



Synthesis and characterization of novel biobased polyester-imides from natural amino acids, as precursors of polyester-imide urethane coatings

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By Frank van der Donk S3855872

Assessors Dr. Patrizio Raffa Prof. Dr. Cor Koning

Abstract

This thesis aims to show a way of synthesising a polyester-imide, which then is crosslinked with polyisocyanate in order to make polyester-imide urethane coatings, using amino acids and citric acid as a starting material for an imide-containing diethyl ester and using 1,3-propanediol as diol. This goal was achieved, as a properly crosslinked bio-based polyester-imide urethane coating was created using glycine and citric acid as a starting material.

Based on previously published work, different amino acids were converted into cyclic di-acid imides, by reacting the amino acids with citric acid. After the imide formation the cyclic di-acid imides were esterified, as the cyclic imide will not survive the harsh reaction conditions of esterification condensation polymerization. The cyclic imide is polymerized via transesterification polymerization with 1,3-propanediol, which provided a low molecular weight polyester. In order to improve the molecular weight the polymerization was optimized. This significantly increased the molecular weight and precipitation yield. After the polymerization, the polyester-imide was crosslinked using a trifunctional isocyanate. Different crosslinking tests showed a properly crosslinked polyester-imide urethane, as the crosslinker reacted with the primary hydroxyl end-groups and probably also with the tertiary hydroxyl groups of the repeating units. The polyester-imide urethane coating, showed a poor chemical and scratch resistance. However, these physical properties of the polyester-imide urethane can likely be improved in future research.

List of abbreviations

DSC Differential scanning calorimetry
FT-IR Fourier transform infrared spectroscopy
GPC Gel permeation chromatography
H-NMR Proton nuclear magnetic resonance
M_n Number averaged molecular weight
M_w Weight average molecular weight
PEG Polyethylene glycol
P-NMR Phosphorus nuclear magnetic resonance
\$\vec{P}\$ Poly dispersity
TGA Thermogravimetric analysis
T_g Glass transition temperature

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1. Introduction

Ever since the discovery of fossil fuels the world has heavily relied on them as a source of energy and as a building block for polymers. However, for the last five decades scientists have been warning the world for the potential harm of these fossil resources ^[1]. Unfortunately, only in the last two decades this warning was taken serious by the world, as the world was starting to see the negative effects that these fossil fuels and their products have on the environment. One of the main negative effects of the usage of the fossil fuels is that it has been shown to have a severe effect on climate change, due to the high carbon emissions during the production and usage of these fossil fuels, and the production of petrochemical plastics ^[2].

However, this is not the only problem associated with fossil fuels, as most of these petrochemical plastics were not selected with recycling or biodegradability in mind. This results in an accumulation of plastics in landfills and nature ^[3]. In order to counteract the accumulation of landfills, people are forced to incinerate these plastics, which results in even a higher level of carbon emissions ^[3].

These are not the only problems that the plastic industry is facing, as legislatures are attempting to ban certain single use plastics, like food containers, due to the harm these plastics are causing to the environment ^[4]. Another problem the plastic industry is facing is that fossil fuels are becoming less abundant by the day, which could start to create price increases in the near future ^[5-9]. So, with all these different problems associated with petrochemical plastics, companies are shifting towards greener materials. This creates a substantial interest in biobased fuels and materials, as the expectation is that these novel biobased materials will solve most of the problems that are associated with the current petrochemical polymers. These biobased materials could even potentially show better chemical and physical properties compared to their fossil fuel counterpart ^[5,6].

Interesting feedstocks for these biobased plastics are citric acid and different amino acids, as both are widely abundant in nature and relatively inexpensive ^[5,9]. These feedstocks are also interesting when one considers them from a chemical perspective, as they contain multiple functional groups, giving them a wide range of applications ^[5,10].

The aim of this thesis is to show that the citric acid and different amino acids can be converted into polyester-imides, which then can be crosslinked with polyisocyanates in order to create a novel polyester-imide urethane coating. Firstly, in Chapter 2 the necessary background information regarding the polymerization of amino acids is provided, and the research statement is introduced. Thereafter, in Chapter 3 the experimental procedures are described and in Chapter 4 the experimental results are discussed. In Chapter 5 the final conclusion of this research is given and lastly, in Chapter 6 recommendations are given for future research.

2. Background and research statement

As mentioned in the introduction, amino acids are an interesting feedstock for the production of biobased plastics, as they are widely abundant in nature and are a relatively inexpensive feedstock. The incorporation of the amino acids into polymers can significantly improve the biodegradability of the polymer, which will be discussed in section 2.1. This is followed by the introduction of an original way of converting amino acids into polyester-imides in section 2.2 and 2.3. During the reaction several side reactions could occur which could affect the polymerization. Section 2.4 discusses these side reactions and their effect. Lastly, based on the background provided, in section 2.5, the research statement of this proof of concept is introduced.

2.1. Biodegradable and biobased plastics

Ideally, most of the plastic should be able to be recycled after their life time, in order to reduce the impact that they have on the planet. However, currently most of the plastic waste isn't recycled, as there are only very limited amounts of polymers that are actually suitable for the current way of recycling ^[3]. This means that large portion of the plastic waste ends up in a landfill ^[3]. As the plastic waste starts to accumulate, an increasing demand for biodegradable polymers starts to form. The demand for biodegradable polymers is especially strong for applications where polymers are hard to recover after their use. So, biodegradable polymers are especially interesting for industries, like agriculture, fishery, construction and food industries ^[3].

An interesting option for the production of biodegradable polymers are amino acids, as amino acids are widely abundant in nature and are relatively inexpensive. Converting the amino acids into polycondensates is especially interesting, as these polycondensates will contain an easily hydrolysable backbone ^[11]. This means that over time the polymer will start to degrade back to their monomers, which are biodegradable ^[12,13]. However, the relative biodegradability is dependent on which kind of amino acid that is used in the polymerization. This is because D-amino acids based polycondensates are less biodegradable than their L-amino acids counterpart, as the D-amino acid based polycondensates do not fit in the active side of different enzymes ^[9]. Fortunately, the L-amino acids are much more abundant in nature compared to their chiral counterpart ^[14]. The difference in biodegradability suggests that the amino acid based polycondensates are also degraded via enzymatic hydrolysis ^[9].

So, since the amino acid based polycondensates are degraded via enzymatic hydrolysis, the flexibility of the polymer chain becomes important, as the ease of biodegradability of polycondensates via enzymatic hydrolysis is dependent on the flexibility of the polymer structure ^[3,15]. The reason for this is that the polymer needs to fit into the active side of the enzyme ^[15]. The effect of flexibility of the polycondensates can be seen when comparing the biodegradability of aliphatic polyesters and aromatic polyester, as the more flexible aliphatic polyesters are more biodegradable, than aromatic polyesters ^[3]. Fortunately, the less flexible aromatic polyesters are still biodegradable, as over time the polyesters will still degrade over time in nature via non-enzymatic hydrolysis ^[3,11,16-18], however the aromatic polyesters also show a lowered degradation due to their hydrophobic nature ^[18].

The usage of amino acids as a starting material gives the opportunity to make fully biobased and biodegradable polymers ^[19]. Another positive effect of the usage of amino acids as a feedstock for polymers is that, they are present in agricultural waste, like corn stover and sugar beet pulp, which is currently used as a feed for farm animals ^[20,21]. This means that usage of amino acids does not directly compete with food industry, but instead is a waste product from the food industry. Therefore, amino acids can be considered a second generation feedstock ^[22], which makes them ideal for the production of bioplastics

2.2. Using amino acids as a starting material for polymers

As hinted in the previous section, amino acids are an ideal starting material for biobased and biodegradable polymers. The research of Fumio and Endo shows that incorporating amino acids into the polymer structure can enhance the biodegradability of the polymer ^[23]. Fortunately, there are different ways amino acids can be incorporated into the polymer structures, as depicted in *figure 1*. The amino acids contain multiple functional groups, which enables them to be used as a feedstock for a wide variety of materials, as some of the polymers have shown to be capable of electron transfer, information transfer, photo reactivity and selective catalytic function ^[24].

For the production of the polyamides, amino acids can directly be used as monomers during the polycondensation of the polyamides. By converting natural occurring amino acids into polyamides the biodegradability of the polyamide improves ^[24]. This was also the case when amino acids were incorporated into different nylon structures ^[24]. The increased biodegradability gives these polyamides a wide range of applications, from food packing to possible drug delivery systems ^[24,25].



