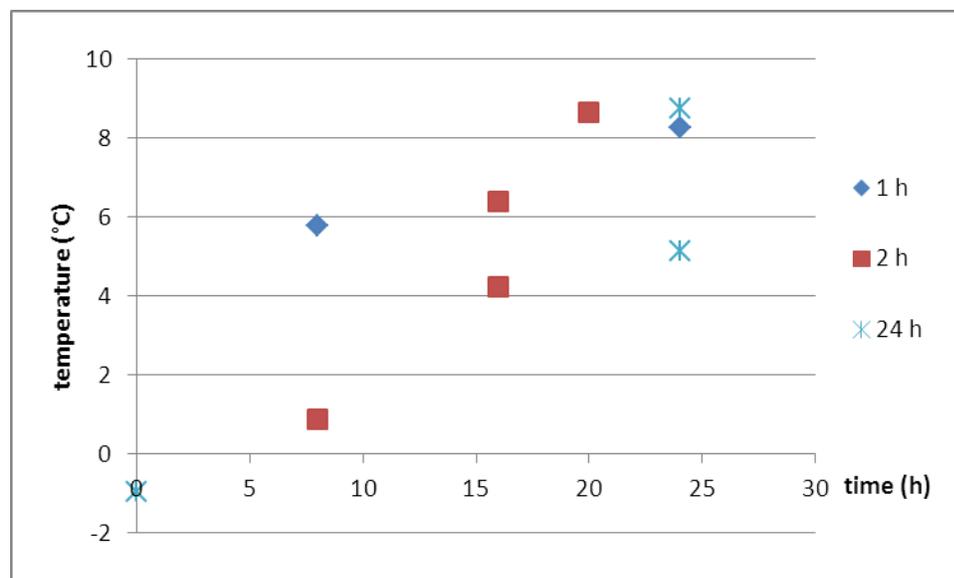


Figure 21. T_g graph of all the T_g s depending on their time of pressing categorized by preheating time.

3.5 *p*-Xylylenediamine

pXD was tested in three different mol ratios (1:1.65, 1:3.3, 1:6.6) as possible crosslinker for EJO. They were tested by stirring the mixture for 24h at 150°C. The 1:6.6 mol ratio gave a brown liquid, but did not work, probably because of the great excess of diamine. The 1:1.65 mol ratio gave an orange brown gum and over time a white solid appears at the surface. The 1:3.3 mol ratio took the amidation reaction into account and had the most promising result after 28.5h of reaction time. A bright yellow solid (T_g 8°C). After 24h of pressing the T_g increased to 11.2°C.

3.5.1 FT-IR

The FT-IR spectrum of the 1:3.3 mol ratio mixture of EJO and pXD after 21h is shown in figure 22. Only the amide vibrations at 1636 and 1547 cm^{-1} were visible. The ester vibration and the epoxy vibrations were not visible, indicating that amidation and aminolysis occurred.

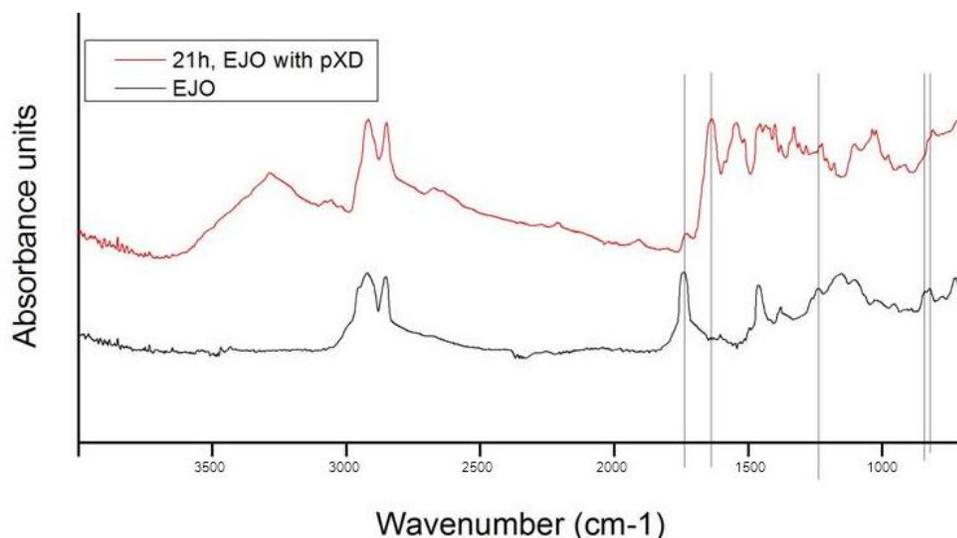


Figure 22. FT-IR spectra of EJO and the reaction product of EJO with pXD after 21h

