Functional PET based oligomers and polymers for cross-linked systems: Synthesis and Characterization

Ph. D. Thesis

by

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Chapter 1

Introduction

The ever-increasing amount of plastic use and the general carelessness of humans ensued the heavy accumulation of waste plastics around the globe (Figure 1.1). Starting from that late 1980s and early 1990s sustainability, being environmentally conscious has become increasingly important to our society. Therefore, researching and improving recycling methods became inevitable and a growing trend. The European Union became a leading party in this field with its legislation concerning waste management. Even companies like Coca-Cola, BASF and MOL in cooperation with APK AG have started their own projects concerning plastic recycling. Their excellent and diverse properties allowed plastics to became part of our everyday lives and became a compulsory, almost irreplaceable part of every industrial field. But these properties also caused problems at the end of their life cycle. A significant portion of plastics is intended to be used only once or for a short time (packaging materials, cutlery, medical equipment, etc.). Without a deliberate solution to repurpose, reuse or recycle these materials a vast amount of plastic waste accumulates with every year. Some of the single-use plastics such as straws, cotton swabs made from plastic, plastic plates and cutlery, plastic coffee stirrers and plastic balloon holders will be banned by the European Union’s Single-use Plastics Directive*. Other products such as plastic bottles will have to be collected separately by 2025. One of the greatest disadvantages of plastic recycling derives from it being a mixed waste material. If the purpose of recycling is to regain the pure plastics – and maintain sustainability – from the waste material than several separation and purification steps must be implemented into the recycling lines. As a result, recycled plastics usually have a higher price than virgin materials. Due to the possibility of degradation their properties might not even reach the requirements for certain fields of application1,2

![Figure 1.1 The global plastic waste generation by industrial fields and type in 2015. Total waste production was 302 million tons. Data was published by Geyer et al.2](image-url)

Poly(ethylene terephthalate) (PET) has become one of the most recycled polymers among the commodity and engineering polymeric materials.\textsuperscript{3–10} Several patents and research papers have focused on its recycling methods. Most of these solely discussed or focused on the regaining of pure PET from the waste material. One of the hardest challenges in recycling is to gain material with at least equal properties to the virgin polymer and maintain sustainability. As a result, a large number of researchers and research groups investigated the possibilities of chemical recycling and doing so produced new polymeric materials, chemicals, and virgin PET as well. The goal of our research group was to develop environmentally more friendly chemical recycling methods and find uses for the raw reaction products in cross-linked systems.

In the following sections, we discuss plastic recycling methods (1.1) in detail, especially chemical recycling, solvolysis (1.2). In subsection 1.3 we describe design and characteristics of cross-linked systems and the use of terephthalic acid derivates.

### 1.1. Plastic recycling methods

Plastic recycling is one of several waste management strategies to deal with the emerging problem of plastic waste\textsuperscript{11}. Landfilling is one of the conventional approaches that does not deal with sustainability. Well-maintained it could minimalize the environmental issues, but it is still a one-way linear approach that just deferments the problem. Reusing and/or repurposing the materials can lengthen the lifetime of certain products. In some cases, exchanging to alternative environmentally more friendly materials and/or downgauging the volume of used materials could prove to be a solution as well. Incineration and pyrolysis can be used to gain energy or chemicals from waste plastics.

Plastic recycling methods can be classified by several means. The ISO 14044 standard for environmental management distinguishes them into two groups: open looped or closed looped methods. By their definition, a recycling method is open-looped when the end-product is used in a different system, for example, the waste PET bottle scrap is used to produce fibres for the textile industry. Nevertheless, the quality of such materials are not considered in this standard as it was pointed out by Huysman et al\textsuperscript{1}. Huysman and his colleagues suggested the use of “circular economy performance indicator” (CPI) to characterize the quality of the recycled product. Doing so they classified the waste materials into four groups: high-, medium-, low- and very-low-quality. High-quality materials can substitute virgin materials in a 1:1 ratio and can be used in the same or similar products. Medium quality materials can only substitute the virgin material in a certain ratio, these can be used in similar or lower quality products. Low-quality materials can only substitute other lower quality materials and cannot be used in the same products as the virgin material. By their classification, very-low-quality materials should only be used for incineration. This classification generally summarizes the problems and opportunities in plastic recycling. This sorting mostly considers mechanical recycling and incineration, not other techniques such as chemical recycling that could be used to produce new materials with equal or better properties than the original virgin material. The separation, sorting of waste plastics plays a significant role in the quality of the waste material. Most of the recycling methods – except energy recovery – require a certain level of purity from the process materials. The mixed plastic waste is usually separated, shredded and cleaned to remove any contamination (glue, paper, metals). The plastic waste is thoroughly washed in aqueous and/or organic solvent medium.\textsuperscript{1,12}
Certain pollutants, impurities could cause degradation and/or side reactions that could significantly reduce the quality of the recycled product. Hence separation techniques are essential in plastic waste recycling, unfortunately, they are also one of the most expensive processes. The total separation of waste plastics is a yet to be solved problem. The sorting technologies can be classified into five types: spectroscopic-, density based-, tribo-electrostatic-, flotation- and other separation methods. Spectroscopic methods are mostly based in FTIR spectroscopy and are capable to sort most of the plastic waste materials. The dark colored object cannot be identified with FITR spectroscopy since they absorb infrared light. Due to the relatively small density interval of polymeric materials gravitational separator systems are not effective enough to separate all plastic types. For example, PVC and PET are almost inseparable by such methods (1.30-1.35 g cm\(^{-3}\) density range). Tribo-electrostatic and froth flotation systems nowadays are capable of separating PVC/PET mixtures with over 99% precision. In recent years new labelling methods such as fluorescent labelling with up-converters were tested. Upconverter nanoparticles are capable of emitting different colors of light depending on their composition. If standardized they could be used as labels and enhance the separation of plastic waste materials.

Figure 1.2 The recycling technologies of solid plastic waste based on the classification of Singh et al.

Plastic recycling methods can be sorted into four categories: primary, secondary, tertiary and quaternary (Figure 1.2). Primary recycling covers the in-plant recirculation (closed-loop) of industrial plastic scrap. Usually, this industrial scrap is mixed with the virgin material to assure product quality or used for a secondary purpose. Secondary recycling includes the mechanical recycling of industrial and domestic, consumer plastic waste. The purified plastic waste is either separated to different plastic types and processed or either processed without any segregation, into pellets. Unseparated plastic pellets can only be used for lesser quality products. The properties of such blends greatly depend on the type and ratio of the different plastics, the morphology/structure of the blend and the interaction forces between the components. The miscibility of the plastic components is governed by the interaction forces between the components and it could
be tailored by using compatibilizers. The tertiary, chemical recycling is used to turn the plastic waste into raw materials that can be used for new plastic and chemical production. Quaternary recycling is the incineration of plastic waste to gain energy. These techniques will be discussed in the following paragraphs.

1.1.1. Mechanical recycling

Thermoplastic polymers such as PET are processed at high temperatures. PET is a crystalline polyester with a melt temperature of 260 °C and it is usually processed at 265-280 °C. Polyesters, polyamides and other polymers produced with polycondensation require 3-4 hour drying session at 110-140 °C before processing, otherwise, the residual water content (over 0.01-0.02 m/m%) causes scission in the polymer backbone. After the separation and shredding the plastic scrap is usually processed with an extrusion machine into pellets to avoid aching in later processes. Depending on the implemented use of the recycled material, stabilizing agents and other additives (pigments) are added during processing. The new pellets can be processed with any thermoplastic processing method (extrusion, injection molding, blow molding). The intrinsic viscosity (determined by its molecular weight) of PET scrap determines its later use. The plastic scrap is used to produce packaging materials such as bottles, containers and fibres. Fibres are used in the textile industry and often they are mixed with other natural and synthetic fibres.

![Figure 1.3 Contaminants and their effects on chain scission during mechanical recycling](image)

The repeated recycling of thermoplastics results in the loss of mechanical properties due to the degradation processes occurring during processing and use. Thermal-, thermo-oxidative- and hydrolytic degradation processes are most likely to degrade PET and other polycondensates. Certain type of contaminants can enhance, catalyze the scission of the polymeric backbone (Figure 1.3), thus lowering the molecular weight of the plastic. Any residual impurities, Bronsted acids, and bases can catalyze the hydrolysis of PET to creating carboxylic acid and 2-hydroxyethyl terminated lower molar weighed
PET derivates. Ethylene vinyl acetate and adhesives derive from the soda, beverage bottle labels. The thorough cleaning and washing of the waste plastic remove most of these components from the bottles. The separation of PET and poly(vinyl chloride) (PVC) from mixed plastic waste is rather difficult and almost impossible to achieve complete separation.\textsuperscript{16,19,29–31} The degradation of PVC and the dehydrochlorination is unavoidable at higher temperatures.\textsuperscript{32–34} Therefore, the forming of hydrochloric acid can easily break ester bonds at the processing temperatures and degrade PET. The thermal ageing leads generally to two main kinds of structural changes: changes in lateral groups (hydroxyl and carboxylic group formation), and modification of molecular structure (chain scission, branching, extension and cross-linking). These changes even at low conversion rates significantly decrease the viscosity in molten state fractural behaviour.\textsuperscript{10} Although the changes in lateral groups mostly affect the optical and electrical properties that derive from the formation of chromophore groups. The chain scission reactions cause the production of aldehydes, formates, carboxylic acids and vinyl-esters. If these derivates form near the chain ends they might form low molar weight volatile compounds such as carbon dioxide and -monoxide, methane, ethylene, benzaldehyde, formaldehyde, and acetaldehyde.

To counter the effects of degradation solid state polycondensation and chain extenders are used the increase melt strength during processing and facilitate further processing. Solid state polycondensation is carried out at 210-240 °C in vacuum to forward the reaction of terminal functional groups and remove volatile side products. Chain extenders such as glycidyl-ethers are used to increase the molar weight of the plastic melt by extension and/or branching of the polymeric backbones.\textsuperscript{5,35,36}

Nevertheless, mechanical recycling is one of the economically most favorable ways to recycle thermoplastic polymer waste. It is relatively simple, and it uses already well-established technologies. Beside incineration and energy recovery mechanical recycling is the most prevailing technique to recycle. Chemical recycling in comparison is still in its infancy in practical use.

1.1.2. Incineration for energy production

Incineration is one of the easiest ways to deal with waste materials. There is almost no need to separate the waste materials or even treat them to remove contaminants. Since the separation of plastics is the most expensive part of all the recycling technologies incineration will be the most cost efficient as long as a separation maintains its high price.\textsuperscript{37} In some cases, mechanical recycling is not an option, some materials cannot be efficiently separated, too heavily degraded or hazardous to recycle.\textsuperscript{12,38–40} Hospitals and other medical faculties produce million tons of medical waste a year, just the USA produces 3.5 million tons a year.\textsuperscript{41} Most of the medical waste comes from single-use mixed plastic equipment. Incineration is the most common way to deal with such hazardous materials, in every other case, they must be decontaminated the minimize the potential health hazard.\textsuperscript{41} Incineration is one of the most effective ways to harness any benefit from waste materials. It significantly reduces the volume of solid wastes and it is quite profitable since plastic waste has a high calorific value.\textsuperscript{42–44}
Incineration is the combustion of organic waste materials in a controlled environment in the presence of oxygen (usually air). By the Waste Incineration Directive of the European Union† incineration plants are required to minimize their effects on the environment and human health from possible pollutants to air, soil, surface and ground waters. Incomplete combustion of organic materials at relatively low temperature can result in the production of several toxic, carcinogenic materials such as dioxins, furans, polycyclic aromatic hydrocarbons, NO\textsubscript{x} and SO\textsubscript{x} gases and metals.\textsuperscript{45-52} PVC and other chlorine-containing polymers must be incinerated at 800 °C or higher temperature to avoid the production of dioxins.\textsuperscript{47} However, such high temperatures can only be achieved at large-scale plants.

1.1.3. Chemical recycling

The chemical recycling of plastics aims at producing, regaining raw materials, fuels, and chemicals from plastic waste. The following technologies were developed in this regard: pyrolysis, fluid catalytic cracking, hydrocracking and hydro-pyrolysis, KDV process, gasification, and solvolysis. All these processes, except solvolysis, are based on the controlled thermal degradation of organic waste materials due to high temperatures in an inert, oxygen-free atmosphere. The solvolysis of PET will be discussed in detail in sub-chapter 1.2.

The thermal degradation of polymers is a combination of several processes with a different mechanism. These mechanisms are the random scission of the polymeric backbone, depolymerization and elimination of low molar weight fragments.\textsuperscript{53,54} The dominating degradation process is determined by the molecular structure of the polymer. Random scission of the backbone is characteristic of polyolefins. The degradation process is statistically governed, and the polymer chain breaks up to shorter chains. The molar weight of the polymer drastically drops. The depolymerization starts at the end of the polymer chains and monomers eliminate step by step. The molar weight of the polymers slowly decreases. This mechanism is characteristic of polyacetals and poly(methyl-methacrylate). The elimination of lower molar weight components due to thermal degradation is mostly associated with poly(vinyl chloride). This mechanism dominates the degradation process if the substituent of the polymeric backbone has relatively low dissociation energy. The length of the polymeric backbone barely changes during this degradation process, but the molecular weight decreases due to the elimination of low molar weighed volatile compounds. The thermal degradation of polymeric materials takes place at the 300-500 °C temperature interval and is heavily influenced by the polymer type.\textsuperscript{53,54}

The pyrolysis is a versatile technology that can be fine-tuned with the reaction parameters and reactor types. The pyrolysis products can be classified into three distinct groups: char, oils and gas. The operation temperature determines the constitution of the end products. If the production of char and gas components is preferred, then the reaction should be carried out higher than 500 °C. The 300-500 °C interval is recommended for oil compounds.\textsuperscript{55} The kinetics of the reaction can be tuned by the catalyst and the used

technology to gain the desired end products. Batch-, semi-batch-, continuous- (fluidized bed, fixed-bed or conical spouted bed) reactors can be utilized as well. The properties of the plastic pyrolysis oil are comparable with gasoline and diesel. Their properties depend on the source of waste plastic. Polyolefin-based pyrolysis oils have as high calorific as gasoline and diesel (40-43 MJ/kg). PVC and PET derived pyrolysis oils have a lower calorific value (20-30 MJ/kg). The viscosity of these oils approximates the standard values of diesel. The char can be used as absorbents, feedstock for activated carbon production and solid fuel. The composition of the gas compound depends on the pyrolyzed waste material. Polyolefins barely produce volatile gas compounds (5-10%) during pyrolysis, on the other hand, PET and PVC produce large amounts of gases (hydrogen, alkanes, alkenes, CO, CO$_2$ and hydrochloric acid).