Figure 1. Different ways of using amino acids as a starting material for different polymers. Image adopted from Sanda et al. ^[9]

Another way of using amino acids as a starting material of polymers is to convert them into amino alcohols, which can be obtained via reduction of the carboxylic acid of the amino acid ^[9]. The conversion to amino alcohols is an interesting building block for biobased polymers, as can be seen in *figure 1*. The work of Emiko et. al. shows that different amino alcohols, derived from natural occurring amino acids, can be polymerized with dicarboxylic acids, via polycondensation ^[26]. The work of Emiko et. al. also shows that via polycondensation, thermostable and biodegradable poly ester amides can be made while using natural occurring amino acids as a starting material ^[26]. These polyester amides have a similar range of applications as the previously mentioned polyamides ^[26].

By converting amino acids into isocyanates, polyamide imides can be made. The work of Mallakpour and Khani shows that polyamide imides made from amino acid based isocyanates are moderately thermostable ^[27]. The follow up work of Mallakpour and Rafiemanzelat shows that the thermostability can strongly be improved by converting the polyamide imides into polyamide imide ether urethanes, using a twostep polycondensation ^[28]. Mallakpour and Rafiemanzelat suggests that these poly(amide imide ether urethane)s could be biodegradable due to their amino acid, urethane and polyether linkages ^[28].

The work of Koning et. al. shows that different amino acids can be converted into cyclic imides, using succinic and citric acid ^[5]. They used these amino acid based imides for the production of renewable alkyd resins, which showed improved drying and hardness compared to standard high performance alkyd resins. However, the cyclic imides based on amino acids and citric acids could also be used for the production of novel biobased polyester-imides, which is not described by Sanda et al. ^[9]. So, by reacting the amino acids with citric acid, a cyclic imide di-acid is formed, which can be polymerized with an opportune diol, via condensation polymerization. The formation of the cyclic imide di-acid is represented in *scheme 1*.



Scheme 1. Imide formation, by reacting citric acid with an suitable amino acid

However, polycondensation is generally unsuitable for these molecules, as it generally requires harsh reaction conditions, for instance, reactions temperatures can reach up to 250 °C ^[29-31]. Such reaction conditions will start to degrade the cyclic imide during the reaction. The degradation of the cyclic diacid imide can cause problems during the polymerization as dehydration and decarboxylation can occur. These reactions are further explained in section 2.4. Fortunately, the cyclic imide can also be polymerized via transesterification polymerization, which uses less harsh reaction conditions. In order to do so, however, the cyclic imide needs to be esterified with an alcohol. The esterification of the cyclic imide di-acid is represented in *scheme 2*, which is catalysed with p-toluene sulfonic acid.



Scheme 2. Esterification of the cyclic imide with ethanol, which is catalysed via p-toluene sulfonic acid (PTSA)

2.3. Polymerization

The transesterification polymerization is a step-growth polymerization, meaning that during the transesterification the molecular weight of the new polymer chains are slowly built up ^[17]. When using transesterification polymerization the chain length is strongly dependent on the ratio between the di-ester and the diol, which should be equimolar ^[32]. The chain length is also dependent on the purity of the monomers ^[32]. Because, if not all the carboxylic acids of the cyclic imide are esterified, the chain growth will be stopped.



Scheme 3. Transesterification polymerization with 1,3-propanediol

Transesterification reactions are equilibrium reactions. So, in order to obtain a high conversion, and thereby also a high molecular weight, the equilibrium needs to be shifted to the right ^[33], as can be seen in scheme 3. However, while normally this can be done by adding an excess of one of the reagents, this cannot be done for transesterification polymerization. The reason for this is that the excess of one of the reagents will slow down the polymerization ^[34] and if the excess is too large it could potentially even stop the transesterification polymerization and result in depolymerization. Therefore, one of the reaction products should be removed in order to shift the reaction to the right. In order to do so, the cyclic imide needs to be esterified with a volatile alcohol, like ethanol. This needs to be done because, the volatile alcohol can then easily be removed during the transesterification. By using a volatile alcohol, a higher conversion and molecular weight will be obtained.

A way to remove most of the volatile alcohol from the reaction mixture, is to reduce the pressure in the reactor. However, when using smaller diols this could have a negative effect on the polymerization. The reason for this is that smaller diols, like 1,3-propanediol, could start to evaporate during the polymerization and alter the monomer to diol ratio, which will slow down the reaction rate of the polymerization. Therefore, when using smaller diols the reactor pressure should not be reduced until all the diols are bonded. Once all the diols are bonded the pressure can be reduced to help remove the newly formed ethanol to obtain a higher conversion.

2.3.1. Crosslinking

Coatings are used in order to protect the underlaying substrate on which it is coated, so that the application can be used in environments were high levels of durability are required ^[35]. In most applications the coating should protect against deformation, toughness and natural weathering ^[35]. Therefore, the lifespan of the coating is determined by either a change in appearance or protective properties of the coatings. The work of Allen et. al. shows that the degradation of polyester urethane coatings is caused by oxidation, photolysis and hydrolysis of the urethane bonds, which were confirmed using UV spectroscopy ^[35]. The loss of the urethane crosslinking bonds over time caused the coating to show adverse mechanical properties, which indicates the necessity of a properly crosslinked polyester urethane coating. The work of Krumova et. al. showed that the thermo and mechanical properties actually decreases with a low amount of crosslinking bonds, but

as the amount of crosslinking bonds increased the thermo and mechanical properties strongly increased. However, the increase in thermo and mechanical properties levelled off after a 20% of crosslinking density was reached, which implies that the crosslinking can only enhance the thermo and mechanical to a certain point. Therefore, in order to obtain a coating with the wanted properties, a polymer needs to be used which already has good thermo and mechanical properties, as the crosslinking can only enhance the properties to a certain point. Therefore, it is important that the starting polymer should have a high enough molecular weight and contain at least two functional groups per chain, which can react with the trifunctional crosslinker.

For this thesis, the trimer of hexamethylene tri-isocyanate will be used as a crosslinker, this crosslinker is more commonly known as Desmodur N3600. The reason for the use of this crosslinker is that the isocyanate end groups of the crosslinker react with the primary alcohol end-groups of the polyester chains, to form a polyester urethane coating ^[37]. In order to form a good coating the starting material needs to have a high hydroxyl end-group concentration, as a low hydroxyl end-group concentration will lead to a low concentration of urethane bonds, which means that the thermo and mechanical properties of the polyester are actually not enhanced. The poor crosslinking of the polyester urethane coating will not create one giant molecule, which means that the coating is much more prone to cracking and deterioration by chemicals.

A low hydroxyl end-group concentration is not the only way that could lead to a poor polyester urethane coating, as the isocyanate groups of the crosslinker also react with water. The presence of water during the crosslinking can have two negative effects. Namely, it transforms the isocyanate into an amine and it creates carbon dioxide. The transformation into an amine means that the crosslinker only has two reactive sides for the crosslinking. The formation of carbon dioxide also has a negative effect on the crosslinking, as the carbon dioxide gas will form bubbles which could be trapped during the curing process. In order to keep the polyester urethane coating away from water the crosslinking needs to be done under pure nitrogen, as even the water that is present in the air could negatively affect the crosslinking.



Figure 2. Chemical structure of the trimer of hexamethylene tri-isocyanate, known by the product name Desmodur N3600. Image obtained from Gustini et. al.^[37]

2.4. Side reactions

There are several side reactions that could occur during the imide formation, esterification and polymerization reactions. In this section these side reactions and their effect on the different reactions are discussed.

The work of Koning et. al. shows that during the imide formation two kind of side reactions can occur ^[5]. The first reaction is the dehydration of the tertiary alcohol, which originates from citric acid. The dehydration of the alcohol creates a double bond at either the linear part or the cyclic part of the imide. The other side reaction that the work of Koning et. al. shows, is the decarboxylation of the carboxylic acid which originates from the citric acid ^[5]. When the decarboxylation occurs, the cyclic imide changes from difunctional carboxylic acid into a monofunctional carboxylic acid, which causes problems during the polymerization reaction, as the monofunctional imide will act as a chain stopper during the polymerization, such as described in *section 2.3*. The dehydration of the tertiary alcohol can also cause problems during the polymerization, which will be discussed later on in this section.



Figure 3. Dehydration and decarboxylation during the imide formation, figure adopted from Koning et. al.^[5]

During the imide formation another side reaction can occur. The work of Noordoever et. al. shows that the starting material citric acid is also prone to dehydration and decarboxylation ^[38]. However, their work shows that these side reactions noticeably start to take place at 180 C°. However, when the imide formation is done with xylene as an azeotropic solvent, the reaction temperature will not exceed 138 C°, meaning that the citric acid will not degrade during the imide formation ^[5,39].