3.5.2 $^1\text{H-NMR}$

Figure 23 shows the $^1\text{H-NMR}$ spectrum of pXD with EJO after 21h. The proton signals at 4.39, 3.6-3.86 and 2.18 ppm indicate amidation of the triglyceride ester. The decrease of the proton signals at 1.48 and 2.8-3.2 ppm indicate that aminolysis took place. The $^1\text{H-NMR}$ spectra gives a rough indication of the reaction because the formed product did not completely dissolve in CDCl_3 and the amidation results in a lot of different protons shifts, caused by the formation of glycerol, di- and mono glycerides.

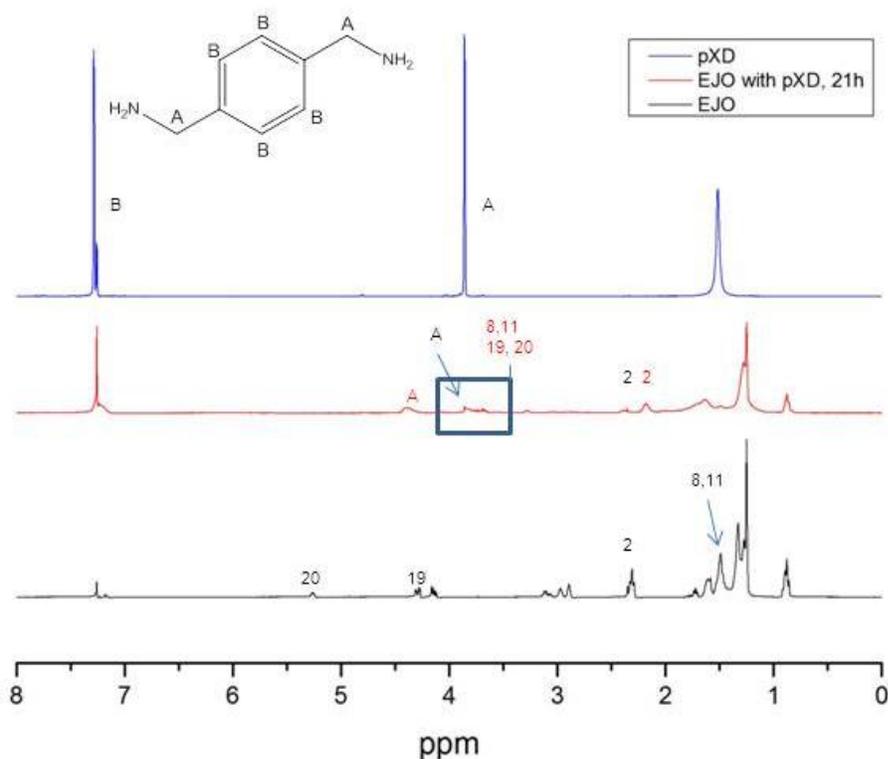


Figure 23. $^1\text{H-NMR}$ (CDCl_3) spectra of EJO, pXD and their reaction mixture after 21h.

3.5.3 Press Parameters

In order to find the best preheating and pressing time for this mixture, several combinations of the 1:3.3 mol ratio were tested. In figure 24 and table 5 the preheating and pressing times of the mixture and their T_g were shown. The trend is that until 24h of press time the T_g increases, but the T_g decreases with increasing pressing time. This is probably caused by degradation of the material in the press over a longer time. Of the 2.5h preheating series there is also a sample of 8h pressing, this sample had a T_g of 2.5°C, 24h of pressing increased this T_g towards 22.4°C. Because of the great difference in T_g as a function of the pressing time, is decided to test specimens with two different pressing times of the 2.5h preheating series on mechanical properties.