Fluid catalytical cracking (FCC) technologies enhance the pyrolysis of waste materials with narrowing the spectra of end-products and allowing the use of more moderate reaction conditions. The product spectra can be directed to more valuable fine or commodity chemicals and fuels. FCC technologies can be distinguished as a liquid and vapor phase. FCC utilizes porous solid zeolite-based catalyst such as silica-alumina (ZSM-5) and Y-type zeolites.

Hydrocracking differs from standard cracking just in the presence of hydrogen. Relatively high pressure of 70 atm is used for these reactions at 300-500 °C. Hydrocracking yields a higher-quality fuel, the formation of toxic side products in minimalized or eliminated. Integrated hydro-pyrolysis and hydroconversion (IH$_2$) is a catalytic conversion process that is cable of turning a wide range of organic materials (organic green waste, municipal waste, plastic waste) to fuel components. It was developed by the Gas Technology Institute of Des Plaines (Illinois, USA). The process consists of three steps hydropyrolysis, hydroconversion, and reforming. Hydropyrolysis is carried out with a fluidized bed reactor with catalyst particles at 400-500 °C at 15-35 atm. The hydroconversion step operates at similar reaction parameters. It further reduces the oxygen content of the product flow. Following the hydroconversion step the product is condensed and the gas stream (alkanes, alkenes, CO and CO$_2$) is fed into a steam reformer. IH$_2$ is a self-maintaining due to the fact that the last reforming stage of the process produces the required amount of hydrogen for the first two steps. It has been shown to be economically favourable due to its integrated nature, simplicity and efficiency. It integrates already existing well-known technologies. This technology mostly operates with biowaste feedstock, the use of plastic waste as a feedstock is under investigation.

KDV process (Katalytische Drucklose Verölung) or the catalytic pressure-less depolymerization process was developed by Alphakat GmbH (Germany). This technology is capable of removing all the oxygen content of the produced oils. Thus, the end-products are completely compatible with the standard combustion engines regardless of the plastic feedstock. Another advantage of the KDV process is its mild reaction conditions compared to pyrolysis.

Gasification converts almost any organic feedstock (natural gas, coal, oil, green waste, plastic waste, etc.) to a mixture of hydrogen, CO, CO$_2$, methane and other hydrocarbons. This mixture is also known as Syngas, its quality is determined by the ratio of its main components (H$_2$:CO). Syngas reaction used widely used for methanol production that is a cornerstone of organic chemical production. The type of gasification...
depends on the oxidizing medium: partial oxidation with air, partial oxidation with oxygen enriched air, partial oxidation with pure oxygen, by steam, and by plasma. The gasification of organic materials consists of the following steps. Heating and drying that takes place up to 160 °C. Devolatization that takes place up to 700 °C. During this step thermal cracking, pyrolysis of organic materials occurs and light volatile gases, tar and char are produce. Hydrogen gas is produced from the cracking of the various organic degradation products. The partial oxidation of the mixture allows the occurrence of exothermic reaction that generates enough heat for the thermal cracking to occur. 12,62,66

1.2. The solvolysis of PET

The solvolysis of PET is a versatile chemical method specially designed to break up the ester bonds in the polymeric backbone and gain terephthalic acid derivates and ethylene-glycol (Figure 1.4). In most of the cases, the main goal of solvolysis is to utilize its products in the polycondensation of PET. Therefore, sustainability is maintained, and new virgin polymers are produced that have identical or better properties than the original PET. Terephthalic acid, dimethyl-terephthalate (DMT), and BHET can be used as raw materials for the polycondensation of PET. Terephthalic acid and dimethyl-terephthalate are used to produce BHET via direct esterification of condensation. Then BHET is used for the polycondensation step at 280°C bellow 1 mmHg pressure. 67 Thus the end-products of hydrolysis, methanolysis and glycolysis can be directly fed to PET production.

![Figure 1.4 The end-products of PET solvolysis](image)

Several studied have focused on the optimization of the solvolysis processes to increase the purity and yield of the reaction products. In other cases, the solvolysis products were repurposed to produce other valuable polymeric materials or fine chemicals. One of the main goals in the development of solvolysis techniques is to achieve and maximize high yields (90%<) at mild reaction conditions. Regarding the further use of the solvolysis products solvolysis possesses the same kind of problems as mechanical recycling. A certain level of purity is required of the feedstock components, thus separation, purification steps must be introduced into the production line. High volumes of chemicals
are needed to reach high levels of yield and conversion. As a result, the solvolysis of PET is an expensive technology. In this section, we discuss the methods, reaction mechanism, kinetics, and catalyst of PET solvolysis.

1.2.1. Solvolysis methods

The scission of ester bonds can be carried out with water, alcohols or amines and can be classified into the following methods: hydrolysis (a), methanolysis (b), glycolysis (c), aminolysis (d) and ammonolysis (e) (Figure 1.4).

*Hydrolysis* is one of the most common methods to scission ester bonds. Esters, polyesters are hydrolyzed in water, aqueous or organic solutions to separate the organic acid and alcohols from the ester bonds. Hydrolysis is carried out at high temperatures (190°C<) at atmospheric or higher pressures at acidic, basic or neutral pH. It is capable of regaining high yields of terephthalic acid and ethylene-glycol from PET waste. Although hydrolysis is a relatively simple technology, high amounts of chemicals are needed for the purification and separation of the reaction products. Terephthalic acid must be recrystallized in several steps and ethylene-glycol must be separated via extraction, distillation or salting out from the aqueous reaction medium. 68–70 Acids and bases catalyze the hydrolysis reaction and change the reaction mechanism. Consequently, it is a severely expensive method that considerably relies on finding the optimal reaction parameters and catalyst to be economically profitable. The applied concentration of acids and bases varies with the technology and desired reaction time. With the increasing concentration of acids or bases, the depolymerization can be carried out at a lower temperature, at relatively milder concentration. 68,71–77 Aturi et al. demonstrated the potential of solvolysis via hydrolytic depolymerization of cross-linked unsaturated polyester resins with acetone/water mixture. They recovered various organic compounds including the building blocks of the unsaturated ester such as maleic anhydride, phthalic acid and propylene-glycol. 78

Aqueous or organic alkaline hydroxide solutions (KOH, NaOH) are usually used in a wide concentration range (~4-25%) for alkaline hydrolysis. The dissolved terephthalic acid salts can be precipitated from the solution by acidifying the reaction mixture after filtration. The alkaline hydrolysis is usually carried out over 100°C in atmospheric or pressurized conditions. 71–74 Phase transfer catalyst was shown to effectively enhance PET hydrolysis and promote the use of milder reaction conditions (70-90 °C). 79,80 The cationic phase transfer catalyst, mostly quaternary ammonium salts (e.g.: trioctyl methyl ammonium bromide) selectively adsorb to the surface of the plastic scrap and attract the hydroxyl ions. Thus, the anionic hydroxyl groups migrate to the plastic surface and hydrolyze the ester bonds. 81 Although the phase transfer catalyst allows the use of milder conditions, they considerably lengthen the reaction time up to 4-6 hours to reach high yields of terephthalic acid (~90%). 82

Acidic hydrolysis is usually carried out with concentrated sulfuric acid, although other inorganic acids such as nitric acid and phosphoric acid have also been utilized as well. 68,75–77 The oxidative effect of nitric acid produces oxalic acid out of ethylene-glycol. 77 The use of concentrated acids significantly shortens the reaction time (less, then an hour) and lowers the reaction temperature (room temperature) and allows the reaction to be carried out at atmospheric pressure, on the other hand, the reaction mixture becomes
highly corrosive. Lower acid concentrations elongate the reaction even up to 6 hours and higher reaction temperature must be used ($150 \, ^\circ\mathrm{C}$) to reach total depolymerization. At the end of the hydrolysis, the oily viscous reaction mixture is filtered to remove the terephthalic acid and other solid components. The filtrated is mixed with water, the pH level is set to 6-13 to dissolve the terephthalic acid. Any impurities that remain in solid state or precipitate are filtered, if necessary, the solution is treated with activated carbon to gain a clear solution. At the last, terephthalic acid salt solution is acidified to pH 1-2 to precipitate the organic acid. The terephthalic acid washed and dried. Ethylene-glycol can be removed from the filtrates via extraction with trichloroethylene or salting out with sodium sulfate.

Neutral hydrolysis process is carried out with water or steam at 2-300 $^\circ\mathrm{C}$ at 1-4 MPa pressure, despite its name around 3.5-4 pH levels. The acid pH is sad to be the results of the water-soluble monoesters of terephthalic acid and ethylene-glycol. The high reaction temperature in the melting range of PET results in relatively quick reactions ($\sim 1$ hour). Terephthalic acid precipitates from the reaction mixture and it can be easily filtered at the end of the reaction. Compared to alkaline and acidic hydrolysis neutral hydrolysis yields terephthalic acid with lower purity. Solid contaminants and residual PET particles must be removed from the product so it can be utilized as higher quality material.

*Methanolysis* yields dimethyl-terephthalate (DMT) and ethylene-glycol (EG) as end-products. It is usually carried out at a high temperature at the 100-300 $^\circ\mathrm{C}$ interval at high pressures, even at super critical conditions. Transesterification catalyst such as metal salts are usually applied to enhance the reaction at mild conditions. The reaction mixture must be cooled down at the end of the reaction otherwise the transesterification of the dimethyl-terephthalate starts to occur. Dimethyl-terephthalate precipitates from the cooled down reaction mixture and it can be easily filtered. Methanolysis can be carried out in a batch and continuous reaction setups as well. Side-products such as co-esters with ethylene-glycol, dimers and oligomers could also be found in the reaction product depending on the depolymerization parameters. Yang et al. have shown that the yield significantly increases with increasing the weight ratio of the methanol and PET. Above 1:6 weight ratio the increase moderates. Increase in reaction temperature and pressure considerably enhances the reaction rate and shortens the reaction time. Yang et al. have shown that at 250°C 11 MPa PET methanolysis takes circa 40 minutes to reach near 100%. Meanwhile, Mishra et al. performed methanolysis at much milder conditions below the critical point of methanol at 120 $^\circ\mathrm{C}$ 7-9 atm (0.7-0.9 MPa) and reach the same yield after 120-150 minutes.

*Glycolysis* is usually carried out with diols such as ethylene-glycol, diethylene-glycol, propylene-glycol. Any kind of diol could be utilized in this reaction, nevertheless, ethylene-glycol (EG) is the most important since it yields bis(2-hydroxy-ethyl)-terephthalate (BHET). Glycolysis can be carried out at high temperatures (160-300 $^\circ\mathrm{C}$), ambient or higher pressures, even in or near supercritical conditions. At the end of the reaction the BHET it extracted with boiling hot water and recrystallized. Higher molar weighed side products remain in the organic phase. The organic phase (EG) is usually purified via extraction or distillation. The mayor difference between methanolysis and glycolysis comes from the bishydroxyl functionality of the reagents. Any component
with hydroxyl groups could participate in the transesterification reaction, even oligomers or the final monomer, product. As a result, 100% yield of BHET selectivity is rarely achieved, an equilibrial mixture of BHET, dimers and even longer oligomers make up the depolymerization products. Consequently, developing new, advanced catalyst became the most frequently researched aspects of PET glycolysis to increase the monomer yield.\(^90\)–\(^96\) The advancements in catalyst development will be thoroughly discussed in subsection 1.2.2. Without a catalyst, glycolysis is slow and has a poor yield. Güçlü et al. investigated the possibility of solvent assisted glycolysis with xylene.\(^97\) The purpose of xylene was to selectively dissolve the glycolysis products from the ethylene glycol phase to shift the reaction towards depolymerization. The extensive use of xylene resulted in an even more expensive technology with severe health hazard, hence, became a dead end in PET glycolysis.

PET glycolysis derivates are versatile materials that could be used as building blocks in various products beside PET. The use of these materials was thoroughly investigated in numerous projects in cross-linked systems such as unsaturated resins, polyols for polyurethanes, alkyd resins, epoxy resins.\(^98\)–\(^100\),\(^108\)–\(^110\),\(^100\)–\(^107\) Cross-linked systems will be further discussed in subchapter 1.3.

Initially aminolysis was only used to treat the surface of PET fibres to enhance the compatibility with the matrix component. It was carried out with dilute aqueous amine solutions at mild conditions.\(^111\),\(^112\) Compared to the previously discussed hydrolysis and transesterification based techniques aminolysis is thermodynamically more favorable due to the more nucleophile nature amines.\(^113\) These reactions can be carried out at ambient conditions. Tawfik et al. ingeniously demonstrated this via using open-air sand-baths at the hot summer months in Egypt.\(^114\) At these conditions the depolymerization takes several weeks and catalyst are crucial to reach high yields. At higher temperature, the reaction time significantly shortens, although catalyst is still necessary for high yields.\(^115\) PET aminolysis requires catalyst similar/identical to glycolysis and follows the same trends concerning the effects of synthesis parameters on the rate of the reaction.