During the polymerization, similar to the imide formation, dehydration of the tertiary alcohol can occur, which means that a double bond is formed. The newly formed double bond can be initiated by a free radical, as the free radical can be formed via oxidative degradation ^[40]. When a high amount of dehydration occurs during the polymerization this could lead to the initiation of an uncontrolled chain growth polymerization. The uncontrolled chain growth polymerization will lead to an uncontrolled crosslinking of the growing chains. The uncontrolled crosslinking is undesirable, as premature crosslinking will make the polymer completely insoluble in different solvent, thus making it impossible to mix the polymer with an organic solvent. To prevent the uncontrolled crosslinking a free radical scavenger can be added to the reaction mixture, like Irganox, which protects the polymer against thermal-oxidative degradation and free radical formation ^[40].

Discolouring can occur during the different reactions via thermo-oxidation ^[41]. So, in order to reduce the discoloration all reactions must be done in the absence of oxygen, as the presence of oxygen will cause a strong yellow discoloration of product ^[41,42]. The discolouring can also be reduced by reducing the reaction temperature for the different reactions, as this generally will reduce the amount of side reactions that occur during the different reactions. Preventing the discoloration is necessary as the discolouring is irreversible ^[41]. The negative effects of a small amount of oxygen can be countered by adding a small amount of antioxidant, like Irganox, which protects the polymer against thermal-oxidative degradation and free radical formation ^[40]. However, a slight discolouring is not as fundamental of a problem compared to the other discussed side reactions, as there are many applications where the colour of the end product does not really matter, like in fertilizer coatings.

2.5. Research goal

This research will be in the form of a "proof of concept" to show that amino acids and citric acid can be used as a starting material for polyester-imides, which can then be crosslinked in order to create a polyester-imide urethane film. The aim of the project thus is:

• To create a fully biobased polyester-imide from amino acids and citric acid as starting materials. Subsequently, the intermediate product obtained from amino acids and citric acid needs to be polymerized into polyester-imide by reaction with a diol. Furthermore, it should be possible to convert the fully biobased polyester-imide into a polyester-imide urethane coating via crosslinking.

In order reach the aim of this project, different side goals were set. The first side goal is to produce the monomers for the transesterification polymerization, using amino acids and citric acid as a starting material. This thus yields the following side goals of this research:

- Producing different cyclic imide di-acids, by reacting different amino acids with citric acid. For the different amino acids, glycine and I-phenylalanine are used.
- Producing different cyclic imide di-esters, by reacting the cyclic imide di-acids with ethanol. This is done so that the cyclic imides can be polymerized via transesterification polymerization with a diol.

As the monomers are produced, the polyester-imides can be created by reacting the di-ester with 1,3-propanediol via transesterification polymerization. The different polyester-imides need the following properties in order to be able to convert the polyester-imides into polyester-imide urethane coatings:

- The polyester-imides need to have a high enough conversion in order to produce a polymer with a molecular weight (M_n) of around 3000g/mol
- The polyester-imides need to have a high amount of -OH end groups which can be crosslinked with polyisocynates in order to be able to create polymer films with good properties.

3. Experimental

This chapter will discuss the different experimental procedures and different characterization procedures that were used during the experimental work of the thesis.

3.1. Materials

Acetone (technical grade) and Dimethyl sulfoxide (DMSO, technical grade) were purchased from Biosolve. Citric acid anhydrous (CA, <99%), p-toluene sulfonic acid (PTSA, <98.5%), glycine (Gly, <98.5%), l-phenylalanine (<98%), 1,3-propanediol (<98%), dibutyl tin(IV) oxide (<98%), Dibutyltin dilaurate (<95%) Methyl sulfonic acid (MSA, <98.5%), deuterium oxide (D₂O, <99%) and deuterated dimethyl sulfoxide (D-DMSO, <98.5%) were purchased from Sigma Aldrich. Tetrahydrofuran (THF, technical grade), toluene (technical grade) and xylene (technical grade) were purchased from Boomlab. High vacuum silicone grease was bought from Dow Corning. For heating an oil bath is used, which was heated by IKA RET basic IKAMAG and IKA RCT standard IKAMAG heating plates. For the mixing either a magnetic stirring bar or a Heidolph mechanical stirrer was used for stirring during the reactions. As a crosslinker Desmodur ultra N3600 was used, which was gifted by Covestro.

3.2. Synthesis of the cyclic imide di-acids

The formation of the different cyclic imide di-acids is based on the work of Koning et. al. ^[5] and on the patent US10189767B2 ^[43]. For the formation a 250 ml round-bottom flask, 10ml dean-stark trap and a standard glass cooler were used. The used setup can also be seen in *Figure 4*.

The flask was loaded with 15g citric acid and either 5.88g glycine or 12,89g Lphenylalanine, dependent on which specific cyclic imide was produced. The flask was also loaded with 50ml of either xylene or toluene. The reaction was heated with an oil bath and a IKA RCT standard IKAMAG heating plate and stirred with a magnetic stirring bar. The reaction mixture was heated until the citric acid was fully converted, which can be measured by the amount of water that is being trapped in the dean-stark trap, which corresponds to 2.8ml of water. Once the reaction was done the reaction mixture was cooled down and the xylene was removed under reduced pressure, using a rotary evaporator. This results in the production of the cyclic imide di-acid as a product. The cyclic imide di-acids were analyzed using FT-IR and H-NMR. For the H-NMR measurements the products were dissolved in D₂O.

3.3. Synthesis of the cyclic imide di-ester

The esterification of the cyclic imide di-esters is based on the standard transesterification reaction that is described in the work of Otera ^[44]. For the reaction a 250 ml round-bottom flask and a standard glass cooler was used. The used setup can be seen in *Figure 5*.

The flask was loaded with either 18.04g (glycine) or 25.09g (L-phenylalanine) cyclic imide di-acid. The flask was also loaded with 1%mol of p-toluene sulfonic acid (PTSA) and an excess of anhydrous ethanol (50ml). The mixture is refluxed at 80 °C for 5-6 hours under nitrogen. After the reaction was done the mixture was cooled down and the ethanol was removed under reduced pressure using a rotary evaporator. After that the product is dried even further in vacuum oven over night at 80 °C, in order to completely remove all traces of ethanol from the product. The cyclic imide di-esters were analyzed using FT-IR, H-NMR and TGA. For the H-NMR measurements the product were dissolved in d-DMSO.



Figure 4. Setup of the Imide formation



Figure 5. Esterification setup

3.4. Transesterification polymerization

For the transesterification polymerization 5 gram of glycine di-ester cyclic imide and 1.65 gram of 1,3 propanediol were used. For the polymerization 1 mol% of dibutyltin(IV) oxide was added to the reaction mixture. The mixture was stirred using a Heidolph mechanical stirrer and heated with IKA RCT standard IKAMAG heating plate to 142 °C . The polymerization is performed completely under a nitrogen atmosphere. The polymerization set up consists of a specialized glass reactor, water cooler, heating tube, vacuum pump and a mechanical stirrer. The heating tube is heated up to 99 °C in order to help the removal of ethanol during the reaction. The set up that has been used for the polymerization can be seen *Figure 6*.

The first three hours of the polymerization were done under nitrogen and the last three hours were done under reduced pressure. The pressure, was reduced using a vacuum pump. After six hours the reaction mixture was cooled down and then dissolved in 40ml acetone. Once the polymer was fully dissolved, the polymer was precipitated in 400ml of ice-cold water. After precipitation the polymer is dried overnight at 80 °C in a vacuum oven to completely remove the acetone and water from the polymer. The polymers were analyzed using FT-IR, H-NMR, P-NMR, GPC, TGA and DSC. For the H-NMR measurements the polyester-imides were dissolved in d-DMSO.



Figure 6. Transesterification Polymerization setup

3.5. Crosslinking

Figure 7, shows the crosslinking set-up which was used during the practical work. The crosslinking set-up consists of a IKA RET basic IKAMAG heating plate and a upside down glass funnel. The glass funnel was used to keep air away from the curing polyester-imide urethane coating, This was achieved by leading a continuous flow of nitrogen gas through the upside down glass funnel.

For the crosslinking Desmodur ultra N3600 was used with dibutyltin dilaurate as a catalyst. Before the crosslinking 0.4 gram of polyester-imide was dissolved in 0.7ml of acetone. The crosslinker amount was determined from the amount of alcohol end groups of the polyester, which was 0.012ml. The crosslinker was mixed with 0.4ml of acetone and for the catalyst 0.0018ml was mixed with 1ml of acetone. Once the polymer was fully dissolved, the three solutions were added to each



Figure 7. Crosslinking setup

other. After quickly mixing the mixture was spread out over the substrate surface, which is an aluminium sheet as can be noted in *Figure 6*. After that the mixture was heated at 60 $^{\circ}$ C for 30

minutes, whereafter the temperature was slowly ramped up to 140 $^{\circ}$ C in 30 minutes. After ten minutes at 140 $^{\circ}$ C the polymer coating was cooled down and carefully removed from the substrate.