Table 5. The press results of the pXD series.

mol ratio	preheating (h)	press time (h)	T_g (°C)
1:3.3	1	24	13.26
1:3.3	1	88	12.78
1:3.3	2.5	8	2.49
1:3.3	2.5	16	-
1:3.3	2.5	24	22.44
1:3.3	2.5	88	19.62
1:3.3	3.5	24	21.73
1:3.3	28.5	0	7.96
1:1.65	30	24	4.68

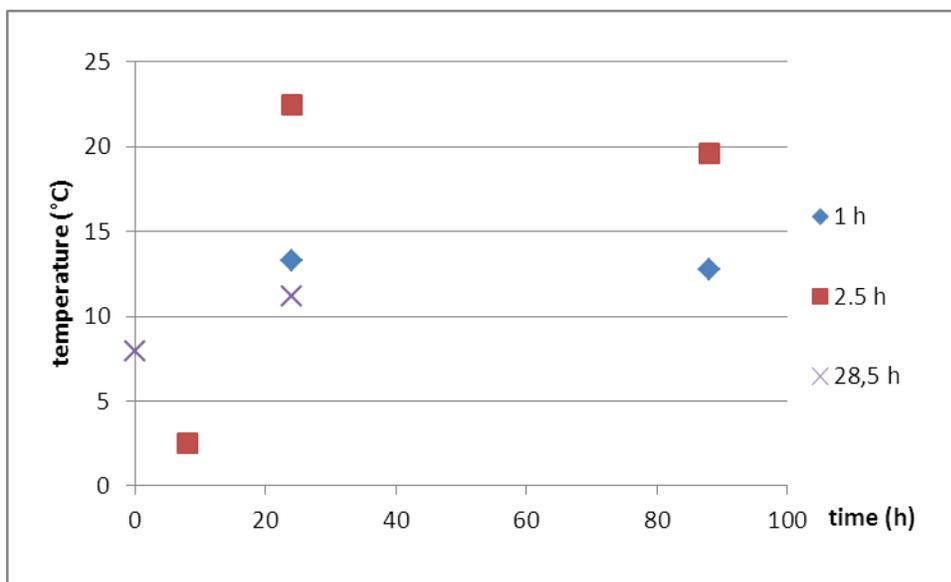


Figure 24. T_g graph of all the T_g s depending on their time of pressing categorized by preheating time.

A batch of 1:3.3 mol ratio of EJO and pXD of 2h preheating was made. This mixture was pressed into specimens according ASTM standards for micro tensile stretching (D 1708-06), for 8 and 24h.

3.6 Mechanical Properties

Three series, one based on TETA with EJO, the other two based on pXD with EJO, were tested on mechanical properties. In table 6 all results of the tensile stretching and the T_g 's of the materials are shown. The mechanical properties of the three series were determined at room temperature, which is above T_g for all series. Normally mechanical properties are determined of materials under their T_g , as materials are then in their 'solid' state. Now the mechanical properties of the materials were determined in the rubbery state of the polymers, which will influence the mechanical properties. In appendix 1 the tensile test graphs and pictures of the test specimens are shown.

Table 6. The tensile testing results together with the T_g of the corresponding materials. All preheated at 150° and pressed at 150°C and 200kN.

Series		Modulus	T_g	Stress (Mpa)		strain (%)	
		(Mpa)	(°C)	max load	auto break	max load	auto break
TETA	NH2_24	1.6	8.7	0.82	0.82	86.9	86.9
pXD	NH2-5_8	18.3	3.1	0.99	0.35	29.1	126.2
pXD	NH2-5_24	52.4	6.4	1.7	0.77	43.9	299.4

The first series contained a 1:1.65 mol ratio of EJO and TETA, prepared by 2h of preheating and 24h of pressing time. The final material showed elastic behavior. On average the material could handle a stress of 0.82 MPa with a strain of 86.9% at max load. The modulus of the material is 1.6MPa and is has a T_g of 8.7°C After breaking (failure) the material reshaped to it is original size.