Any amine functional organic molecule could be used for aminolysis as long as it is in a liquid phase at the reaction conditions. Although bi or polyfunctional amines are preferred over mono functional amines since they could be further modified via the residual functional groups. Given the versatility of amine reagents aminolysis products can be finely tailored for numerous applications. Terephthalamides are highly sought materials that could be used to produce high temperature resistant polyamides, polyimines, polyyureas, polyurethanes and epoxy hardeners.\(^115\) Natarajan et al used N,N’-bis(2-hydroxyethyl)-terephthalamide to produce biodegradable polyesters-amides that could be used in bone regeneration and controlled drug release.\(^116\) Beside polymeric materials several unique uses were developed. Parab et al. and More et al. synthesized biesters of N,N’-bis(2-hydroxyethyl)-terephthalamide and tested them as plasticizers in PVC. The synthesized plasticizers were comparable with commercial compounds such as dioctyl phthalate.\(^117\),\(^118\) Palenkar et al. used PET derived terephthalic-dihydrazide to produce heterocyclic bis-1,3,4-oxadiazole, bis-1,2,4-triazole and 4-thiazolidinone derivates that showed moderate antibacterial activity.\(^119\) In a separate study Palenkar et al. synthesized several azo-dyes from terephthalic-dihydrazide that showed moderate light and excellent wash fastness on polyester and nylon fabrics.\(^120\)
Ammonolysis can be carried out with the aqueous solution or anhydrous ammonia at mild conditions, even at room temperature. The use of aqueous ammonia results in the production of terephthalamide and ethylene-glycol. Depending on the mildness of the conditions it could take 40-50 days to approximate full conversion. The terephthalamide is insoluble in the reaction mixture, therefore it can be easily filtered and recrystallized to reach the desired purity levels. Pyrolytic dehydration can be used to produce terephthalonitrile that can be converted to p-xylylenediamine or 1,4-bis(aminooethyl)cyclohexane.

1.2.2. Mechanism and reaction kinetics

![Figure 1.5](image)

Figure 1.5 The general mechanism of organocatalyzed PET solvolysis based on the mechanism published by Horn et al. Poly(ethylene terephthalate) (PET) is the polyester of terephthalic acid and ethylene-glycol, by doing so it shows the characteristic reactions of esters. The scission of ester bonds can be carried out with the hydrolysis (uncatalyzed, base or acid catalyzed); transesterification with alcohols; and amidation with ammonia or amines. The mechanism of these reactions is similar: addition-elimination nucleophilic substitution (Figure 1.5). The electrophile hydrogen of the catalyst molecule (marked as H) connects to the oxygen atom of the carboxyl group allows the nucleophilic attack of the reagent molecule on the carbon atom of the carboxyl group. The hydrogen atom of the reagent molecule (~XH) connects to the nucleophilic atom of the catalyst molecule. As the bond between the nucleophilic X atom and the carboxyl carbon forms the hydrogen atom originally belonging to the catalyst connects to the oxygen atom of the ester. The bond between the carbonyl carbon and ester oxygen atom scissions. As a result, a 2-hydroxyethyl group terminated PET derivate and a new PET derived acid/ester/amide, molecules are produced. The catalytic acceleration of the solvolysis reaction is crucial: the depolymerization can be carried out at lower temperatures and shorter reaction time. The mechanism published by Horn et al demonstrates both catalytic ways simultaneously to activate the components of the solvolysis. Electrophile catalyst might coordinate with the carbonyl oxygen, nucleophile catalyst coordinate with the hydrogens of the EG to enhance the nucleophile attack.
Due to the poor solubility of PET in water, alcohols and amines, the solvolysis of PET is a heterogeneous reaction. The reaction speed considerably depends on the reaction parameters (temperature, pressure, particle reactant ratio, catalyst), especially the reaction temperature (Figure 1.6).\textsuperscript{92,126,127} Up to the melting point of PET, the reaction is heterogeneous, but as the crystalline phase melts (above 240-250 °C) the polymer dissolves in the reaction medium and the solvolysis reaction becomes homogenous. Even below the melting point of PET after a certain degree of conversion, the plastic dissolves in the reaction medium.\textsuperscript{128} Most of the solvolysis reactions are carried out in the 180-210 °C temperature interval at atmospheric pressure, bellow 170°C the conversion and reactions rates are mostly too low for practical use. The boiling point of most solvolysis reagents is below 220°C, therefore melt phase reactions are carried out at high pressures. As a result, the kinetic modelling of the solvolysis reactions and its dependence on reaction parameters is still in debate. Pressurized reactors are mostly used in hydrolysis, methanolysis and ammonolysis.\textsuperscript{68–71,129,130} Although, supercritical glycolysis has been investigated as well.\textsuperscript{90} In most cases the increase in pressure enhances the reaction via increasing the boiling point of the reagents. The heterogeneous reaction kinetics of PET solvolysis has been analyzed by several authors. Changes in morphology and fragmentation were reported; and an initial delay in the depolymerization reaction (Figure 1.6).\textsuperscript{125,131–134} The conversion and yield levels of solvolysis products considerably decline in function of the scrap size (Table 1.1).\textsuperscript{70,135} Collins et al. divided the depolymerization process into four stages: \textsuperscript{136}

- The attack on the unordered amorphous phase with no mass loss, no oligomer formation, just molecular weight reduction
- The continuous attack on the amorphous initiates mass loss
- Attack on the ordered non-crystalline amorphous phase
- Attack on the crystalline phase
Table 1.1 The effect of PET scrap particle size on the PET conversion and yield of methanolysis reaction products. The methanolysis was carried out at 120°C at 5-7 atm pressure. The samples were collected after 120 min.\textsuperscript{70}

<table>
<thead>
<tr>
<th>Particle size (µm)</th>
<th>PET conversion (%)</th>
<th>DMT yield (%)</th>
<th>EG yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>97.8</td>
<td>97.64</td>
<td>97.62</td>
</tr>
<tr>
<td>64</td>
<td>97.8</td>
<td>97.64</td>
<td>97.62</td>
</tr>
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<td>97.8</td>
<td>97.64</td>
<td>97.62</td>
</tr>
<tr>
<td>127.5</td>
<td>97.8</td>
<td>97.64</td>
<td>97.62</td>
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<td>81.54</td>
<td>81.51</td>
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<td>256</td>
<td>62.4</td>
<td>62.36</td>
<td>62.33</td>
</tr>
<tr>
<td>362.5</td>
<td>37.1</td>
<td>36.86</td>
<td>36.82</td>
</tr>
</tbody>
</table>

Figure 1.7 The schematic steps of PET glycolysis with diethylene-glycol (DEG)\textsuperscript{131}

The nature of this phenomenon was thoroughly investigated by Pardal and his colleagues. They found that the ratio of the solid phase decreases via random scission until an equilibrail molecular weight is reached. The molecular weight distribution shifts without change to lower molar weights. The ratio of the amorphous phase gradually approximates zero.\textsuperscript{131} They interpreted their findings as to the following: the reactant diffuses into the solid PET and depolymerizes it. The lower molar weight soluble components dissolve into the reaction medium. Thus, bigger scrap particles elongate the solvolysis. This process continues until highly crystalline microphases are obtained that will degrade in the final step (Figure 1.7). The initial stage of the reaction greatly depends on the reaction conditions. Sangalang and his coworkers reported that their studies did not fit the exponential decrease of molecular weight via random scission \((M_n(t) = M_\infty \exp(-k_r t))\). An initial period was found in both catalyzed and uncatalyzed reactions where the molecular weight stagnated.\textsuperscript{125} In their argument they stated that the statistical scission of the ester groups is based on the assumption that all ester groups are equally accessible and reactive.
Introduction

Due to the fact that ester groups in the highly organized crystalline phase are not as accessible as the ones in the amorphous phase, the amorphous phase is more likely to degrade in the same conditions. Therefore the ratio of the crystalline phase in the residual PET should increase at the initial stages of the reaction which they have proven with FTIR spectrometry. This recrystallization was observed in amorphous and crystalline PET samples as well and it coincided with the time scale of the depolymerization. The catalyzed depolymerization reactions closely resembled other solid-state kinetic models matching the mechanism of a second-rate mechanism. The non-catalyzed glycolysis kinetics data closely resampled nucleation and growth theory-based models such as the Avrami equation. The nucleation-controlled reaction mechanism was confirmed by SEM (Figure 1.8 (a) and (b)). The surface of PET become rough at the initial stages of the depolymerization. Thin, rod-like segments on the surface grew and become more prominent. The thickness of these rods was found to be really close to the lamella size of PET (8 nm). The calculated activation energy by Sangalang et al. (29 kJ mol⁻¹) is significantly lower than other reported in the literature (80-110 kJ mol⁻¹). Their calculated value is closer to the theoretical values of transesterification and degradation (12-19 kJ mol⁻¹).

\[ K = \frac{[BHET]}{[PET][EG]} \]  

The solvolysis of polyesters is an equilibrium-based reaction that considerably depends on the reaction conditions and the concentrations of the reactants (equation 1). To be able to reach full depolymerization and gain products such as DMT, BHET, or N,N'-bis(2-hydroxyethyl)-terephthalamide with high yields high ratio reagents must be used. Otherwise residual ester linkages between the terephthalic acid and ethylene-glycol will remain in the reaction product. In the case of bifunctional reagents, any terminal functional group might take part in the depolymerization. The high reagent concentration decreases the possibility of such reactions occurring. In the case of transesterification with diols – due to the equilibrial nature of transesterification – dimers tend to
form decreasing the yield of the desired monomer. Thus, coesters, dimers and oligomers will be present beside the desired end-products (Figure 1.9). Utilizing certain catalyst can push the reaction towards depolymerization and minimize the ratio of side-products. They are essential in reaction parameter optimization. Nevertheless, separation steps must be included to gain pure products regardless of the yield. In the case of aminolysis, the equilibrium is considerably shifts towards the amidation process due to the nucleophile nature of amines. Nevertheless, a high ratio of the amine reagent is required for these reactions, otherwise, residual ester linkages may remain in the product (Figure 1.10).

Figure 1.9 Gel permeation chromatography (GPC) chromatogram of PET glycolysis with different molar ratios of diethylene-glycol:PET

Figure 1.10 FTIR spectra of N,N’-bis(2-hydroxyethyl)-terephthalamide prepared with different ratios of PET and ethanol-amine showing the presence of residual ester groups
1.2.3. Catalyst

The catalytic enhancement of solvolysis reaction has been a center of focus for the last 20 years. Due to the cost-heavy circumstances of chemical recycling, it is essential to optimize this process and fasten the otherwise slow and time-consuming reaction. Any transesterification enhancing catalyst can be used for the depolymerization of PET as well. These can be sorted into several categories such as metal salts, acids, bases, organocatalyst, heterogeneous catalyst and other catalyst. Several authors focused on the development, characterization of heterogeneous catalyst. They can be easily separated from the reaction mixture and utilized repeatably which considerably impacts the economic evaluation of chemical recycling. One of the greatest challenges in PET solvolysis results from the use of ethylene-glycol and other diols for PET solvolysis. Due to the equilibrial transesterification reaction BHET can participate in the transesterification. As a result, an equilibrium between monomer and dimer is reached at the end of the reaction, the yield of BHET curve has a maximum in the function of reaction time.\(^2,4\) In most of the cases, the goal of the depolymerization is to maximize the yield of the monomer. Therefore, most catalysts were developed to enhance the reaction speed of depolymerization and minimize the time for the 100% conversion of PET. Hence the shortened reaction time decreases the possibility of transesterification via the hydroxyl terminated monomers, thus preventing the monomers to turn into dimers.\(^2\)

Most of the catalyst described in the following sections were tested in the glycolysis with EG, thus their effectiveness will be compared via their yield to BHET production (\(Yield = (\text{moles of BHET})/(\text{moles of depolymerised PET units})\)) (Table 1.2). Nevertheless, the differences in the reaction parameters must be taken into account as well. These parameters are the average size and distribution of the PET scrap; the ratio of EG; the concentration of the catalyst; reaction temperature, time and pressure; and the design of the reactor.

The average size and distribution of the PET scrap are not necessarily addressed in PET solvolysis studies, although it has a considerable effect on the reaction kinetics. Most of the catalyst studies utilized ground PET powder with an average size in the micron range that is considerably smaller than the commercial scrap of soft drink bottles. Usually, in catalyst studies, the ratio of EG is significantly higher (over 1:10) than a study focusing on new product development and characterization (~ 1:4 – 1:7). These extremely high ratios push the reaction towards depolymerization, although they might be too high for practical use. Usually, the catalyst is tested in small reactions – total weight of reaction mixture is less than 30 g – therefore the effectiveness of the catalysts is still unknown even in larger laboratory scales. The catalyst is the most expensive components in these reactions. It is essential to recycle them and minimize their concentration. So homogenous catalyst such as the metal salts or organocatalyst might be too expensive without binding them to a support material. Otherwise they are too expensive to regain from the reaction medium. The higher reaction temperature and the use of pressure can significantly shorten the reaction time. Nevertheless, milder reaction condition is usually preferred so they could be widely established even in industrial scales and allow the use of already existing equipment. In conclusion, direct comparison between studies is not trivial. All parameters must be considered to come to the right conclusions.
Table 1.2 Comparison of transesterification catalyst in PET glycolysis. The PET:EG ratio is calculated to the molar ratio of PET repeating units and the mols of EG. The reactions were carried out at atmospheric pressure, unless indicated otherwise. The particle size of the PET varies in publications.