3.6. Characterization

In order to characterize the different products in this thesis, several different methods were utilized. This section describes the characterization procedures that were followed.

3.6.1. Fourier transform infrared

Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu IR-trancer-100 with the Happ-Genzel method. The transmittance spectra were measured between the wavelength range 600 cm⁻¹ and 4000 cm⁻¹, with a resolution of 1-8 cm⁻¹ for 32-64 scans.

3.6.2. Proton nuclear magnetic resonance

Proton nuclear magnetic resonance (H-NMR) spectra were recorded at 400 MHz in a Varian mercury plus spectrometer. For the H-NMR measurements 1-2 mg of the sample were dissolved in 1 ml solvent. For the H-NMR measurements the samples were either dissolved in d-DMSO or deuterium oxide. The range of the H-NMR spectra were done between the range of -2 to 12 ppm with a relaxation time of 1 second.

3.6.3. Gel permeation chromatography

Gel permeation chromatography (GPC) spectra were recorded on Mixed-E column. For the GPC measurements, the samples for the GPC were dissolved in GPC grade THF at a concentration 2mg/ml. For the internal standard toluene was used.

3.6.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) spectra were recorded on PerkinElmer TGA machine. For the measurements 1mg of sample was heated under nitrogen from 30 $^{\circ}$ C to 600 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C per minute.

3.6.5. Differential scanning calorimetry

Differential scanning calorimetry (DSC) spectra were recorded on PerkinElmer DSC machine. For the measurements 1mg of samples were heated from 30 $^{\circ}$ C to 200 $^{\circ}$ C and then cooled down to -60 $^{\circ}$ C and then heated back to 200 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C per minute.

3.6.6. Phosphorus nuclear magnetic resonance

Phosphorus nuclear magnetic resonance (P-NMR) spectra were recorded on Bruker NMR machine. The method for the P-NMR analysis was based on the work of Dias and Spyros ^[45]. For the P-NMR measurements a stock solution was prepared by dissolving 0.6 mg chromium acetylacetonate and 13.5 mg cyclohexanol in 10 ml of a pyridine and deuterated-chloroform solvents (1.6:1.0 volume ratio). For the measurements 30 mg of polymer was dissolved in 2ml of the stock solution. Once the polymer was fully dissolved, 70 μ l of phosphorylation agent was added and let to react for 30 minutes.

4. Discussion of the results

4.1. Formation of cyclic imide di-acids

4.1.1. Glycine

The citric acid and glycine based cyclic imide di-acid were successfully synthesised via the method of Koning et. al. ^[5] using xylene as an azeotropic solvent. The conversion could be followed by observing the evolution of water in the Dean-Stark trap during the reaction. Doing so showed that 15% of the total amount of water was formed during the first 20 minutes of the reaction and that the reaction was finished after four hours, as no more water was being trapped in the dean-stark trap. However, the amount of water that was being formed is only a rough indication of the conversion, as during the reaction, water can also form by the dehydration of the tertiary alcohol. Whether the dehydration of the tertiary alcohol occurs during the imide formation will be discussed further in this chapter.

During the reaction a yellow discolouring occurred, which was caused by a small presence of oxygen in the reactor, as it is almost impossible to completely remove the oxygen from the reactor in a lab setting.

The citric acid and glycine based cyclic imide di-acid were compared to the starting materials using FT-IR. *Figure 8*. shows the comparison between the product and glycine, which shows the strong formation of the C=O of the imide at 1690 cm⁻¹. *Figure 7*. also shows the disappearing of the H-N of the amine group of the glycine at 1580 cm⁻¹ and 1650 cm⁻¹, which confirms the formation of a cyclic imide.



Figure 8. FT-IR analysis of the citric acid, glycine based cyclic imide di-acid (blue) compared to glycine (orange). The desired product can be confirmed by the formation of the strong peak at 1690 cm⁻¹ which indicates the C=O bond of the imide, that are not present in the glycine and the disappearing of the amine peaks at 1580 cm⁻¹ and 1650 cm⁻¹ which represent the amine peaks of the glycine

The FT-IR comparison between the cyclic imide and anhydrous citric acid can be seen in *Figure 9*. In *Figure 9* it can be seen that the acid peaks largely overlap with the newly formed imide peak at 1705 cm⁻¹. However, in *Figure 9* it can be seen that the anhydrous citric acid has two carboxylic acid peaks, as the peak at 1705 cm⁻¹ corresponds to the dimer of the citric acid and the 1760 cm⁻¹ to the lone carboxylic acid [^{46]}. *Figure 8* also shows the disappearance of the lone carboxylic acid peak. So, from the disappearance of the amine and the lone carboxylic acid it can be concluded that the imide ring is

fully closed. The spectrum of the anhydrous citric acid also shows a clear shift of the tertiary alcohol from 3500 cm^{-1} to 3450 cm^{-1} .



Figure 9. FT-IR of the citric acid, glycine based cyclic imide di-acid (blue) compared to anhydrous citric acid (orange). The comparison shows a clear shift of the tertiary OH group, as the peak is sifted from 3500 cm⁻¹ to 3450 cm⁻¹



Figure 10. H-NMR spectrum of the citric acid and glycine based cyclic imide di-acid, using deuterium oxide (D2O) as a solvent. Wherein the following chemical shifts originate from citric acid: 2.79 ppm, 2.84 ppm, 3.14 ppm, 3.19 ppm and 4.20 ppm and the chemical shift at 2.94 ppm originates form the glycine. The spectrum also shows a small amount of xylene at 2.20 ppm and 7.05 ppm. The full spectrum can be seen in appendix A

The successful synthesis of citric acid and glycine based cyclic imide di-acid was further confirmed via H-NMR. *Figure 10* shows the H-NMR spectrum of the cyclic imide, the spectrum also shows that there is still a small amount of xylene present and that during the reaction a small amount of side products is formed. However, the H-NMR spectrum did not show a clear formation of the double bond at 6 ppm, which means that no dehydration, and no decarboxylation are taking place during

the imide formation. This means that the progression of the reaction can be traced by the amount of water that is being trapped during the reaction.

4.1.1.1. reduced temperature

The imide formation with xylene as an azeotropic solvent showed a high reaction rate at the start of the reaction, as after 20 minutes roughly 15% of the total amount of water was formed. This means that the temperature of the reaction can likely be lowered, which will reduce the formation of side products. In order to reduce the reaction temperature, either the azeotropic solvent needs to be changed or the reactor pressure needs to be reduced to lower the boiling point of the xylene. In order to reduce the reaction temperature the azeotropic solvent was changed. Therefore, the xylene was replaced by toluene, effectively lowering the reaction temperature from 138 °C to 111°C. Choosing to replace the solvent to toluene has also another positive effect as toluene is more volatile than xylene. Hence toluene is easier to remove from the reaction mixture than xylene is.

By changing the azeotropic solvent to toluene the reaction rate was reduced, which increased the reaction time by two hours. *Figure 11* shows a comparison between the H-NMR spectra of the products when using toluene and xylene as azeotropic solvents. The comparison shows a slight decrease of side reactions when using toluene as an azeotropic solvent. Also, by lowering the reaction temperature the yellow discoloring slightly decreased.



Figure 11. comparison of the H-NMR spectra of the citric acid and glycine based cyclic imide di-acid's when using xylene (red) or toluene (blue) as an azeotropic solvent the full spectrum can be seen in appendix A.

4.1.2. L-phenylalanine

The synthesis of the citric acid and the I-phenylalanine based cyclic imide di-acid synthesis was confirmed using FT-IR, as can be seen in *Figure 12*. The FT-IR spectrum shows a clear disappearance of the amine group of the I-phenylalanine at 1480 cm⁻¹ and 1560 cm⁻¹ The FTIR spectrum also shows a clear formation of the imide peak at 1695 cm⁻¹.