Two series of pXD and EJO in 1:3.3 mol ratio were made, both series had a preheating time of 2.5h and were pressed for 8 or 24h. The 8h series had a T_g of 3.1°C and a modulus of 18.3MPa. The material showed necking after a stress of 0.1MPa and a corresponding strain of 29.1%. After neck formation the stress reduces to an average of 0.4MPa and the corresponding strain to an average of 126.2%. Most of the specimens did not break, but the tensile test was stopped by the measuring program, the stress was reduced to the lower detection limit.

The 24h series of pXD had a T_g of 6.4°C and a modulus of 52.4MPa. All samples of this series showed necking after an average stress of 1.7MPa and a strain of 43.9% at max load. After necking the max strain the material could handle differs a lot from 217.3 to 479.1%. On average it had a strain of 299.4%. The stress is reduced after the neck forming to an average of 0.8MPa, but showed significant differences in values from 0.4 to 1.4MPa.

From comparing the results of the three test series as shown in table 6 it is clear that the modulus and stress at max load are increasing from the TETA series to the pXD 8h, to pXD 24h series. The TETA series could handle the highest strain at max load. Both pXD series showed necking and elongate to much higher values before breaking. The strain is increasing with the pressing time within the pXD series, for the strain at max load and the strain at breaking.

Based on the measurements it can be said that an increasing pressing time leads to a higher T_g , which probably corresponds to a higher crosslink density. The TETA mixture resulted in an elastic polymer, while the pXD mixtures showed necking, with a tremendous remaining deformation after the neck formation.

4. Conclusion

Jatropha oil was successfully epoxidated with performic acid (formed in an *in situ* reaction of formic acid and peroxide in toluene). The epoxidation reaction had a high yield >92%. The difference between JO and EJO is clearly visible in the corresponding FT-IR and ¹H-NMR spectra.

EJO was crosslinked with HMD, TETA and pXD in different mol ratios via aminolysis. Characterization of the products with FT-IR and ¹H-NMR revealed aminolysis and amidation. The amine ratios were increased to overcome the amidation. HMD had the highest reactivity and resulted in a dark brown sticky material after 24h. TETA had a similar reactivity and in 24h reacted to a yellow brown rubbery material. The reactivity of pXD was slightly lower, this diamine needed 28.5-30h under similar reaction conditions (150°C) to form a hard yellow material. Only the TETA 1:1.65 mol ratio and pXD 1:3.3 mol ratio resulted in promising materials. These materials were investigated further in order to find the best preheating and pressing time at 150°C.

Tin(II)methylhexanoate was tested as catalyst of the aminolysis reaction of Bis A and HMD. A minimum of 10wt% of catalyst was necessary for a decrease in reaction temperature and an increase in reaction speed. The lower amount of catalyst (5wt%) had no influence on the reaction according to the DSC thermogram. Probably the catalyst was poisoned by the water present in the amine. When used with EJO and HMD, the catalyst was not selective for the ring opening reaction and even increased the amide formation. Therefore, it was not investigated further.

MeO was investigated as model compound in the amidation with HMD. Based on this reaction the amide signals in ¹H-NMR could be investigated. They are found at 3.46 and 2.10 ppm. To the best of our knowledge the proton signal at 2.10 ppm is not identified in literature.

The mechanical properties were determined for the TETA 1:1.65 mol ratio and pXD 1:3.3 mol ratio. A 2h preheating and 24h pressing time series of TETA was performed at 150°C. The TETA series resulted in a transparent elastic material with a T_g of 8.7°C. The pXD mixture was tested in two series of 2.5h of preheating and 8 or 24h of pressing time at 150°C. The final products had a T_g of respectively 3.1 and 6.4°C. Within the pXD series the modulus and T_g increases with increasing pressing time and the pXD specimens show necking with a long elongation before breaking. A higher T_g in comparison with the TETA series was expected for the pXD series because of the benzene ring present in the structure of this amine.

Of all tested materials, the TETA mixture gave the most promising result. However, all mechanical properties were determined above the T_g of the material (in the rubber state), the values will be different when measured under the T_g .