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>PET:EG (1:x)</th>
<th>Temperature (°C)</th>
<th>Time (h:min)</th>
<th>Catalyst (m/m %)</th>
<th>BHET yield (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>No catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>16</td>
<td>190</td>
<td>40:00</td>
<td>-</td>
<td>96</td>
<td>139</td>
</tr>
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<td>30.9</td>
<td>190</td>
<td>2:00</td>
<td>-</td>
<td>~5</td>
<td>92</td>
</tr>
<tr>
<td>-</td>
<td>41.29</td>
<td>195</td>
<td>3:00</td>
<td>-</td>
<td>4.3</td>
<td>140</td>
</tr>
</tbody>
</table>

**Metal Salts**

- Zn(OAc)$_2$ 6 190 8:00 0.5 67.63 141
- Pb(OAc)$_2$ 6 190 8:00 0.5 65.91 141
- NaHCO$_3$ 6 190 8:00 0.5 66.22 141
- Na$_2$CO$_3$ 6 190 8:00 0.5 65.43 141
- Ti(PO$_4$)$_3$ 8.6 195 3:15 0.05 95.3 142

**Organocatalyst**

1,5,7-triazabicyclododecene 16 190 0:08 10 n/n% 94.9
1,8-diazabicyclo[5.4.0]undec-7-ene 16 190 0:07:30 10 n/n% 98.9
1,5-diazabicyclo[4.3.0]non-5-ene 16 190 0:07 10 n/n% 98.5
4-(N,N-dimethylamino)pyridine 16 190 1:40 10 n/n% 93.6
1,4-diazabicyclo[2.2.2]octane 16 190 2:00 10 n/n% 93.1
N-methylimidazole 16 190 5:00 10 n/n% 92.6
N,N-dimethylamine 16 46:00 10 n/n% 92.4

**Ionic liquids**

- [bmm][Cl] 10 190 8:00 13.8 83 143
- [bmm][Cl] 10 190 2:00 5 6 126
- [bmm][OH] 10 190 2:00 5 70
- [bmm][ZnCl$_2$] 10 170 4:00 3.9 89.5
- [bmm][FeCl$_3$] 10 170 4:00 3.9 76.4 144
- [bmm][CoCl$_3$] 10 170 4:00 3.9 89.7

**Inorganic particles**

- ZnMn$_2$O$_4$ tetragonal spinel 11.5 260 (0.5 MPa) 2:00 1 92.3 145
- CoMn$_2$O$_4$ tetragonal spinel 11.5 260 (0.5 MPa) 2:00 1 89 145
- Supermagnetic $\gamma$ Fe$_2$O$_3$ 10.3 300 (1.1 MPa) 1:00 1 ~90 94
- Fe$_3$O$_4$ 31 190 2:00 5 ~60 92
- Protonated titanate nanotube 4 196 3:00 1 88 146
- (Mg-Zn)-Al hydrotalcites 10 196 2:00 1 ~75 147
- SO$_4^{2-}$/Co-Zn-O (SCZ-300) 15.5 180 3:00 0.05 75 148

**Composite carbon nanoparticles**

- grapeneoxide-Mn$_3$O$_4$ A 115 300 (1.1 MPa) 1:20 0.7 95 149
- Multivalved carbon nanotube (MWCNT) 31 190 2:00 5 ~80 92
- MWNT-Fe$_3$O$_4$ 31 190 2:00 5 100
- $\gamma$-Fe$_2$O$_3$/N-doped graphene 41.29 195 3:00 0.6 100 140

**Special catalyst**

- MOF ZIF8 4 196 1:30 0.16 76.75 91
- Polyoxometalate 4 180 0:30 0.13 84.1 150
- $\alpha$-K$_3$SiW$_{11}$ZnO$_{39}$ 86 60 14 days 0.05 g g PET 60-70 151
**Metal salts** are the most conventional transesterification catalyst widely utilized in PET solvolysis. Transition metals were considered most active among metal catalysts. These metals yield circa 60-75% BHET at the 180-190 °C range. Their effectiveness may be limited at a higher temperatures. Campanelli et al. found that Zn(OAc)$_2$ cannot enhance the reaction rate at temperatures higher than 245°C. Hence their widely established use, they also serve as a reference point in new catalyst developments. Alkali metal salts were tested as a catalyst since their extended use does not result in various medical issues. Certain alkali salts were proven to be comparable with the heavy transition metals. Troev et al. reached a seemingly significant breakthrough with use of Ti$_3$(PO$_4$)$_4$ and reach exceptional yields over 90% under 4 hours reaction time. Troev tested the glycolysis of fibre and bottle grade PET scrap with EG, diethylene-glycol, propylene-glycol. Troev's experiments showed a significant difference in the glycolysis of the fibre and bottle grade PET. The low molar weighed fibre grade PET yielded 96.4 even without a catalyst while the bottle grade PET could only yield near 60-65% with catalyst.

Polyoxometalates are polyatomic ions composed of metal-oxygen clusters, with broad applications. They have high thermal and chemical stability, high acidity, low toxicity, and they can take part in redox reactions. Geng et al. investigated transition metal substituted polyoxometalates (K$_6$SiW$_{11}$MO$_{39}$; M: Zn, Mn, Co, Cu, Ni). The polyoxometalates significantly shortened the depolymerization time up to 30 minutes with yields over 80%. In addition they were able to recover the catalyst via vacuum distillation and use it over 8 cycles without loss of catalytic activity.

Metal organic frameworks (MOF) consist of metal ions or clusters coordinated to organic ligands. They are porous solid materials similar to zeolites with a finely-tunable structure and active sites. Suo et al. investigated three types of self-assembly MOFS (ZIF-8, ZIF-67, and MOF-5). They have found that the ratio of the organic ligands and the metal ions influence the specific surface area and acidity of the ZIF-8 type MOF, thus affecting the catalytic activity of the catalyst. The higher the specific area of the MOF, the higher the concentration of the acidic active sites, thus the more active the catalyst becomes. The reaction time was significantly shortened to 90 minutes to reach a plateau of 70-80% yield.

Organocatalyst has become the focus of attention in organic chemistry in the last 15 years. One of their greatest advantages is the exchange of traditional metal catalyst, thus contributing to green chemistry. Organocatalyst can be finely engineered for any organic synthesis. They can even reach selectivity levels only obtainable by enzymes. Aminolysis and glycolysis of PET was tested with various strong base organocatalyst and demonstrated excellent selectivity and yield. Most of the catalyst in optimized concentrations yielded in the 80-90% interval. The reaction time was significantly shortened due to their activity. Most metal-based catalyst required at least two or three hours to reach high conversion and yields. Only polyoxometalates compare to their magnitude of reaction rate. Since they are homogenous catalyst their recycling is cost heavy, although affixing them on support could increase their already excellent potential in the future.

Up to our knowledge enzymes were tested on few occasions in PET glycolysis. Since enzymes cannot endure high temperatures, the reaction was carried out at mild conditions with high PET:EG ratio. Despite that 60-70% BHET yield was obtained. All things considered such a high yield at 60°C is a remarkable achievement in glycolysis.
Ionic liquids are organic molten salts that have a melting point lower than 100°C. They are excellent solvents with considerable electrochemical and thermal stability, low flammability and non-volatility. They have been considered for various uses including catalyst. Ionic liquids dissolve in the liquid phase of glycolysis. They can be purified via vacuum distillation of the residual EG. They can be recycled and used several times without any activity loss. Compared to other catalyst high concentrations are necessary for high yields, that might be too expensive at higher scales. Wang and his research group were the first to publish the use of ionic liquids in PET glycolysis in 2009. Since then several papers have been published concerning the development of these type of catalyst. 1-butyl-3-methylimidazolium chloride cation [bmim]+ derived ionic liquids were thoroughly examined in these studies, and the effects of different anions were investigated. [bmim]Cl and [bmim]Br neutral ionic liquids (not acidic nor basic) demonstrated catalytic ability in glycolysis, although their effectiveness was limited. Concerning their selectivity and yield of BHET they overtook the conventional metal salt, nevertheless, long reaction times were necessary. Basic ionic liquids such as [bmim]OAc and [bmim]OH exceeded the activity of [bmim]Cl and significantly reduced the reaction time. Although only [bmim]OH was able to maintain high selectivity and yield. Metal salt modified ionic liquids proved to have even higher activity as a catalyst, especially with transition metals (Zn, Co, Mn). [bmim]2(ZnCl4) and [bmim]2(CoCl4) yielded near 90% in similar conditions, but at a lower temperature. Although [bmim]2(FeCl4) could only reach 70-80% yield, they also had magnetic properties that could significantly further the separation of the ionic liquid. Inorganic silicates, oxides, and other metal derivate particles are well-known catalyst widely used in industrial, research and development settings as well. Since these inorganic particles do not dissolve in the reaction medium of glycolysis they can be easily recovered from the organic phase via filtration, sedimentation or other methods. Sodium and protonated titanate nanotubes are a cost-efficient and relatively easy
to make. Compared to other metal oxides it demonstrated excellent efficiency even at 196°C and low PET:EG ratio. Compared to other catalyst titanate nanotubes are one of the most efficient.

Solid base and acid characteristic materials have been recently investigated and applied for transesterification and hydrolysis reactions. Both solid acids and bases demonstrated higher catalytic activity than conventional metal salts. Solid acid catalyst, sulfated oxides such as $\text{SO}_4^{2-}/\text{ZnO}$, $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$, $\text{SO}_4^{2-}/\text{Co}_3\text{O}_4$ and $\text{SO}_4^{2-}/\text{Co–Zn–O}$ yielded in the 70-80% range. Eshaq et al. investigated layered double hydroxides (hydrotalcites or anionic clays). Compared to metal salts they have a higher catalytic activity that resulted in shorter reaction times, although the reaction yield barely rose higher than 75%.

Figure 1.11 The proposed mechanism of synergic catalysis with $\text{Fe}_3\text{O}_4$ doped MWCNT composite particles in PET glycolysis by Al-Sabagh.

Carbon-based nanoparticles are exceptionally robust materials that have been thoroughly investigated in various fields, including catalysis. Carbon nanoparticles such as nanotubes, graphene, graphene-oxide could be modified, finely tuned for specific uses. Via the precipitation of metal oxides on the carbon nanoparticles exceptionally active catalyst were obtained with over 90% BHET yields. Park et al. utilized $\text{Mn}_3\text{O}_4$ doped graphene oxide nanocomposites in PET glycolysis and obtain a 96.4% yield at 300°C, 1.1 MPa. In comparison, $\text{Mn}_3\text{O}_4$ particles yielded 82.7 at the same conditions. Nabid et al. used $\gamma$-$\text{Fe}_2\text{O}_3$/N-doped graphene as a catalyst at milder reaction conditions (195°C) and obtained 100% yield. Nabid and his coworkers showed that the $\gamma$-$\text{Fe}_2\text{O}_3$ particles and N-doped graphene on their own could only reach 30-40% yields. Al-Sabagh et al. carried out similar experiments with multiwalled carbon nanotubes (MWCNT) and $\text{Fe}_3\text{O}_4$ particles. In their case the $\text{Fe}_3\text{O}_4$ and the MWCNT reached near 60% and 80% yields. According to the Al-Sabagh, the effectivity of these nanocomposites is the result of a synergic effect (Figure 1.11). The EG glycol molecules interact with the carbon nanotubes, this way the hydrogen bonding between the EG molecules is enhanced and the oxygen in the hydroxyl groups become more electron negative. While the metal particles
interact with the oxygen of the carbonyl-group the more electronegative oxygen attacks the nucleophilic carbonyl carbon atom. Thus both the nucleophile and the electrophile components are in an activated state via the interaction with the two catalytic components. It must be noted that exceptionally high ratios of PET:EG were used. These types of catalyst must be tested with lower ratios to correctly estimate and compare their catalytic activity. Nevertheless, these catalysts exceed most of the previously developed catalyst. In addition, their magnetic properties allow an easy, reliable recovery and reuse.

1.3. Application in cross-linked systems

Cross-linked systems have been in the focus of development ever since their discovery in the 19th century. Their production essentially differs from linear polymers. The molding of these materials takes place during the polymerization, cross-linking. Fundamentally there are two ways to produce cross-linked structures: the cross-linking of long polymeric chains; or to use small functional molecules to form high molecular weighed branched, eventually cross-linked networks. Unsaturated resins or vulcanized rubbers are an example of the former, while polyurethanes, phenolic-, amino-, furan- or epoxy resins are examples of the latter.

This subchapter focuses on the design and characteristics of cross-linked systems and how do their properties depend on their production parameters. Furthermore, we discuss the potential role of PET solvolysis derivates in these systems.

1.5.1. The connection between structure and properties

The nature, characteristics of the components just as with linear polymers determine the properties of the cross-linked systems (Figure 1.12). The structure of the polymeric backbone, the size of substituents and inter- and intramolecular forces between the polymeric chains influence the relaxation capabilities of the polymeric chains, thus the glass transition temperature. Although it must be noted that these parameters are rarely independent of one another. Glass transition temperature \((T_g)\) is attributed the temperature where the segments of the polymer chains – the smallest part that can move independently – starts to move. Flexible backbone structure results in lower \(T_g\) while the stiffer the chains becomes the higher the \(T_g\) raises as well. Smaller substituents allow an easier relaxation of the polymeric chains, and as the size of the substituents is increased the movement of chains is becomes impeded. The strength of the secondary forces between the chains increases the barrier energy of conformation change, thus the stronger these forces are the higher the \(T_g\) shifts. The molar weight (M) of also influences the \(T_g\), although it must be noted that the molar weight of commercial polymers is high enough that it has almost no effect at all on \(T_g\). In case of oligomers, and low molar weight polymers \(T_g\) increases with M and it reaches a plateau after a critical value. These criteria and observations were proven to be true in all polymeric systems, although in the case of cross-linked materials another parameter must be taken into account: cross-link density. Cross-links between the polymeric chains can restrain the relaxation of the chains, thus the higher the number of the cross-links the higher the \(T_g\) shifts. Cross-link density can be fine-tuned via changing the length of polymeric chains between cross-link points, or changing the functionality or concentration of the cross-link forming agent.
Due to the functionality of the PET solvolysis derivates, they are mostly utilized as building blocks for oligomeric/polymeric components in various cross-linked systems. Via polycondensation with diacids they could be used to produce polyols (ester, ester-amide) for polyurethanes or to produce unsaturated polyester resins comparable with commercial products. Duque-Ingunza et al. demonstrated the effects of condensation conditions on the molecular weight distribution and how it affects the produced unsaturated resin. They have shown, that utilizing milder conditions for the polycondensation reaction results in lower molar weigh polyesters and significantly lower $T_g$ in the final resin product from $120^\circ C$ to $65^\circ C$. With changing the ratio of aromatic and aliphatic components in the polyester chains the mechanical properties could be finely tuned. Although a considerable number of studies were carried out examining the use of PET derivates only a few of them address the sustainability of these syntheses. The high ratio of reagents and the necessary purification steps exacerbate the cost these new materials.

PET derivates have rarely been utilized other than a building polymeric chains, such as forming epoxy functional resin precursors. Terephthalamides have been claimed to be usable as cross-linkers before. Yet their use and characteristics have rarely been described in practical systems. Dutt et al. experimented with PET derived N,N-bis(2-aminoethyl)terephthalamide, but it was only usable in high cure-temperature epoxy systems.

1.5.2. The effect on reaction kinetics and conversion

Since the cross-linking and the molding take place at the same time the conversion $(\alpha)$ of the cross-linking reaction considerably influences the properties of the final product. The obtainable properties, the reaction kinetics of the cross-linking reaction substantially depend on the curing parameters (Figure 1.13 b). The TTT diagram of a
cross-linking system indicates the phase of matter depending on the cross-linking time and temperature. Just as the TTT diagram indicates (Figure 1.13 a) cross-linking systems go through phase changes as reaction approximates the equilibrial rate of conversion at a certain temperature. Since the applied reaction times are always shorter than the needed for equilibrium, learning the change of reaction rate over the reaction time, the kinetics of the reaction is essential.