Figure 12. Comparison of the FT-IR spectrum of the citric acid and I-phenylalanine based cyclic imide di-acid and I-phenylalanine. Which shows the formation of the cyclic imide at 1695 cm⁻¹ and the disappearance of the amine peaks at 1480 cm⁻¹ and 1560 cm⁻¹

The H-NMR spectrum of the product was analysed with the help of the supplemental data of Koning et. al. ^[5], which can be found in appendix B. However, on the H-NMR spectrum of the product it is much harder to precisely identify the product compared to the glycine based imide, as most chemical shifts happen between 2.5 ppm and 3.5 ppm, causing them to overlap each other. The overlapping is largely caused by the protons which show coupling with the aromatic part, which originates form the I-phenylalanine. The H-NMR spectrum also shows that a small amount of dehydration occurs during the imide formation, which can be seen by the double bond formation at 6.7 ppm. The spectrum also shows that a small amount decarboxylation occurs during the reaction, which can be traced back to the chemical shift at 1.24 ppm. So, the H-NMR spectrum shows that during the reaction a small amount of dehydration and decarboxylation occurs, which is in line with the findings of Koning et. al. ^[5].

4.1.1.2. reduced temperature

The H-NMR spectrum of the citric acid and I-phenylalanine based cyclic imide di-acid showed the decarboxylation of the cyclic imide, which has a negative effect on the polymerization. In order to reduce the decarboxylation, the reaction temperature was reduced, and xylene was replaced with toluene, like in the glycine reaction. However, unlike the glycine reaction, this did not work as intended for the I-phenylalanine reaction, considering that after the reactions the same starting products remained.

Due to the covid-19 pandemic there was limited lab time available for master students. Therefore, no further research was done for the l-phenylalanine reaction and the full focus was shifted towards the glycine reaction, as the glycine reaction showed not traces of decarboxylation.



Figure 13. H-NMR spectrum of the citric acid and l-phenylalanine based cyclic imide di-acids. Using deuterium oxide (D2O) as a solvent. The spectrum was worked out with the help of the supplementary data of the work of Koning et. al. ^[5] The full spectrum can be seen in appendix A and the supplementary data can be seen in appendix B.

4.2. Formation the citric acid and glycine based cyclic imide di-ester

The citric acid, glycine based cyclic imide di-acid was successfully esterified with ethanol using ptoluene sulfonic acid (PTSA) as a catalyst. After drying a solid product was obtained, which was slightly more yellow than the starting material. This means that the yellow discolouring also occurs during the esterification reaction. *Figure 14* shows H-NMR spectrum, which shows the formation of the diester. The formation can be seen in the appearance of the chemical shifts of the diester at 1.1 ppm and 3.4 ppm. The H-NMR spectrum also shows the formation of side products at 1.2 ppm and 2.8 ppm. These side products could be decarboxylation of the product, however this is very unlikely as the H-NMR spectrum does not show a clear dehydration of the tertiary alcohol at 6 ppm.



Figure 14. H-NMR spectrum of the citric acid and glycine based cyclic imide di-ester. For the measurement the product was dissolved in d-DMSO. The H-NMR spectrum shows the formation of the esters at 1.1 ppm and 3.4 ppm the full spectrum can be seen in appendix A.

After drying, the product was washed with cold water, as to remove the PTSA catalyst from the product. However, after washing the product it needs to be dried again and during the washing some loss of product takes place. This way of removing the catalyst is far from optimal, therefore the esterification reaction was also tested with methane sulfonic acid (MSA) as a catalyst. This was done because MSA can be removed from the product during the drying of the product, due to the relatively low boiling point of the MSA catalyst.

However, when using MSA as a catalyst an orange liquid was obtained after drying, which indicates the formation of side products during the reaction. This was confirmed by the H-NMR spectrum which shows a lot of overlapping chemical shifts between 2.5 and 3.5 ppm, which indicates that the product is not pure. This is an indication of the formation of side products. It remains unknown what caused these side reactions, but unfortunately due to the lack of lab time this could not be further investigated.



Figure 15. Comparison between the MSA (blue) and the PTSA (red) catalyst for the esterification of the citric and glycine based cyclic imide di-acid with ethanol full spectrum can be seen in appendix A.

The thermal stability of the citric acid, glycine based cyclic imide di-ester, which was catalysed by PTSA, was measured using the TGA. *Figure 16* shows the TGA spectrum of cyclic imide di-ester. The TGA spectrum shows that the new di-ester is stable to 190 °C with a 5% mass loss at 248 °C. This makes the citric acid, glycine based cyclic imide di-ester stable enough for transesterification polymerization up to approximately 160-170 °C, however as expected not stable enough for polycondensation at 220-250 °C. The TGA of the cyclic imide showed an improvement in thermostability when comparing it with citric acid, as the citric acid will start to degraded at 177 °C ^[47]. However, the thermostability decreased when comparing the cyclic imide with glycine, as the glycine will start to degrade at 230 °C ^[48].



Figure 16. TGA spectrum of the citric acid and glycine based cyclic imide di-ester

4.3. Transesterification polymerization

The TGA analysis showed that the citric acid and glycine based cyclic imide di-ester is thermally stable enough for transesterification polymerization. So, for the transesterification polymerization 1,3propanediol was selected as a diol. The transesterification polymerization was done at 142 °C for six hours at a 1:1 ratio (imide:diol). Figure 17 shows the H-NMR spectrum of the product, which shows the formation of the polyester. However, the H-NMR spectrum also shows that during the reaction a strong dehydration of the tertiary alcohol occurs, as the H-NMR spectrum shows a strong formation of the double bond at 6.42 ppm. This means that the dehydration is likely catalysed by the dibutyltin(IV) oxide, as the TGA showed that dehydration of the monomer start to occur at roughly 190 °C. The H-NMR spectrum also shows a strong ethyl peak of the ethyl ester at 1.20 ppm, which is an indication for a low molecular weight of the polymer. The reason for this is that the ethyl esters are end groups, so a high intensity of the ethyl ester peaks, indicates a low amount of repeating units. So, not all the ester end groups have been transesterfied with 1,3-propanediol. Another indication is the low precipitation yield of 26% in ice-cold water. The low precipitation yield is an indication of a low conversion of the polymerization, as the reaction mixture still contains a large amount of low molecular weight material, which is lost during the precipitation of the polyesterimide in ice-cold water.



Figure 17. H-NMR spectrum of the transesterification polymerization of the 1,3-propanediol and the citric acid and glycine based cyclic imide di-ester. The H-NMR spectrum shows a strong formation of the double bond at 6.42 ppm, which is cause by the dehydration of the tertiary alcohol. The full spectrum can be seen in appendix A

The low molecular weight was confirmed by the GPC data, which showed a low molecular weight (M_n) of 1408 g/mol. However, in order to be suitable for the intended application, the molecular weight (M_n) of the polymer should be around 3000 g/mol. The reason for this is that a high amount

of low molecular weight material will need a lot of crosslinking agent, which could negatively affect the properties of the polymer coating. Furthermore, these crosslinking agents are relative expensive.

In order to increase the molecular weight of the polymer, the reaction was optimized by changing three parameters. The following parameters were changed one at a time: reaction time, reaction temperature and monomer to diol ratio. Results of the optimization are shown in table 1.

Increasing the reaction time: Generally, by increasing the reaction time the overall conversion of the polymerization increases, unless equilibrium is already reached. However, by increasing the reaction time of the polymerization the amount of side reactions is also increased, such as the dehydration of the tertiary alcohol. For the optimization the reaction time is changed from six to twelve hours.

Increasing the reaction temperature: By increasing the reaction temperature the reaction rate of the polymerization is increased. The increased temperature will also help with the removal of the ethanol, which will shift the equilibrium to the right, thereby, increasing the overall conversion of the polymerization. However, due to the thermostability of the cyclic imide di-ester and the boiling point of the 1,3-propanediol the temperature will only be increased in the second half of the polymerization. This means that only during the during the vacuum phase the temperature is increased, and is slowly ramped up to 172 $^{\circ}$ C.

Changing the monomer ratio: in theory a 1:1 (imide:diol) mol ratio is already the most optimal for the transesterification polymerization ^[32]. However, due to the low boiling point of the 1,3-propendiol the actual ratio could be changed during the polymerization. To counteract the loss of the 1,3-propanediol, due to evaporation of the 1,3-propendiol, the ratio is adjusted. For the optimization an excess of 10 wt% of 1,3-propanediol is used. The increase in the diol amount will also positively affect the hydroxyl end-group concentration of the polymer, as an increased diol amount will increase the hydroxyl end-group concentration of the polymer.

By increasing the reaction time to twelve hours (polyester-imide 2), the molecular weight slightly increased to 1577 g/mol. However, the biggest change was visible in the precipitation yield, which increased significantly to 62%. Increasing the reaction temperature during the second half of the polymerization (polyester-imide 3) increased the molecular weight to 1526 g/mol and the precipitation yield increased to 31%. Changing the monomer ratio (polyester-imide 4), resulted in a significant increase in the molecular weight, as it increased to 1782 g/mol. However, by changing the monomer ratio the precipitation yield lowered slightly. This is most likely caused by experimental error during the precipitation of the crude polyester.