In this research, only three diamines were tested. This is not enough to give an overview on the structure properties relationships of the amine for the resulting network after crosslinking with EJ-oil. Therefore, more amines should be tested for this matter. Furthermore, the ¹H-NMR and FT-IR spectra of the diamines revealed the presence of water and the aminolysis is expected to be more efficient without water. The performed reactions should therefore be repeated with dried amines, to exclude any negative effects of water on the crosslinking. The pressing of the pXD mixture indicated negative effects of water as a lot of bubbles were formed in the test specimens. These bubbles were not formed in later specimens that were made with dried pXD.

All the materials synthesized in this research, had a T_g below room temperature. The T_g can be influenced by using different amines. More rigid diamines (such as 4,4'-diaminodiphenylmethane) are expected to result in a higher T_g . The crosslink density also influences the T_g to some extent. A higher crosslink density will lead to a higher T_g , however the crosslink density of the synthesized materials was not determined.

The catalyst tested in this thesis was Tin(II)methylhexanoate and was found not selective for the epoxy or ester group. According to literature $ZnCl_2$ would be a suitable catalyst for the aminolysis reaction. For any further experiments the use of this catalyst is advised.

It is possible to perform the crosslink reaction in a special cell in the FT-IR spectrometer. This way it is possible to follow the reaction directly with FT-IR and this could shine new light on the reaction speed of the aminolysis and amidation. It would be interesting to investigate this further.

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Appendix 1

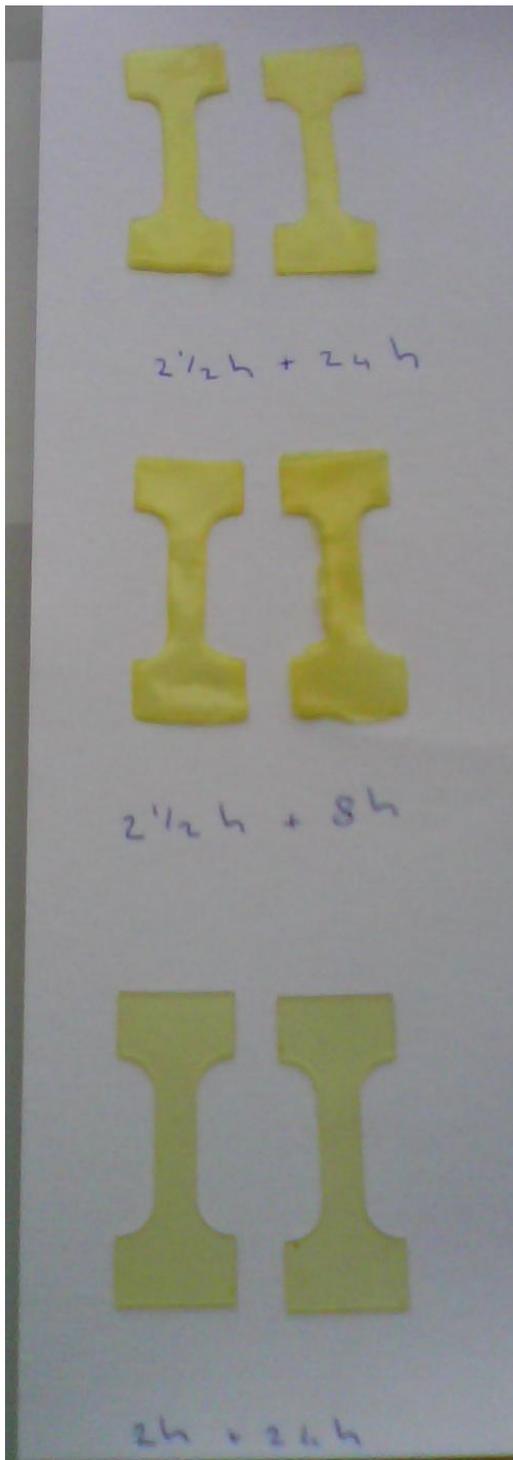
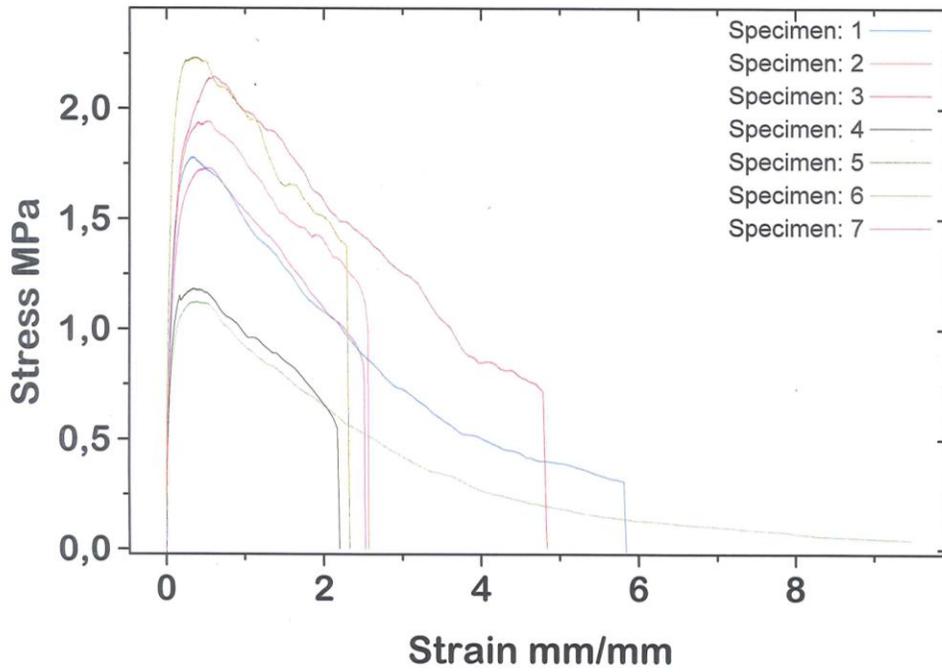