Figure 1.13 The Time-Temperature-Transformation (TTT) diagram of a cross-linked system (a). And the dependence of glass transition temperature on the curing time and temperature of an epoxy system (b). The later diagram was digitally reproduced based on the data published by Deng et al. Adapted with permission from Macromolecules 27, 18, 5147-5153 (1994). Copyright (1994) American Chemical Society.\textsuperscript{172}

Figure 1.14 Relaxation spectrum (a) and peak relaxation time of a curing epoxy systems.\textsuperscript{173} The parameter on (a) is the conversion. The diagrams were digitally reproduced based on the data published by O’Brien et al. Adapted with permission from Journal of Composite Materials 35, 10, 833-904 (2001). Copyright (2001) SAGE journals.
The dependence of the reaction rate can be separated into two distinct regimes in all cross-linked systems. At the beginning of the reaction, the reaction rate is only restricted by the concentration and reactivity of the active sites (chemically controlled regime). As the reaction progresses further the appearance of macromolecules in the reactive systems the diffusion coefficient gradually increases and diffusion becomes the decisive factor (diffusion controlled regime). The exact dependence of the diffusion coefficient on the reaction rate is still in debate. Several models have been developed to take into account the restrictive nature of the diffusion controlled regime in autocatalytic reactions. Most of them were modifications of the classic Horie and Kamal-Sourour models for autocatalytic reactions. Since resinous systems go through vitrification as they cure the glass transition theories (WLF equation, free volume model, configurational entropy theory) served as inspiration for model development. The Rabinowitch model \( k_{r}^{-1} = k_{i}^{-1} + k_{d}^{-1} \) allowed the separation of reaction rate constants to an intrinsic rate constant (determined by the chemistry of the system) and a diffusion rate constant \( (D) \). Thus the influence of the diffusion coefficient and the proportions of the rate constants could be expressed in kinetics modelling. \( k_{d}(\alpha) \sim D(\alpha) \sim \tau^{-1}(\alpha) \) assumption was used for further developments where \( \tau \) is the structural relaxation time, since \( D(\alpha) \) function is unknown. The relaxation time was proven to increase with conversion (Figure 1.14). As a result the reaction rate starts to decrease after a certain degree of conversion (Figure 1.15), the cross-linking reaction becomes diffusion controlled. Thus, post-curing above the \( T_g \) is needed to further the reaction to full cure.

![Figure 1.15 The conversion rate-change of an epoxy system during curing](image)

Ratio of components not just effects the properties of resinous materials, but also the reaction kinetics, especially in the case of resin produced via stepwise polymerization techniques. Any shift from the equimolar ratio can drastically decrease cross-link density and worsen the properties of the endproduct.
1.4. Scope

In previous sections, we have addressed the main characteristics and issues of plastic waste recycling. Mechanical recycling is the most commonly used and cheapest way to recycle plastic materials. It utilizes already existing and well-known techniques that make it a favorable choice in the plastic industry. Nevertheless, the separation of the raw plastic streams and deteriorating effects of contaminants cause a never-ending war with degradation. These issues could be managed, but after a certain number of cycles, the waste materials cannot substitute the high-quality, virgin materials. Energy recovery through incineration can deal with any type or quality of plastic waste. Up to this date is it still an economically favorable way to deal with waste materials. It can completely exclude the expensive purification and separation of the waste stream. In certain cases, it is the only way to deal with waste streams such as contaminated medical wastes. Unfortunately, smaller incineration plants cannot reach high enough temperatures to exclude the possibility of producing toxic, carcinogenic volatile compounds. In addition, incineration does not contribute to a circular, greener economy.

Chemical recycling, on the other hand, could maintain a circular economy via regaining the building blocks of the waste materials. These building blocks could be utilized to reproduce high-quality plastics, resins or other fine chemicals. Solvolysis of waste plastics especially PET has become one of the main focuses of green chemistry. Over 30 years of research and development lead to the discovery of exceptional solvolysis catalyst and engineering new, highly valued specialized products. The high volumes of chemicals needed for the depolymerization, then the separation and purification of the end-products considerably increase the cost of recycling. In the case of reproducing PET, these purification steps are necessary, but they might not need be in the case of other products such as cross-linked systems. In our investigations represented in this thesis, we investigated the use of raw solvolysis products. Our goal was to engineer reactive systems where there is no need, or it might be even advantageous to exclude the purification of the solvolysis products. We utilized the theoretical minimum of reagents to reach 100% depolymerization of the original PET to reduce, minimize the volume of needed chemicals.

In standard glycolysis, the reaction mixture reaches an equilibrial constitution of bishydroxy esters of terephthalic acid, its dimers, oligomers and residual diol which includes the eliminated EG. In most of the cases, dimers and oligomers are discarded. Since glycolysis with a low ratio of diol yields in a wide range of molecular weigh the end-product is inhomogeneous. To deal with this issue we decided to introduce diacids into the depolymerization reaction to incorporate low molar weight volatile components and produce oligoesters. In Chapter 2 we experimented with this technique, acido-alcoholysis and compared it conventional glycolysis and acidolysis (transesterification with acids). The results confirmed our assumptions but have given no explanation about the fine molecular structure of the depolymerization products. In the next Chapter 3 of our investigation concerning acido-alcoholysis we carried out two series reactions in a similar fashion to thoroughly characterize the reaction products and to find a connection between structure and properties. A straightforward connection was found between the applied ratio of diacid and the properties of the depolymerization product that allowed us to fine tune the end-products. One-pot type depolymerization and polycondensation reactions were engineered based on our findings.
In the following sections we attempted find a potential use for raw aminolysis products. Raw aminolysis products of PET consist of terephthalamides, the eliminated EG from PET and residual amines that were used as a reagent. Amine functional compounds are well known for their use as epoxy cross-linkers, and as a matter of fact, hydroxyl functional compounds are capable of catalyzing the curing of epoxy resins with amines. Thus all the components in raw aminolysis products could fulfill a purpose in epoxy curing. The aminolysis reactions were carried out with a well-known amine cross-linker, isophorondiamine. In Chapter 4 our goal was to design a cross-linker system with the raw aminolysis product that could be processed at lower temperatures. The aminolysis product was dissolved in isophorondiamine and a solution series was designed to investigate the effects of the aminolysis product on the curing and the viscoelastic properties. Gelation and DSC studies indicated a significant accelerative effect on epoxy curing that we further investigated in Chapter 5. A thorough characterization was carried concerning the aminolysis products with NMR and MALDI-TOF. The effects of reagent ratio on the molecular weight of the oligoamides were investigated. The accelerative effects of the aminolysis products on epoxy curing was investigated with DSC reaction kinetics and computational chemistry studies.

Chapter 6 contains a standalone study independent of the previous chapters concerning the solvolysis of PET. We have synthesized aliphatic random polyester amides and characterized their molecular structure and thermal and crystalline properties. We have investigated the effects of small substituents on the fine structure of the produced polyester amides with NMR. And we have given a possible explanation of the formation of different crystalline phases in random polyester amides. This study served us as the cornerstone in learning the fine structure characterization of oligomers and polymers with NMR combined other techniques.

In Chapter 7 we summarized the main results concluded in the previously chapters without going into specific details. This chapter is restricted to present a summary of our work as thesis points.
1.6 References

Introduction

2008, 42, 249–255.


71. GB822834, 1959.


76. US4355175, 1981.


Introduction


Introduction

Chapter 1

Chapter 2

Oligoester and polyester production via acido-alcoholysis of PET waste

2.1. Introduction

The alcoholysis, glycolysis of PET by its nature as a transesterification reaction is equilibrium based. Through the modification of several parameters it could be pushed to gain terephthalic ester monomers that could be utilized in new polymer production. The equilibrium of the reaction could be push towards the monomer production with increasing the ratio of the used alcoholic reagent such as ethylene-glycol, propylene-glycol or methanol. The production of the so-called side products of this reaction dimers, or oligomers cannot be evaded, their ratio could only be minimalized. Depending on the goal of the chemical recycling such as new PET or other terephthalic acid derivate production the reaction can be modified. More efficient catalyst or the removal of the monomers during the reaction and higher reagent ratios could increase the yield of the reaction.

If the goal of the recycling is to gain new value-added materials, and not new PET, then it is not inevitably needed to use these expensive methods. In most cases the oligomeric side products are discarded during the purification processes or just refed to the solvolysis reaction system.

![Glycolysis of PET](image)

**Figure 2.1 Glycolysis of PET**

The transesterification of PET could also be done with carboxylic acids as well. It is a classical reaction well known in organic chemistry and it could be used to break the existing ester bonds and form new with the reagent carboxylic acid. Similarly to hydrolysis, terephthalic acid and esters of ethylene-glycol and the reagent acid are expected to form. It has two possible routes, alkyl-oxygen and acyl-oxygen scission. Via acyl-oxygen scission an anhydrite intermediate is produced that can react with an alcohol (Figure 2.2). Via the alkyl-oxygen scission the mid-product could react with any alcohol in the reactive system to form a new ester.

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If we introduce excess alcohol into an acidolysis system acidolysis, alcoholysis and esterification reactions could occur in the same reaction. Thus mixed esters, oligoesters of the used reagents, terephthalic acid and ethylene glycol should be produced. In this study we would like to propose a new technique that is a combination of standard glycolysis and acidolysis. The acid components could act as chain lengthening agents during the depolymerization reaction and react with the free diols in the system. Thus, hydroxyl and carboxyl group terminated mixed oligoesters form that could be utilized as mid-products in various systems. These oligoesters can be further used without any purification steps, hence shortening the recycling process.

In this study the amount of acid and alcohol are comparable to each other, both acidolysis, alcoholysis and esterification of acids can occur in the same system. Organic acids (adipic, succinic and sebacic acid) and 1,4 buntanediol as solvolitic agents were applied in PET acidolysis and acido-alcoholysis reactions. Diglycidyl ethers were used to obtain high molecular weight polyesters. Diglycidyl ethers can be used as chain extenders. These compounds can react with hydroxyl-, carboxyl- and amine groups as well, although their reactivity differs for each functional group. The presence of carboxyl group in our system was expected to result in higher molecular weight products and fast reactions.

2.2. Experimental

2.2.1. Materials

PET flakes from HUKE Kft. (Sárvár) were used for solvolytic reactions. The consumer (bottle) PET waste was washed and ground to small flakes (thickness 0,41±0,08 mm; (9,9±2,9 mm)x(6,8±2,2 mm)). Adipic acid, sebacic acid, succinic acid and butane-1,4-diol were purchased from Sigma Aldrich. 1,4-butanediol diglycidyl ether (RD3), cyclohexane-1,4-dimethanol diglycidyl ether (RD11) and hexane-1,6-diol diglycidyl ether (RD18) are products of Ipox Chemicals. Zinc-acetate (Zn(OAc)$_2$.2H$_2$O) was purchased from BDH Chemicals and was used as catalyst. Tetrahydrofuran (THF) and N,N-
dimethylformamide (DMF) were purchased from Molar Chemicals and were used as solvents. Dibuthyltin-dilaurate, perchloric-acid, methyl-cellosolve and di-n-buthylamine were purchased from Molar Chemicals and were used for hydroxyl group measurements. All the reagents were used without further purification.

### 2.2.2. PET solvolysis

All the solvolytic reactions were carried out in a 250 cm$^3$ four-necked round bottom glass flask equipped with mechanical stirrer, inert gas inlet, thermometer and reflux condenser. All the reactions were carried out at 210 °C in argon atmosphere at atmospheric pressure. All the components were weighed into the reactor at the beginning of the reactions. The ratio of the reagents was calculated to the repeating unit of PET (192,18 g$\cdot$mol$^{-1}$). Acidolysis reactions were conducted with 1:1 PET:acid molar ratio with adipic acid, succinic acid and sebacic acid. Alcoholysis reaction was carried out with 1:1 PET/alcohol molar ratio with 1,4 butanediol. Acidico-alcoholysis reactions were carried out with 1:0,5:0,5 PET:acid:alcohol molar ratio with each one of the acids and 1,4 butanediol. The complete disappearance of the PET flakes was considered as the end of the reactions. The reaction time varied with each reaction, in average it was 1,5-2,5 hours.

### 2.2.3. Chain extension

Chain extension of the acidico-alcoholysis products was carried out in a 250 cm$^3$ four-necked round bottom glass flask equipped with mechanical stirrer, gas inlet, thermometer and reflux condenser. The reactions were carried out at 180 °C in argon atmosphere. All the components were weighed into the reactor at the beginning of the reactions. The ratio of the reagents were stoichiometric, calculated to the total functional group content (total hydroxide + total carboxyl content). 1,4 butanediol diglycidyl ether (RD3) for all the solvolysis products. 1,4-hexanediol diglycidyl ether (RD18) and 1,4 cyclohexanedi methanol diglycidyl ether (RD11) were only used with sebacic acid/1,4-butanediol reaction product.

### 2.2.4. Characterization

Solubility was checked in tetrahydrofuran (THF) and in N,N-dimethylformamide (DMF) before GPC measurements and functional group analysis. For the acid value 0,5000 g samples were dissolved in 20 cm$^3$ THF or DMF. The samples were titrated with 0,5 M sodium hydroxide solution in methanol using phenolphthalein indicator. Hydroxyl value was determined via a titration method. 1,5000 g of sample were dissolved in THF or DMF. Than 10 cm$^3$ of phenyl-isocyanate solution and 0,2 cm$^3$ dibuthyltin-dialeurate catalyst solution was added to the solutions. After 15 minutes methyl-cellosolve and di-n-buthylamine was added. The samples were titrated with 0,5 M perchloric-acid solution in the presence of methyl red indicator.