So, all three of the parameters showed a positive effect on the polymerization (polyester-imides 2, 3 and 4), as either the molecular weight or the precipitation yield increased, which can be seen in *table 1*. Therefore, the polymerization was done at "optimal conditions", in which all three parameters were changed at the same time, as they all increased the molecular weight (M_n) of the polyester. By changing all three parameter the molecular weight increased to 3290 g/mol and the precipitation yield increased as well to 66% (polyester-imide 5).

Polyester- imide	Time (Hour)	Ratio (imide:diol)	Temp (°C)	M _n (g/mol)	M _w (g/mol)	Ē	Yield after precipitation
1	6hr	1:1	142	1408	2141	1.52	26%
2	12hr	1:1	142	1577	2309	1.46	62%
3	6hr	1:1	172	1526	2180	1.43	31%
4	6hr	1:1.1	142	1782	2133	1.20	23%
5	12hr	1:1.1	172	3290	4521	1.37	66%

Table 1. Optimization of the citric acid and glycine based cyclic imide di-ester, 1,3-propanedioltransesterification polymerization

However, even after the optimization the ethyl ester peak was still strongly visible in the H-NMR spectrum of polyester-imide 5, which indicates that a large part of the ethyl ester end groups are not replaced by the primary -OH groups of the 1,3-propanediol. In order to precisely measure the alcohol end groups of the polyester, the alcohol groups were reacted with the phosphorylation agent, which makes it possible to quantify with P-NMR. The P-NMR spectrum showed that the primary alcohol concentration (end group) was 0.25 mmol/g, which means that slightly less than the half ethyl esters are replaced by 1,3-propanediol, the hydroxyl calculation can be found in appendix C. The hydroxyl concentration is too low for the crosslinking, as for the crosslinking a high hydroxyl end group concentration is needed. The reason for this is that if the crosslinking functionality is to low, then the coating will be poorly crosslinked. The P-NMR spectrum also shows that there are still substantial amounts of tertiary alcohols present, which originate from the citric acid, as the P-NMR shows a tertiary hydroxyl concentration of 1.72 mmol/g.

In order to increase the hydroxyl end group concentration the polymer was further reacted with an large excess of 1,3-propanediol and a new amount of catalyst for three hours and six hours. Both the three- and six hours reaction showed a decrease of the ethyl peak of the ethyl ester, which can be seen in *Figure 19*. However, the H-NMR spectrum also shows a decrease in the intensity of the double bond at 6.42 ppm, as the decreases from 0.85 to 0.68 for the 3 hour reaction and 0.57 for the 6 hour reaction and a strong increase in the bonds which correspond to the chemical shifts of the 1,3-propanediol at 1.9 ppm and 4.2 ppm.

So, the change of the chemical shifts could be an indication that the 1,3-propanediol reacts with the double bond and form an ether bond. The comparison between spectra also shows that more side products are being formed, which makes this method less than ideal for the increase of the hydroxyl end group concentration of the polyester. Another way to increase the hydroxyl end group concentration, is by increasing the diol amount for the polymerization. However, increasing the diol ratio to 1:1.3 (imide:diol) resulted in a completely crosslinked polymer after the polymerization, as the resulting polyester-imide was completely insoluble in: acetone, THF, DMSO, n-pentane, water, ethanol, diethyl ether, dichloromethane, methanol and chloroform.



Figure 18. H-NMR spectrum of polyester-imide 5 at polymerization of the 1,3-propnediol and Citric acid and glycine based cyclic imide di-ester, which still shows a significantly ethyl peak at 1.2 ppm full spectrum can be seen in appendix A



Figure 19. Comparison of the H-NMR spectra of the starting material and the further reacted with 1,3-propanediol polyester-amide. The red spectrum is the starting material, the green spectrum is after three hours and the blue is after six hours



Figure 20. P-NMR spectrum of polymer 5, which is used to determine the concentration of the primary and tertiary alcohols of the polyester. The chemical shift at 132 ppm corresponds to the primary alcohol, the chemical shift at 133 ppm corresponds to the tertiary alcohol and the chemical shift at 137 ppm corresponds to the internal standard

So, by increasing the diol ratio the polyester-imide started to crosslink during the polymerization, but due to the lack of lab time this could not be properly be researched. There are four possible explanations on why the polymer crosslinked, which can be split into two groups. The first group consist of crosslinking options caused by uncomplete ring closing of the cyclic imide. The second group consists of options caused by the double bond that is formed during the polymerization.

As stated, the first option is that the cyclic imide is not fully formed during the imide formation. This can result in two different paths, which both could result in unwanted crosslinking. The first way is that the third acid which should form the cyclic imide, is not used in the ring closure reaction and remains available to be polymerized, via polycondensation. This means that during the polymerization there are a carboxylic acid side groups present in the monomer. The COOH side group could possibly react over time with the 1,3-propanediol via polycondensation, resulting in branching and possibly crosslinking.



Scheme 4. Carboxylic acid side group initiating crosslinking via polycondensation

However, generally, polycondensation occurs at much harsher conditions than compared to the transesterification polymerization, making this option very unlikely, however, the increased reaction temperature and time could make it somewhat plausible. The problem with this hypothesis is that this would assume that during the esterification with ethanol the carboxylic acid is not esterified,

which is very unlikely as the esterification is not done with a selective catalyst. Therefore, it is much more logical that the carboxylic acid is esterified if the cyclic imide is not fully formed, which would result in tri-ester instead of di-ester. This would then start to crosslink with the 1,3-propanediol as the polymerization functionality is increased of each polymer chain. Checking the formation of this is relatively easy, as the ester amount can be measured with H-NMR, as has been showed in the previous section of this chapter. However, none of the H-NMR spectra showed any indication of the formation of the third ester. Hence, it is regarded that it is very unlikely that the unwanted crosslinking is caused by the not fully ring closing of the cyclic imide.



Scheme 5. Crosslinking via transesterification polymerization

A much more plausible option is the second path, which is the result of the double bond formation. During the polymerization dehydration of the tertiary alcohol occurs, which can clearly be seen in the H-NMR spectra of the different polyester-imides. The new formed double bond could react in two different ways. The first option is that the double bond is protonated by a strong acid, which could indicate that there is still PTSA present after washing of cyclic imide di-ester. The protonation of the double bond would form the stable tertiary carbocation, which then is attacked by one of the lone electron pair of the oxygen of one of the alcohols of the 1,3-propanediol in order to from an ether ^[49]. The formation of the ether is hard to analyse using FT-IR as the peaks of the ether and the tertiary alcohol overlap with each other.



Scheme 6. Ether formation during the polymerization, possibly resulting in crosslinking

The other option of the second path, is that during the polymerization a free radical is formed via thermo oxidative degradation, which is caused by the presence of a small amount of oxygen during the polymerization. The free radical attacks the double bond which initiates a free radical polymerization, alongside the step growth polymerisation. This over time, will form a highly crosslinked polymer structure, as there is a high amount of double bonds present in the reaction mixture.



Scheme 7. Initiation of free radical polymerization, possibly resulting in crosslinking

Of the two paths, the second path seems the most likely. The reason for this is that during the polymerization a high amount of double bonds are formed, due to the dehydration of the tertiary alcohol of the citric acid residues. Of the double bond options the radical polymerization is the most logical, as the other option assumes that there is still a strong acid is present during the polymerization, even after washing the cyclic imide di-ester. However, this is still a plausible option until proven otherwise. A way to test which of the two options causes the uncontrolled crosslinking, would be to add a free radical scavenger to the reaction mixture and test if the polymer still starts to crosslink during the polymerization. If after adding the free radical scavenger the polymerization.

The TGA analysis of the different polyester-imides based on citric acid and glycine imide di-ester and 1,3-propanediol showed that they are stable until 250 °C with a 5% mass loss at 290 °C, which can be seen in *Figure 21*. The thermostability shows that the polyester-imides are stable enough to be processed in for example an extruder.



Figure 21. TGA of polyester-imides based on citric acid and glycine based cyclic imide diester and 1,3propanediol with different molecular weights ranging from 1408-3290 g/mol

DSC measurements show that the polyester-imides based on citric acid and glycine based cyclic imide di-ester and 1,3-propanediol are amorphous as the DSC measurements only showed a glass transition temperature (T_g). The T_g of the different polymers ranges between 23.3 °C and 41.5 °C. There is an unexpectedly big difference between the different polymers which could be caused by the entrapment of some acetone in the polymer structure of polyester-imides 2 and 3, as the trapped acetone could act as a plasticizer, thereby lowering the T_g .