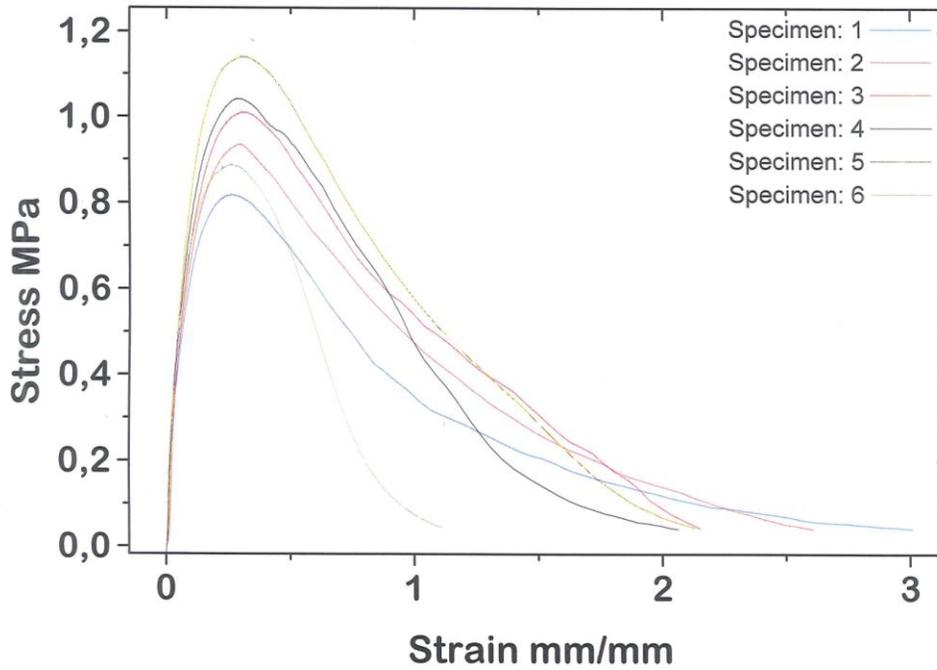
Figure 25. Test specimens.

In figure 25 a picture of the test specimens used with tensile testing, subscript is their preheating and pressing time. On the following pages the tensile test graphs of the corresponding test series are shown.

Sample ID: NH2-5_24



Sample ID: NH2-5_8



Sample ID: NH2_24