The FTIR spectra were recorded using a Bruker Tensor 27 FTIR spectrometer. The wave number range was between 4000–400 cm$^{-1}$, the resolution 2 cm$^{-1}$, the number
of scans was 28 with ATR, 16 with KBr pastilles. Gel permeation chromatographic (GPC) measurements were done using a Jetstream 2 plus thermostat, Waters HPCL Pump 515 and Waters Styragel HR1, 2, 4 column with tetrahydrofuran. Polystyrene standards were used for the calibration. Perkin Elmer TGA 7 was used for thermogravimetric measurements. About 10 mg of samples were weighed in and measured in purging nitrogen gas with 10 °C min⁻¹ heating rate up to 700 °C.

Sheets of 100x100x0.6 mm were pressed in a laboratory press at 150 °C and 150 kN for composting tests. Pressed sheets were laid in compost for 6 weeks carried out by Zöldhíd Régió Kft (Hungary) via Gore™ Cover system. Green waste materials were chopped up and laid down into piles and covered with a semipermeable cover. The pressed sheets were put in nets inside the compost piles. The temperature was monitored and controlled by the automatic ventilation system and was kept at around 75 °C. Weight loss and fragmentation was observed after the composting period.

2.3. Results and discussion

2.3.1. Characterization of solvolysis products

The FTIR spectra of the solvolysis products with sebacic acid and/or 1,4-butandiol are represented in Figure 2.3. The measurements support that the reactions took place. Around 3600 cm⁻¹ wide low intensity peak appeared on the spectrum of PET waste indicating the negligible presence of hydroxyl groups. CH₂ valence vibration peaks at 2940 and 2850 cm⁻¹ have shown increase in intensity compared to PET. The ester carbonyl
valence vibrations at 1721-1700 cm\(^{-1}\) shifted from 1712 to 1720 cm\(^{-1}\) indicating the appearance of aliphatic ester groups. The spectrum of acidolysis products showed double peak or at least shouldered peak for carbonyl valence vibrations. This is an indication of the appearance of at least two kind of carbonyl compounds in the products. Changes between 1500 1300 cm\(^{-1}\) and 1100-900 cm\(^{-1}\) are observable in the IR spectrum indicating changes in molecular structure. The differences and changes in carbonyl and hydroxyl groups after the reactions was further studied with functional group analysis.

Acid values were measured with a standard titration procedure with NaOH solution in THF, the OH values were measured with phenyl-isocianate method (Table 2.1). The theoretical values were calculated according to the added quantity of acid and/or hydroxyl groups. Acid values in acidolysis are close to the calculated ones, while they decreased during acido-alcoholysis. The slight increase in acid value can be attributed to the formation of terephthalic acid. The decrease during acido-alcoholysis can be explained by the occurrence of esterification reaction between the diacids, diols, dimers and oligomers. The major decrease in case of PET:SucAc can be attributed to the longer reaction time. Compared to the other acidolysis reactions it took twice the time (~ 4 hours) for the PET to completely disappear, thus esterification reaction had more time to occur.

White, powdery residuum was observed after dissolving our acidolysis products in THF. The powder was filtered; washed and dried. FTIR spectra was recorded and compared to terephthalic acid (99 %, Molar Chemicals) in KBr pastilles. The spectra were found to be identical, thus proving the formation of terephthalic acid.

Table 2.1. Acid and hydroxyl values of PET solvolysis products

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid value (mmol*g(^{-1}))</td>
<td>OH value (mmol*g(^{-1}))</td>
</tr>
<tr>
<td>PET:AdAc</td>
<td>5.91</td>
<td>-</td>
</tr>
<tr>
<td>PET:SuccAc</td>
<td>6.46</td>
<td>-</td>
</tr>
<tr>
<td>PET:SebAc</td>
<td>5.07</td>
<td>-</td>
</tr>
<tr>
<td>PET:But</td>
<td>-</td>
<td>7.13</td>
</tr>
<tr>
<td>PET:AdAc:But</td>
<td>3.20</td>
<td>3.36</td>
</tr>
<tr>
<td>PET:SuccAc:But</td>
<td>3.36</td>
<td>2.93</td>
</tr>
<tr>
<td>PET:SebAc:But</td>
<td>2.93</td>
<td>2.43</td>
</tr>
</tbody>
</table>

GPC measurement results of PET acidolysis and alcoholysis products are represented in Figure 2.4 and Figure 2.5 and given in Table 2.2. THF was used as a solvent for the GPC measurements, thus PET waste couldn’t be compared directly to the reaction products, due to its insolvency. Thus, the solubility of the reaction products proves the success in depolymerisation. Calibration and the comparison to solvolytic reagents were used to determine the success of the solvolysis. The molecular mass distributions of the pure acidolysis and alcoholysis products showed similarities. The gel permeation chromatograms showed several peaks including the used solvolytic reagent (adipic-, succinic-, sebacic acid and 1,4-butanediol). In case of acidolysis with sebacic acid (Figure 2.4 a)) a new
peak appeared at higher retention volume, indicating a slightly lower molar weight side product than sebacic acid. According to the mechanism of acidolysis (Figure 2.2) the possible eliminates of the reaction are terephthalic acid and ethylene glycol. We put the chromatogram of ethylene glycol as a reference. Hence, we propose, the new peak is attributed to the newly formed terephthalic acid. This result is explained by the fact that the molecular weights of succinic and adipic acid are close enough to terephthalic acid to make their peaks indistinguishable on the chromatograms. The significantly higher molecular weight of sebacic acid allowed the separation of the two acids, thus two separate peaks appeared. Adipic acid was the only acid that remained in significant amount after the acidolysis. The proven elimination of terephthalic acid and high amount of adipic acid residuum could have caused acid value higher than theoretical.

Figure 2.4 b) shows a GPC chromatogram of classical glycolysis products with distinct peaks previously stated in the introduction. The peaks can be connected to oligo- and diesters of terephthalic acid with butane-diol and ethylene glycol. A minor butane-diol residuum can be observed as well. The oligomeric products of acido-alcoholysis (Figure 2.5) have shifted to lower retention volumes indicating an increase in molecular weight. Residual reagents of acido-alcoholysis or any lower molar weighed components cannot be identified in the GCP chromatograms. Most of these components were presumably incorporated into the oligomeric chains of the reaction product. Due to the equilibrial nature of the reaction small concentration of low molecular weighed components is expected to be present in the reaction products.

![Figure 2.4 GPC chromatogram of PET solvolysis product with sebacic-, succinic-, adipic acid (a) and 1,4-butandiol (b)](image-url)
Oligoester and polyester production via acido-alcoholysis of PET waste

Thermogravimetric analysis (TGA) further supports our statement of oligomer production (Figure 2.6). The derivative curves (DTG) were calculated in order to determine the changes in slope in weight loss and starting temperatures of each step. Any early weight loss (1-2%), below 100 °C can be connected to impurities within the PET waste. Solvolysis with 1,4-butanediol resulted in distinct dimers and oligomers causing a constant, multi-stepped weight loss via evaporation starting at 103 °C until it reached its thermal degradation temperature at 312 °C than 392 °C. The acidolysis product with sebacic acid shows a two-step degradation curve with a major change in the slope of the curve around 400 °C. In this case the first degradation step started at 265 °C, then the change of slope occurred at 409 °C. Acido-alcoholysis products showed only one major degradation step starting at 390 °C indicating a more uniform composition than the previously discussed reaction products.

Figure 2.5 PET solvolysis product GPC chromatogram with sebacic acid and 1,4 butanediol
Table 2.2 Molecular weight averages of the solvolysis products of PET waste

<table>
<thead>
<tr>
<th>Sample</th>
<th>(M_n) (g*mol(^{-1}))</th>
<th>(M_w) (g*mol(^{-1}))</th>
<th>(M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET:Adac</td>
<td>590</td>
<td>920</td>
<td>1.6</td>
</tr>
<tr>
<td>PET:Sucac</td>
<td>650</td>
<td>970</td>
<td>1.5</td>
</tr>
<tr>
<td>PET:Sebac</td>
<td>640</td>
<td>1000</td>
<td>1.6</td>
</tr>
<tr>
<td>PET:But</td>
<td>710</td>
<td>980</td>
<td>1.4</td>
</tr>
<tr>
<td>PET:Adac:But</td>
<td>2100</td>
<td>4200</td>
<td>2.0</td>
</tr>
<tr>
<td>PET:Sucac:But</td>
<td>1800</td>
<td>3400</td>
<td>1.9</td>
</tr>
<tr>
<td>PET:Sebac:But</td>
<td>2400</td>
<td>4700</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Figure 2.6 TGA measurements and DTG curves of solvolysis products

2.3.2. Chain extension of PET solvolysis products

Each of the chain extenders show multiple peaks on the GPC chromatograms. These extenders are commercial reactive diluents recommended for epoxy resins. The exact composition and components are unknown, except their main components given previously. They were weighed in and used according to the functionality given in the technical data sheets available from the manufacturer.
Oligoester and polyester production via acido-alcoholysis of PET waste

Figure 2.7 GPC chromatograms of the chain extended products

The GPC chromatograms of the chain-extended samples and the reagents are represented in Figure 2.7. The molecular mass value averages and polydispersity are given in Table 2.3. The GPC results unequivocally proved the molecular weight increase after chain extension. Our GPC column system’s effective molecular range according to the manufacturer is about 600000 but a calibration curve with polystyrene standards up to 2 520 000 could be done.

Table 2.3 Molecular weight averages of the chain extended products

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (g/mol$^{-1}$)</th>
<th>$M_w$ (g/mol$^{-1}$)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET:Adac:But+RD3</td>
<td>3800</td>
<td>318 000</td>
<td>83.7</td>
</tr>
<tr>
<td>PET:Sucac:But+RD3</td>
<td>3500</td>
<td>148 000</td>
<td>42.3</td>
</tr>
<tr>
<td>PE:Sebac:But+RD3</td>
<td>6200</td>
<td>380 000</td>
<td>61.3</td>
</tr>
<tr>
<td>PET: Sebac:But+RD11</td>
<td>5600</td>
<td>232 000</td>
<td>41.4</td>
</tr>
<tr>
<td>PET: s Sebac:But +RD18</td>
<td>5600</td>
<td>30 000</td>
<td>5.4</td>
</tr>
</tbody>
</table>

The chain lengthening was successful and polymers with broad molecular weight distribution were produced containing polymer chains higher than 100 000. We have to note that the samples only partially dissolved for the GPC measurements, thus the data only represent the dissolved components of the products. The extreme difference in number and weight average molecular weights can be connected to this problem. RD3 and RD11 caused extremely wide distribution in all cases. These reactive diluents might have components with higher epoxy functionality than 2 that could have caused branching during chain lengthening.
The FTIR spectrum of a chain-extended product are shown in Figure 2.8. The FTIR diagrams prove that the diglycidyl ethers reacted with the solvolysis products. The solvolysis products showed no traces of epoxy group. The characteristic valence vibrations of epoxy groups (912 and 840 cm\(^{-1}\)) were absent in the chain extended products. Due to the presence of carboxyl groups the reaction with the glycidyl ethers was rather intense. The carboxyl groups have catalytic effect in the reaction of epoxy with hydroxyl groups [51-53].

![FTIR spectrum of the chain extended product]

Figure 2.8 FTIR spectrum of the chain extended product

### 2.3.3. Composting

The used composting method provides an insight into the practical degradability of these materials. Naturally propagated microorganisms turned the green waste to compost and degraded the pressed sheets. The pressed sheets were kept in nets to prevent the fragments to fall in and mix with the compost. The produced materials had a reasonable rate of degradation and fragmentation after 6 weeks (Table 2.4). All the studied press compressed plates disintegrated into small pieces (Figure 2.9). The chain extended products showed somewhat lower degradation rate, due to their higher average molecular mass. These degradation rates may be increased with longer composting time.

![Composting residuum of PET:Sebacic acid:1,4-butanediol (paperclip for scale)]

Figure 2.9 Composting residuum of PET:Sebacic acid:1,4-butanediol (paperclip for scale)
Oligoester and polyester production via acido-alcoholysis of PET waste

Table 2.4 Weight loss of solvolysis- and chain-extended products after compostation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight loss in compost (m/m %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET:Adac:But</td>
<td>50.8</td>
</tr>
<tr>
<td>PET:Sucac:But</td>
<td>62.0</td>
</tr>
<tr>
<td>PET:Sebac:But</td>
<td>51.5</td>
</tr>
<tr>
<td>PET:Adac:But+RD3</td>
<td>35.6</td>
</tr>
<tr>
<td>PET:Sucac:But+RD3</td>
<td>36.9</td>
</tr>
<tr>
<td>PET:Sebac:But+RD3</td>
<td>24.7</td>
</tr>
</tbody>
</table>

2.4. Conclusions

A new method, acido-alcoholysis was successfully developed for the chemical recycling of PET. Acido-alcoholysis was investigated and proved to be efficient in incorporating the solvolytic agents and producing higher molecular weight oligoesters. The GPC data suggest that both acidolysis and alcoholysis products contain the used reactants, and consist of distinct oligoesters while in the products of acido-alcoholysis no trace of the reagents could be detected by GPC analysis. The functional group analysis, GPC chromatograms and FTIR spectra proved the success of the depolymerization. Thermogravimetry has also supported our theory on acido alcoholysis resulting in products of more uniform structure. Semi-aromatic polyesters were prepared via chain-lengthening with glycidyl ethers. Substantial increase in molecular weight was achieved. Reasonable weight loss and fragmentation were observed after 6 week-long composting of poly- and oligoesters.