	1			1	r		
Polyester	Time	Ratio	Temp (°C)	Mn	Mw	\overline{P}	T _g (°C)
	(Hour)	(imide:diol)		(g/mol)	(g/mol)		0.0
	(nour)	(innac.aioi)		(6/1101)	(8/1101)		
1	6hr	1:1	142	1408	2141	1.52	41.2
2	12hr	1:1	142	15//	2309	1.46	23.3
3	6hr	1:1	142-172	1526	2180	1.43	33.9
4	6hr	1:1.1	142	1782	2133	1.20	41.1
5	12hr	1:1.1	142-172	3290	4521	1.37	41.5
5	12.11		112 172	5250	1321	1.57	11.5
			1				

Table 2. Glass transition temperatures (T_g) of the different polyester-imides based on citric acid and glycine based cyclic imide and 1,3-propanediol polyester-imides

4.4. Crosslinking

Before, the crosslinking of the polyester-imide made from the citric acid and glycine based cyclic imide, 1,3-propanediol, a test was done with polyethylene oxide (PEG), which contains two hydroxyl end groups per chain, and Desmodur ultra N3600 as a crosslinker. For the crosslinking test the PEG was dissolved in acetone and mixed with the crosslinker and the catalyst. The mixture was spread out on the aluminium substate. The curing of the PEG coating was done at 60 °C for half an hour to evaporate most the acetone, after that the temperature was slowly ramped up to 140 °C over half an hour. The PEG coating became insoluble in acetone and became slightly elastic, which are indications that the PEG was successfully crosslinked. So, if OH end groups are present, Desmodur ultra N3600 is a suitable crosslinker.

Since, the PEG crosslinking test was successful, the same method was used for the crosslinking of the polyester-imide 5 was used, of which less than half of the ethyl ester end groups are replaced by primary alcohols. Polyester-imide 5 was crosslinked with Desmodur ultra N3600 using aluminium as a substrate. However, during the curing at 60 °C bubble formation started to occur, as can be seen in *figure 22*. There are two possible reasons why bubble formation started to occur during the crosslinking. The first option is that the bubble formation was caused by the fast evaporation of the acetone solvent. The other option is that the acetone has taken up water over time, which means that during the crosslinking carbon dioxide gas was being formed, as the isocyanate groups reacted with the water, which is present in the solvent. In order to investigate the bubble formation a new coating was made at a lower starting temperature of 50 °C , which showed a similar bubble formation as the previous coating, which can be seen in *figure 22*. The second crosslinking also showed bubble formation, which is a strong indication that bubble formation was caused by the presence of water.

The second coating was also crosslinked on a different substrate, which showed that the polyesterimide urethane coating adheres well to aluminium substrate and poorly to a Teflon substrate. This could be seen during the removal of the coating from the substrate, as when aluminium was used as a substrate the coating kept on breaking, whereas when Teflon was used the coating could cleanly be removed from the substrate without breaking. The crosslinked polyester-imide urethane coating showed a similar flexibility as the PEG based coating.



Figure 22. Citric acid and glycine based cyclic imide and 1,3-propanediol polyester-imide urethane films. The left coating was cured on an aluminium substrate at a starting temperature of 60 °C. The right coating was cured on a Teflon substrate at a starting temperature of 50 °C

The different polyester-imide urethane coatings were properly crosslinked as both coatings were insoluble in acetone, chloroform, DMSO, ethanol, THF and water. The complete crosslinking was



confirmed using FT-IR, as *figure 23* shows the complete disappearance of the isocyanate groups of the crosslinker at 2250cm⁻¹.

Figure 23. FT-IR spectrum of the polyester-imide urethane coating

The successful formation of the polymer coating was somewhat unexpected, due to the low amount of primary alcohol end-groups in the polyester. This could be a strong indication that the crosslinker not only reacts with primary alcohol end-groups, but also with the less reactive tertiary alcohol, resulting in a properly crosslinked polyester-imide urethane film.



Figure 24. Left: The removed polyester-imide urethane film. Right: Insoluble polyester-imide urethane coating in DMSO

Changing the substate to Teflon made it possible to cleanly remove larger parts of the polymer film. This makes it possible to test how scratch and chemical resistant the crosslinked polymer film is. For the scratch resistant the pencil test was used as described by Gustini et. al. ^[37]. For this method lead pencils with different harnesses were used. Each pencil was used to make a scratch on the surface of the crosslinked polymer film. This test showed that the polymer film started to scratch at a B5 and significantly scratched at a B4, which were the fourth and fifth softest pencils. This indicates that the polymer film is prone to scratching. Unfortunately, the scratching could not be seen clearly on pictures, therefore these pictures are not included in this thesis.

For the chemical resistance test the acetone wipe test was used as described by Gustini et. al. ^[37]. To execute this test a cotton washcloth was used. The acetone wipe test showed that film started to show visible damage after 15 back and forth wipes and started to fall apart after 30 back and forth

wipes, which can be seen in *figure 25*. This test was done multiple times in order to test the effect of different wiping techniques, which all showed similar results. So, from the pencil test and acetone wiping test it can be concluded that the polymer coating is not very scratch and chemical resistant, which are strong indications of a low crosslinking density.



Figure 25. Chemical resistance test of the polyester-imide urethane coating. The left picture is the coating before the test and the right picture is after 30 back and forth swipes with an acetone drenched cotton washcloth.

5. Conclusion

Over the last several decades, the world became aware of the negative effects that fossil fuels and their products are having on nature and the global climate. Many of the plastics now in use have a petrochemical origin, and were not selected with recycling and biodegradability in mind, resulting in discarded plastics accumulating in nature and landfills. To prevent the different problems that these plastics are causing, a great amount of research is being done on biodegradable and biobased polymers. This thesis aims to add to this stock of literature by attempting to create a fully biobased polyester-imide from amino acids and citric acid, as well as 1,3-propanediol as starting materials. This polyester-imide is made via transesterification polymerization, and converted into a polyester-imide urethane coating via crosslinking with a polyisocyanate.

The first step taken was to produce the monomers for the different polyester-imides, by reacting the citric acid with amino acids to create a cyclic imide di-acid. The synthesis of the glycine and l-phenylalanine based cyclic imide di-acids were confirmed using FT-IR and H-NMR, of which only the l-phenylalanine cyclic imide di-acid showed a slight amount of dehydration and decarboxylation. In order to reduce the side reactions both reactions were done at a lower temperature by changing the azeotropic solvent to toluene, this only worked for the glycine reaction. Due to the lack of lab time the full focus was shifted towards the glycine reaction.

As the citric acid and glycine based cyclic imide di-acid is not stable enough for condensation polymerization, the cyclic imide was esterified with ethanol using PTSA as a catalyst. The formation of the ester was confirmed using H-NMR. However, the PTSA catalyst could not easily be removed after the reaction. Therefore, MSA was tested for the esterification of the cyclic imide. However, by changing the catalyst a lot of side reactions were formed, as confirmed via H-NMR. The TGA showed that the cyclic imide di-ester, made using the PTSA as esterification catalyst, is stable up to 190 $^{\circ}$ C, meaning that the cyclic imide di-ester is stable enough for transesterification polymerization.

The transesterification polymerization with 1,3-propanediol at 6hr, 142 °C and using a 1:1 (imide:diol) ratio provided a polyester-imide with a M_n of 1408 g/mol and a precipitation yield of 26%. In order to both increase the M_n and precipitation yield, the polymerization was optimized by changing the following parameters: reaction time, reaction temperature and monomer to diol ratio. The three parameters had either a positive effect on the M_n or the precipitation yield. Therefore, the polymerization was done at 12hr, 172°C and 1:1.1 (imide:diol) ratio, which resulted in polyester-imide with a M_n of 3290 g/mol and a precipitation yield of 66%. However, the H-NMR spectrum showed that the polyester-imide still contained a substantial amount of ethyl ester end groups. The low amount of hydroxyl end groups was confirmed via P-NMR, which showed a hydroxyl concentration, however these were unsuccessful, as the polymer started to crosslink during the polymerization or post-modification. The H-NMR spectra of the different polyester-imides showed that a strong dehydration of the tertiary alcohol occurs during the polymerization, which likely causes the crosslinking during the polymerization.