Acido-alcoholysis is a new promising way to chemically recycle PET waste and to produce higher molecular weight oligoesters. These oligoesters can be used as building blocks for new compostable semi-aromatic polyesters. In the future, we would like to further investigate and explore the opportunities of this method and combine it with polycondensation.
2.5. References

Chapter 3

One-pot depolymerization and polycondensation of PET based random oligo- and polyesters

3.1. Introduction

The glycolysis of poly(ethylene-terephthalate) (PET) has been the focus of numerous researches for the past 40 years. A wide range of studies have been made to optimize this reaction and gain yields as high as possible of bis(2-hydroxyethyl)-terephthalate (BHET) or other terephthalic-acid derivate diesters. This technique allowed the recycling of PET waste that could not be further used and recycled by mechanical techniques like extrusion or injection moulding. In most cases, the primary goal of glycolysis and other techniques such as methanolysis or hydrolysis was to reproduce PET and gain a new virgin material with identical or better properties than the original material. Several methods like chain-extension during a reactive extrusion process were introduced to elongate the lifetime of the PET polymer were studied and developed. But the hydrolytic or thermal degradation processes during use and mechanical recycling inevitably degrade the polyester to a level it cannot be used further. Thus, the solvolysis of PET, chemical recycling, in general, should be used in a greater extent, in an industrial scale. The glycolysis of PET is an equilibrial reaction that requires a high ratio of diol reagent and advanced catalysts to push it towards BHET production to gain high yields. Depending on the goal of the solvolysis the reaction parameters can be tailored to produce BHET or oligomers that could be further used in new reactions. Usually, oligomers are discarded during the purification processes, only a few studies used these or the raw solvolysis product. In most of the cases, the purpose of glycolysis is the reproduction PET via BHET. As a result, the development of new, more efficient and recyclable catalyst become the focus of several research groups. Renewable heterogenous catalyst can be easily removed from the reaction mixture, they have a high catalytic activity that easily rival and could exceed traditional transesterification catalysts, such as metal salts. The use of Fe$_3$O$_4$ and Fe$_2$O$_3$ particle based catalyst reached over 90% selective BHET yields even after several uses. The increasing efficiency of these processes maintains, or rather furthers the sustainability of plastics. Despite these advances, chemical recycling is still considered an expensive method due to the high volumes of chemicals and the necessary purification steps.

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Solvolysis products of PET have been considered as feedstock for other plastic types, especially for unsaturated resins (USR). The synthesis of such materials consists of several steps beginning with the solvolysis of PET. The terephthalic acid derivates further processed, modified even with bio-based compounds such as oleic acid and cellulose derivates in separate reactions. The omission of monomer extraction and utilizing oligomers that are mostly perceived as side products could considerably reduce the cost of PET derived unsaturated resins. One-pot type resin production has been considered before and it could prove to be an ideal solution to cut expenses. The control of condensation time allows the fine-tuning of cross-link density. The lower the molar weight of the resin the lower the \( T_g \) and the loser the network becomes. The modification of unsaturated polyesters has been widely carried out with saturated diacids. They have been shown to be able to tune cross-link density and increase impact strength.

Diacid components have been rarely introduced into depolymerization reactions. In our previous work, we experimented with the simultaneous use of diacids and diols during solvolysis (acido-alcoholysis) and compared it to glycolysis and acidiolysis. The simultaneous use of diacids and diols resulted in higher molar weight and the complete absence of reagents in the reaction.

In this study, we have introduced a dicarboxylic-acid component into the glycolysis system to make oligomers and to use the raw solvolysis product to produce polymeric materials (Figure 3.2). Our goal was to design a multiple-step reaction process, that can be easily modified to gain different, fine-tuned products and can be implemented as a one-pot type process. The diacid component was intended to react with the lower molar weight components, thus the low molar weighed components are incorporated into the reaction product. These carboxyl and hydroxyl terminated oligoesters could be further used in polyurethanes or resinous crosslinked systems. As a result, the reaction product (oligomers) can be used without any purification steps and there is no need to use high amounts of diols to gain pure BHET.
3.2. Experimental

3.2.1. Materials

Arnite® D00301 PET homopolymer granules from DSM were used for chemical recycling (28.5±1.5 % crystallinity). Adipic acid (99%) was purchased from TCI (Tokyo Chemicals Industry). Ethylene-glycol (99%), concentrated hydrochloric acid (37%), sodium-hydroxide (99%), methanol (99.18%) and pyridine (99%) were purchased from Molar Chemicals (Halásztelek, Hungary). Zinc-acetate-dihydrate (Zn(OAc)$_2$·2H$_2$O AnalR Normapur®) was purchased from BDH chemicals. Maleic-anhydride (98+%) and phthalic-anhydride (99%) was purchased from AlfaAesar. Deuterated chloroform (DCCl$_3$ 99%), butane-1,4-diol (99%), styrene (99%), titanium$^{IV}$-butoxide (97%) and cobalt$^{II}$-2-ethylhexanoate solution (65% in mineral spirits) was purchased from Sigma-Aldrich. Butanox M50 (33% methyl-ethyl-ketone-peroxide solution, Akzo Nobel GmbH) commercial initiator solution was purchased from Novia Kft. (Halásztelek, Hungary).

3.2.2. Depolymerization of PET

The chemical recycling, depolymerisation of PET was carried out in a 250 cm$^3$ four-necked glass flask equipped with a mechanical stirrer, a gas inlet (inert Ar atmosphere) and a thermometer. The PET granules (80 g), the ethylene glycol (EG)(25.8 g) and the adipic acid (AdAc) were weighed in according to the calculated 1:1:x molar ratio (Table 3.1). The ratio of the PET repeating units, ethylene-glycol and the adipic acid was 1:1:0; 1:1:0.1; 1:1:0.2; 1:1:0.3; 1:1:0.4 and 1:1:0.5... 0.8 g of zinc-acetate (1% of PET) was used as a transesterification catalyst. The reaction mixture was first heated up to 130-150°C, during this phase the esterification reaction of the ethylene-glycol and adipic acid took place. The reactions were followed with the temperature of the distilling apparatus equipped to the reactor. After 30 minutes the distillation stopped, and a reflux condenser was equipped to the reactor. Then the reaction mixture was heated up to 220°C and was kept at that temperature for 4 hours. At the end of the reaction, the transparent/semi-transparent reaction mixture was poured into an alumina pan. Functional group analysis
(hydroxyl and acid content) was done to determine the amount of excess amount of diacid for the one-pot depolymerization and polymerization reaction. The reaction products were white, soap-like materials at room temperature.

The depolymerization reaction was also carried out with butane-1,4-diol (But) with the same molar ratios as listed before (80 g PET, 37.5 g But, x AdAc, 0.8 g Zn(OAc)\(_2\)._2H_2O) and conditions as described previously. This depolymerization series was further reacted with maleic-anhydride to gain unsaturated polyesters. The functional group content of these products was measured. The amount of maleic-anhydride was added to reach 1:0.9 hydroxyl:acid group ratio (Table 3.1). The acid ratio was calculated from the sum of the residual acid groups and the anhydride, that was counted as 2 acid groups. 80 g of the raw depolymerization product was weighed in a four-necked 100 cm\(^3\) glass flask. The reaction product was heated to 150°C to melt it, then the calculated amount of maleic-anhydride was added to the reaction mixture. The reactor was equipped with a gas inlet (argon gas bubbling), thermometer, distillation inlet and a mechanical mixer. The reaction mixture was heated to 180°C and was kept there for 1 hour. The condensation was followed via the thermometer of the distilling apparatus. The distillation usually stopped after 30 minutes. At the end of the reaction the reaction mixture was poured into an alumina pan. It was stored in a plastic container in argon atmosphere at 5°C until further use.

Table 3.1 Feed data table of the depolymerization and the unsaturated polyester condensation reactions. The weight percentages are calculated from the weight of PET (depolymerization) depolymerization product (PET:But:Adac x).

<table>
<thead>
<tr>
<th></th>
<th>Adac 0</th>
<th>Adac 0.1</th>
<th>Adac 0.2</th>
<th>Adac 0.3</th>
<th>Adac 0.4</th>
<th>Adac 0.5</th>
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</thead>
<tbody>
<tr>
<td><strong>PET:EG:Adac system</strong></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>PET</td>
<td>80 g</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(OAc)(_2)</td>
<td>0.8 g / 1 m/m% of PET</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>EG</td>
<td>25.83 g / 32.9 m/m% of PET</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AdAc</td>
<td>0 g</td>
<td>6.09 %</td>
<td>12.17 g</td>
<td>18.27 g</td>
<td>24.37 g</td>
<td>30.43 g</td>
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<tr>
<td></td>
<td>7.61 %</td>
<td>15.21 %</td>
<td>22.83</td>
<td>30.46 %</td>
<td>38.04 %</td>
<td></td>
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<tr>
<td><strong>PET:But:Adac system</strong></td>
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<tr>
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<tr>
<td>Zn(OAc)(_2)</td>
<td>0.8 g / 1 m/m% of PET</td>
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<tr>
<td>But</td>
<td>37.53 g / 46.91 m/m% of PET</td>
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<tr>
<td>AdAc</td>
<td>0 g</td>
<td>6.09 %</td>
<td>12.17 g</td>
<td>18.27 g</td>
<td>24.37 g</td>
<td>30.43 g</td>
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<tr>
<td></td>
<td>7.61 %</td>
<td>15.21 %</td>
<td>22.83</td>
<td>30.46 %</td>
<td>38.04 %</td>
<td></td>
</tr>
<tr>
<td><strong>Condensation of unsaturated polyesters</strong></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>PET:But:Adac x</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA</td>
<td>22.38 g</td>
<td>12.90 g</td>
<td>12.80 g</td>
<td>10.50 g</td>
<td>8.60 g</td>
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</tr>
<tr>
<td></td>
<td>27.90 %</td>
<td>16.12 %</td>
<td>16.00 %</td>
<td>13.12 %</td>
<td>10.74 %</td>
<td>8.87 %</td>
</tr>
</tbody>
</table>

3.2.3. One-pot synthesis of saturated random polyester

The depolymerization part of the one-pot reaction was carried out as explained previously. A 1:1:0.3 ratio of PET (118.5 g), ethylene-glycol (38.30 g) and adipic acid (27.03 g) was used for this reaction. The required amount of excess adipic acid was calculated from the depolymerization reaction series. The excess adipic acid amount was calculated so a stoichiometric (1:1) ratio of acid and hydroxyl groups is present during the polycondensation. After the end of the 4-hour-long isothermal depolymerization period, the reaction mixture was cooled to 110-120°C. Then 2 cm\(^3\) of Ti\(_{IV}\)-butoxide catalyst and 43.5 g
of adipic acid was added to the mixture. A distilling inlet was equipped to the reactor and the mixture was heated to 220°C. Distillation (1 hour) was used to remove the water from the reaction mixture. After the distillation stopped a vacuum apparatus was connected to the reactor through a dry ice-acetone bath trap. The polycondensation reaction in a vacuum (100 mbar pressure) with constant argon bubbling was maintained for four hours. At the end of the reaction, the reaction mixture was poured into an alumina pan.

3.2.4. One-pot synthesis of unsaturated random polyester

The depolymerization part of the one-pot reaction was carried out as explained previously. A 1:1:0.4 ratio of PET (80 g), butane-1,4-diol (37.5 g) and adipic acid (6.08 g) were used for this reaction. The required amount of excess maleic-anhydride (15.11 g) was calculated from the depolymerization reaction series. The excess maleic anhydride amount was calculated so a near stoichiometric (1:0.9) ratio of acid and hydroxyl groups is present during the polycondensation. After the end of the 4 hour-long isothermal depolymerization period, the reaction mixture was cooled to 110-120°C. Then 15.11 g of maleic-anhydride was added to the mixture. A distilling inlet was equipped to the reactor and the mixture was heated to 180°C. Distillation (1 hour) was used to remove the water from the reaction mixture. At the end of the reaction, the reaction mixture was poured into an alumina pan. The reaction mixture was kept in a closed plastic container in argon atmosphere at 5°C until further use.

3.2.5. Preparation of unsaturated resins

The unsaturated polyester (PET:But:AdAc + MA) was weighed in a 50 cm3 four-necked glass flask equipped with a reflux condenser, thermometer, a gas inlet (Ar atmosphere) and mechanical stirrer. The unsaturated polyester was heated to 180°C to gain a homogenous melt, then it was let to cool down to 80°C. Hydroquinone (0.01%) was added as an inhibitor and styrene (40%) were added as a reactive-solvent and cross-linker. CobaltII-2-ethylhexanoate solution (0.03%) was used as an activator during the crosslinking reaction. The mixture was vigorously mixed for 30 minutes to dissolve the unsaturated polyester in the styrene. The clear mildly pink solution was let to cool down to room temperature. The resin solution was immediately used to mould “dogbone” shaped specimens for DMA (dynamic mechanical analysis) measurements. Butanox M50 (3%) (~33% methyl-ethyl-ketone peroxide solution) solution was used as initiator. The specimens were cross-linked in a Heraeus® UT series drying oven at 90°C for 3 hours, then they were heat-treated at 175°C for 1 hour.

3.2.5. Characterization

The acid content of the depolymerization products was determined with a standard titration method. Three samples (1.5 g) were weighed into Erlenmeyer flasks on an analytical balance. 25 cm³ pyridine was used to dissolve the samples. The solutions were heated in an oil bath (110-120°C) to dissolve the reaction products. The solutions were let to reflux for 30 minutes. Then the samples were titrated with 0.1 M methanolic sodium-hydroxide solution in the presence of phenolphthalein indicator. 3 samples and a blank-sample were titrated to calculate the residual acid content.
Hydroxyl group content of the depolymerization products was measured with a back-titration method. 80 g of phthalic-anhydride was weighed and 500 cm³ in pyridine in a brown-glass flask to produce 1 M reagent solution. The mixture was stirred with a magnetic stirrer until the phthalic-anhydride completely dissolved. The reagent solution was let to rest for a day before use. Three samples (1.3-1.4 g) were weighed in into Erlenmeyer flasks. 25 cm³ 1 M phthalic-anhydride in pyridine reagent solution was added to the samples. Then the samples were heated in an oil bath (115 °C) and let to reflux for two hours. 50 cm³ pure pyridine was added to the samples through the condensers. The samples and a blank sample were titrated with 0.5 M aqueous sodium-hydroxide solution. 3 samples and a blank-sample were titrated to calculate the residual hydroxyl content.

An Ubbelohde type capillary viscosimeter was used to compare the intrinsic viscosity of the depolymerization and the polymerization reaction products. Three samples with 0.05 g cm⁻³, 0.075 g cm⁻³ and 0.10 g cm⁻³ were prepared. The samples were dissolved in pyridine and were let to reflux at 115°C until the solutions were clear. The capillary viscosimeter was thermostated at 75 °C during the measurements. Intrinsic viscosity was calculated from extrapolating the relative and reduced viscosity functions to zero concentration.