Even though the low hydroxyl end group concentration of the 3290 g/mol polyester-imide and the certain presence of at least some ethyl ester end groups on the polyester-imide, it was still successfully crosslinked with Desmodur ultra N3600 as the crosslinking agent. This means that most probably not only the primary OH end groups of the polyester-imide, but also the tertiary OH groups of the citric acid residue took part in the crosslinking process. The polyester-imide urethane film was insoluble in acetone, chloroform, DMSO, ethanol and water, thereby confirming the crosslinking. During the polymerization bubble formation occurred during the crosslinking, which is likely to be

caused by the presence of water. The polyester-imide urethane coating adhered well to aluminium substrate and less well to a Teflon coated substrate. The polyester-imide urethane coating showed poor chemical and scratch resistance.

The final conclusion of this thesis is that the research goal was indeed attained, as citric acid and glycine, as well as 1,3-propanediol was used as a starting material for the polyester-imide. This polyester-imide was then turned in to a polyester-imide urethane coating. However, the research was only partially successful, as there are still a lot of unknowns mainly due to different side reactions that occur during the different reactions.

6. Recommendations

Even though the proof of concept was relatively successful, there are still some points of attention for future research that could build upon this work. Therefore, seven important recommendations are given in this chapter to help to direct future research.

The first recommendation is to analyse the different cyclic imides in more depth using liquid chromatography-mass spectrometry (LC-MS), as LC-MS could help with the identification of the different side products. For instance, LC-MS could help identify what precisely happed with the MSA catalysed esterification of the glycine based cyclic imide di-ester and which side products were formed.

A second recommendation is to further investigate the crosslinking that occurred during the transesterification polymerization, as it is currently unknown what precisely is causing the unwanted crosslinking. In part 4.3. four possible explanations were given, which were split up in two paths, however due to the lack of lab time these could not be further investigated. The first path consists of options wherein the imide ring is not fully closed. The ring closing during the imide formation could be confirmed using LC-MS. If the LC-MS shows that the imide ring is fully closed, then two of the crosslink options can be discarded.

Once the first path is disproven, the second path can be analysed. The second path involves the double bond which is formed via the dehydration of the tertiary alcohol. The first option for the crosslinking with the double bond is, that the double bond is initiated by a free radical that is formed during the reaction. The second option is that the double bond is protonated via a small amount of PTSA, which is not fully removed during the washing. The first option can be tested by adding a small amount of a free radical scavenger to the polymerization mixture, which will prevent the initiation of the growing polymer chains. The second option is harder to test, as all traces of the PTSA need to be removed from cyclic imide di-ester, as the PTSA catalyst could protonate the double bond. There are different ways of purifying the cyclic imide di-ester. The first option is to find a crystallization solution in which only the cyclic imide di-ester crystalizes. However, during the practical work different solvents were tested, but none of them were suitable for the crystallization of the cyclic imide diester. Therefore, more extensive methods need to be used for the purification, such as preparative HPLC. If all traces of the PTSA are removed from the product, then the double bond should not be protonated during the polymerization.

The third recommendation is to further research the coating formation, as currently bubble formation started to occur during the curing. It is expected that the bubble formation is caused by the reaction between water and the isocyanate groups of the crosslinker. To test this hypothesis, the crosslinking needs to be done in a more controlled way, in order to keep any traces of water away from the curing of the polyester-imide urethane coating. To completely make sure that the bubble formation is not coming from the evaporation of the acetone, the acetone needs to be evaporated at room temperature. Once almost all the acetone is evaporated the temperature can slowly be increased.

The fourth recommendation is to use a higher amount of Desmodur ultra N3600 for the crosslinking. The reason for this recommendation, is that currently, the amount of crosslinker is determined by the amount primary hydroxyl concentration and not by the total hydroxyl concentration of the polyester-imide, including the tertiary OH groups originating from the citric acid. Since, the results from the crosslinking test possibly indicates that the crosslinker indeed also reacts with the much less reactive tertiary alcohol, basing the amount of crosslinker on the total hydroxyl concentration of the polyester-imide should result in a better crosslinked polyester-imide urethane coatings. This should increase the chemical and scratch resistance of the polyester-imide urethane coating.

The fifth recommendation is to further investigate the crosslinking procedure, as the polyester-imide urethane coating showed poor chemical and scratch resistance. This is most likely caused by a low amount of crosslinking bonds. The coatings also need to be further analysed, as currently only the chemical and scratch resistance was tested. One of the analyses that could be done is to assess the weight loss of the coating when trying to dissolve the crosslinked coating in different solvents (geltest), which could give a better indication of coating characteristics compared to the currently used solubility test. Other test that could be done to further analyse the coating properties is to measure the tensile strength, wetting properties and viscoelasticity of the polyester-imide urethane coatings.

The sixth recommendation is to investigate if the discolouring can be prevented during imide formation, esterification and the polymerization reactions. In order to prevent the discolouring, a strong antioxidant could be added before the reactions and more precautions to exclude oxygen should be taken.

The last recommendation is to measure the biodegradability, as the biodegradability could not be measured during this master thesis. It would however be interesting to investigate what the biodegradability of the polyester-imide based on citric acid and glycine based cyclic imide di-ester and 1,3-propanediol and of the polyester-imide urethane coating are. It would be interesting to see how the biodegradability changes when different amino acids are used as a starting material of the polyester-imides, like l-lysine or l-phenylalanine. It would also be interesting to use different biobased diols, like 1,5-pentanediol, to see how this will change the biodegradability of the polyester-imides and their crosslinked networks.

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Appendix A. Full H-NMR spectra





Figure 27. The full spectrum for the comparison of the citric acid and glycine based cyclic imide diacid's when using xylene (red) or toluene (blue) as an azeotropic solvent



Figure 28. The full H-NMR spectrum of the citric acid and I-phenylalanine based cyclic imide di-acids. Using deuterium oxide (D2O) as a solvent



Figure 29. The full H-NMR spectrum of the citric acid and glycine based cyclic imide di-ester. For the measurement the product was dissolved in d-DMSO



Figure 30. The full spectrum for the comparison between the MSA (blue) and the PTSA (red) catalyst for the esterification of the citric and glycine based cyclic imide di-acid with ethanol



Figure 31. The full H-NMR spectrum of the transesterification polymerization of the 1,3-propanediol and the citric acid and glycine based cyclic imide di-ester



Figure 32. The full H-NMR spectrum of polyester-imide 5 at polymerization of the 1,3-propnediol and Citric acid and glycine based cyclic imide di-ester



Figure 33. The full H-NMR spectrum for the Comparison of the starting material and the further reacted with 1,3-propanediol polyester-amide. The red spectrum is the starting material, the green spectrum is after three hours and the blue is after six hours

Appendix B. Supplementary data



Figure S1: ¹H-NMR spectrum in THF-d8 of the crude reaction product of L-phenylalanine and citric acid and structures of compounds in agreement with the spectrum. The multiplet between 7.1 and 7.5 ppm represents the aromatic hydrogens of the phenylalanine and some xylene. Xylene absorptions are also observed around 2.1-2.2 ppm. The multiplets from 5.66 to 6.56 ppm represent methine double bonds from structures II, III, IV and V. Multiplets at 5.48 and 5.09 ppm represent double bond methylenes of non ring-closed amic-acid structures of II and III. The multiplet at 4.89 ppm represents the methine of the imide (Structures I-V). The multiplet at 4.73 ppm represents the methylene of the benzyl group. The multiplets between 2.2-3.1 ppm represent the methylenes of the ring-closed succimimides and of the glycine residue. The absorption at 1.29 ppm represents the methyl group of structure IV, in line with the occurrence of decarboxylation. The double doublet around 2.8 ppm points to some residual citric acid. Using the five phenyl protons of the phenylene group as reference (corrected for the traces of xylene) gives: ca. 90 mol% imides (Structures I-V), ca. 8 mol% amic-acids. 5 mol% of the imides are present as Structures II, III, IV and V (85 mol% non-dehydrated product). Of the 5 mol% unsaturated imide compounds 0.66 mol% is structure IV.

Appendix C. Calculations

$$[primary OH] = \frac{Peak intensity \cdot Mol_{internal standard}}{Mass_{sample}}$$
$$[primary OH] = \frac{0.71 \cdot (1.1 * 10^{-5})}{0.031}$$
$$[primary OH] = 2.5 \cdot 10^{-4} mol/g = 0.25 mmol/g$$

 $[primary OH]_{max} = \frac{1}{M_n} \cdot (end \ groups \ per \ chain)$ $[primary OH]_{max} = \frac{1}{3290 \ g/mol} \cdot 2$ $[primary OH]_{max} = 6 \cdot 10^{-4} \ mol/g = 0.6 \ mmol/g$

% primary OH =
$$\frac{[primary OH]}{[primary OH]_{max}} \cdot 100\%$$

% primary OH =
$$\frac{0.25}{0.6} \cdot 100\% = 41.7\%$$