Bruker Tensor 27 FTIR spectrometer (ATR, 28 scans) was used to characterize the general molecular structure of the depolymerization and the polymer samples. Bruker Avance 500 spectrometer was used to measure the ¹H NMR spectra of all the reaction products. Bruker Avance 300 spectrometer was used to measure the ¹³C, DEPT, ¹H-¹H COSY, ¹H-¹H NOESY, ¹H-¹³C HSQC and ¹H-¹³C HMBC spectra. The reaction products were dissolved in deuterated chloroform (DCCl₃, ~ 30 mg cm⁻³ concentration). The temperature of acquisition was 30°C. The PET:EG:AdAc depolymerization series products showed limited solubility on the chloroform solvent at room temperature, only ¹H spectrum were recorded. The 2D correlative measurements were done on the one pot polyester product. The solubility of these products increased with the increasing amount of adipic acid used during depolymerization. The one-pot polyester (PET:EG:AdAc) product was easily soluble in chloroform at room temperature. The PET:But:AdAc depolymerization series and its polycondensates showed reasonable solubility in chloroform. The PET:But:AdAc0.4 and PET:But:AdAc0.4+MA were measured with the 2D correlative measurements.

PerkinElmer TGA 6 was used to characterize the thermal stability of the samples. 10 mg of the samples were weighed in the ceramic crucible. The sample was heated from 30 to 700 °C at 10 °C min⁻¹ heating rate in purging nitrogen atmosphere. Then the sample was kept at 700 °C for 10 minutes and the atmosphere was changed to oxygen to clean the ceramic crucible.

PerkinElmer DSC 7 was used to determine the glass transition temperature and crystallinity of the samples. Glass transition temperature was determined with a dynamic measurement. A 3-5 mg sample was kept at -40 °C for 1 minute, then it was heated to 150°C with 20 °C min⁻¹ heating rate. The sample was kept at 150 °C for one minute, then it was cooled to -40 °C with 20 °C min⁻¹. The sample was kept at -40 °C for one minute, then it was heated to 150°C with 20 °C min⁻¹. Glass transition temperature was determined from the last heating period.
PerkinElmer DMA was used to characterize the glass transition and viscoelastic properties of the cross-linked unsaturated resin samples. The “dogbone” shaped specimen (70x1.4x4 mm) were cut to prismatic shape before measurements. The samples were heated with 2 °C min\(^{-1}\) heating rate from -50 °C to 200 °C. 10 µm amplitude and 1 Hz frequency was used during the tension test method measurements. The glass transition temperature was determined from the peak of the tanδ function.

### 3.3. Results and discussion

![Chemical structures](image)

Figure 3.3 Possible diol, mono-ester and diester forms of ethylene-glycol in the acido-alcoholysis depolymerization reaction product

Mixed oligoesters of the terephthalic acid (TpAc), ethylene-glycol and the reagent diol and dicarboxylic acid are produced at the end of the depolymerization reactions (Figure 3.3). Two separate reaction series were designed to explore this reaction route. In both cases adipic acid was (AdAc) used as the dicarboxylic acid component. Ethylene-glycol (EG) and butane-1,4-diol (But) were used as diol reagents. All the reagent ratios were calculated to the number of repeating units of the weighed in PET. The diols were used in a 1:2 ratio to minimize the reagent use. A 5+1 reactions were carried out with increasing amount if adipic acid. The ratio of adipic acid was increased from 0.1 to 0.5. The reaction products were thoroughly characterized with functional group analysis, FTIR, NMR, TGA and DSC measurements to follow the effects of the acid component on the reaction product. Standard glycolysis with only the diols present were carried
out to be used as a reference points. Based on the characterization of the reaction series one-pot type reactions were designed to produce saturated and unsaturated polyesters. The PET:EG:Adac reaction series was used to produce a random copolyester poly(ethylene terephthalate co adipate). The PET:But:Adac reaction series products were reacted with maleic-anhydride in separate steps and also in a one-pot reaction to produce unsaturated polyesters. The ratio of maleic-anhydride decreased with the increasing ratio of adipic acid during the depolymerization steps. The unsaturated-polyester products were dissolved in styrene (40 m/m%) and were cross-linked to produce “dogbone” shaped resin samples for thermomechanical testing.

3.3.1. Functional group analysis and solution viscosity measurements

Functional group analysis was used to initatively characterize the depolymerization reactions and to determine the needed amount of excess diacid or anhydride for the polycondensation reactions (Figure 3.4). The used acid components (adipic acid) were expected to react with any diol component during the depolymerization stage. Any lower molecular weighed components, such as ethylene-glycol are integrated into the oligomer molecules. The residual acid content scattered with the amount of adipic acid used during the depolymerization step. In case of the PET:EG:AdAc series a slight increase, in case of the PET:But:AdAc series a slight decrease was observed. The PET:But:AdAc series had one order of magnitude higher residual acid content than the PET:EG:AdAc series. The differences of ethylene-glycol and butane-1,4-diol might have influenced this. Butane-1,4-diol is more likely to engage in side reactions (acid catalyzed cyclization to tetrahydrofuran) during transesterification reactions. This may also explain the increase of hydroxyl and acid content at the PET:But:AdAc0.5 point, the ratio of adipic acid might have been too high for the system. The AdAc0 and AdAc0.1 point showed only a slight difference in their hydroxyl value. The AdAc0.1 had higher hydroxyl content then implied near linear decrease in both series. The observed decrease in hydroxyl groups suggest an increase in molecular weight as well.

![Figure 3.4 Functional group content of the depolymerization products: ethylene-glycol and adipic-acid (a); butane-1,4-diol and adipic acid (b)](image-url)
The intrinsic viscosity of the depolymerization series and the polycondensation products was measured with solution viscosimetry. The intrinsic viscosity of the depolymerization series was between 0-0.06 cm$^3$ g$^{-1}$ (Figure 3.5). Both depolymerization series showed an increasing trend, that suggest an increase in molecular weight. It can, therefore, be assumed that our hypothesis was correct and adipic acid acted as a chain-lengthening agent during the depolymerization step. The polycondensation reaction in both cases significantly increased the intrinsic viscosity of the samples with one order of magnitude. The unsaturated polyesters (PET:But:AdAc+MA) had a higher intrinsic viscosity than the saturated polyester (PET:EG:AdAc one-pot). The one-pot unsaturated polyester (PET:But:AdAc0.4+MA) had almost identical intrinsic viscosity to its respective pair in the depolymerization series. It is therefore likely that the acido-alholysis method is reproducible and can be engineered to synthesize oligo- and polyesters in a one-pot way.

### 3.3.2. Molecular structure identification

The FTIR and NMR studies further supported the previously described trends. Several characteristic peaks typical of polyesters were found in the FTIR spectra (Figure 3.6). Ester characteristic peaks, 1720 cm$^{-1}$ carbonyl valence vibration and 1250 cm$^{-1}$ -C=O-C stretching vibrations were found. C-H valence vibration characteristic peaks were found at 2960 cm$^{-1}$ and 2880 cm$^{-1}$, aromatic ring stretching vibration characteristic peak was found at 700 cm$^{-1}$. The usually wide peak attributed to the valence vibrations of hydroxyl groups was found between the 3600-3300 cm$^{-1}$ interval. This peak showed a decrease in intensity with the increasing concentration of the adipic acid. In case of the one-pot synthesis product, this -OH groups attributed peak completely disappeared. The PET:But:AdAc depolymerization series showed similar peaks, and the similar decreasing tendency was found for the hydroxyl related valence vibration peak at the 3600-3300 cm$^{-1}$ interval.
NMR measurements allowed us to thoroughly characterize the depolymerization, and the following polycondensation reaction products. 2D correlative measurements on the one-pot polymer product were used to fully assign the peaks of the depolymerization (PET:EG:AdAc) series \(^1\)H spectra. Adipic acid and terephthalic acid related carbonyl, aliphatic and aromatic carbon atom signals were found in the \(^{13}\)C and DEPT spectra. Ethylene-glycol related peaks were found in the 70-60 ppm chemical shift range. 4 separate peaks were found that could be attributed to the diesters and mixed esters of ethylene glycol with terephthalic acid and adipic acid (Figure 3.7). \(^1\)H spectra were quantitively evaluated by integrating the peaks derived from the various mono- and diester forms of ethylene-glycol (Figure 3.8, Figure 3.9). All the possible molecular structures and connections are represented in Figure 3.3. All these structures were organized into three groups: diols (EG), monoesters (Ad-CH\(_2\)-CH\(_2\)-OH; Tp-CH\(_2\)-CH\(_2\)-OH) and diesters (Ad-CH\(_2\)-CH\(_2\)-Ad; Tp-CH\(_2\)-CH\(_2\)-Tp; Ad-CH\(_2\)-CH\(_2\)-Tp).

Increasing the adipic acid content during the depolymerization stage, higher molecular weighted products were expected to appear. Inasmuch as the relative integral of diols and monoesters related peaks showed a decreasing trend and the diester related peaks showed an increasing trend. The slightly increasing trend of the Tp-CH\(_2\)-CH\(_2\)-Tp connection indicates that the use of adipic acid caused a setback in the depolymerization step. The acid component reacted with the diol and lowered its concentration. Despite that, we were able to achieve a decent rate of depolymerization the ratio of the Tp-CH\(_2\)-CH\(_2\)-Tp only raised with 10%. The appearance of adipic acid monoesters confirms our theory on the adipic acid reacting with the ethylene-glycol at a certain degree during the first stage of the depolymerization reaction. Comparison of “Ad-CH\(_2\)-CH\(_2\)-Tp” “Ad-CH\(_2\)-CH\(_2\)-Ad” relative integrals shows that the BHET derivatives have a higher reactivity than EG and its aliphatic monoesters. The major decrease in the ratio of “Tp-CH\(_2\)-CH\(_2\)-OH” structure after the polycondensation reaction further supports this.
One-pot depolymerization and polycondensation of oligo- and polyesters

Figure 3.7 $^{13}$C and DEPT spectra of the PET:EG:AdAc 1:1:0.3 depolymerization product

Figure 3.8 $^1$H NMR spectra of the PET:EG:AdAc depolymerization reaction series
These findings have an interesting implication in developing the one-pot type reactions of this method. The quantitative analysis of the PET:EG:AdAc reaction series clearly indicates that the depolymerization with ethylene-glycol and the condensation with adipic acid can occur in the same system. Thus these reaction can be engineered to reach a certain, desired functional group content and molecular weight.

In accordance with the PET:EG:AdAc series, the PET:But:AdAc series showed the same type of trends. Due to the introduction of butane-1,4-diol the NMR spectra became complicated and caused overlapping in the peaks. This caused these trends to be less straightforward. Nevertheless, a declining tendency for most of the of monoesters correlated peaks and an increasing tendency for the diester correlated peaks was found. The $^1$H NMR spectra of the PET:But:AdAc0.5 considerably differed from the rest of the series. The sample barely dissolved in the deuterated solvent. The relative integral of the Tp-EG-TP linkages (BHET dimer or oligomers) is almost three times higher than the rest of the series. This suggests the presence of longer PET derivative oligomers in the reaction product. High-intensity peaks at the 3.7-3.6 ppm interval imply the presence of alcohol (EG and/or But) components. These results could explain the higher than expected residual functional group content (Figure 3.4). The quantitative analysis suggests, that in this case the ratio of adipic acid was too high. As a result, the depolymerization step couldn’t reach the same level as the other ratios. Nevertheless, this reaction series shows that the acido-alcoholysis concept could be applied to other systems as well. In any given combination of diol and diacid and PET the reaction must be tested to find the interval of applicable reagent ratios.
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The introduction of maleic-anhydride into the products (PET:But:AdAc depolymerization series) further complicated the molecular structure and the NMR spectra. Due to the relatively low amount of used maleic-anhydride only slight changes were observable in the $^1$H spectra between the 5-3.5 ppm interval (Figure 3.12) 2D correlative measurements were used on the PET:But:AdAc04+MA sample. Despite this, we were unable to resolve the new connections made by the maleic-anhydride in the 5-3.5 ppm interval ($^1$H spectra). Certain parts of the $^1$H spectrum (PET:But:AdAc04+MA sample) were circled to show the changes derived from the condensation reaction. Those peaks were attributed to
mono-ester linkages in the depolymerization products (Figure 3.10). The peaks at the 3.8-3.7 ppm interval showed a significant decrease in intensity. These peaks are attributed to the hydroxyl terminated chain ends, thus these indicate an increase in molecular weight. Only the two unsaturation related peaks could be directly linked to the maleic-anhydride in the 7-6 ppm interval. The relatively high temperature of the reaction caused the maleic-acid to change from its cis isomer state to the trans isomer form.

![Chemical Structure](image.png)

**Figure 3.12** $^1$H NMR spectra of the PET:But:AdAc 1:1:0.4 and its reaction product with maleic-anhydride

3.3.3. **Thermal properties**

The thermal stability of the depolymerization series samples was considerably affected by the amount of adipic acid used during the depolymerization step (Figure 3.13). As it was previously stated the adipic acid component was used to connect the low molar weighed components to form oligomers. The TGA curves of the PET:EG:AdAc series support this statement. At lower temperatures (100-300 °C) the weight of the samples significantly decreased due to the evaporation of low molar weighed components like ethylene-glycol. With the increasing amount of adipic acid these components reacted with the adipic acid and formed oligomers. As a result, a more uniform product was gained and the amount of these easily evaporating components was minimalized. The peaks attributed to such components progressively smoothed on the DTG curves as the ratio of the adipic acid was increased. A new peak/shoulder appeared with increasing the amount of adipic acid at 375 °C. the shoulder’s increase could be explained by the fact that the adipic-esters showed an increasing tendency in the reaction product. Aliphatic polyesters have lower thermal stability than aromatic polyesters. They were shown to be able decrease the thermal stability of copolyesters. 58
The PET:But:AdAc depolymerization series showed a similar, but less distinct trend with the increasing amount of adipic acid. The thermal stability of this reaction series showed no significant change with the polycondensation reaction with maleic-anhydride (Figure 3.14). A shoulder can be identified on all the DTG curves at 445 °C that became well-defined increasing the amount of used adipic acid. Especially in the case of PET:But:AdAc 0.5. McNeil and his coworkers have shown that longer alkyl chains in
poly(alkylene-terephthalate)s decrease the thermal stability, doing so butylene-terephthalate esters are less stable than ethylene-glycol esters. The high ratio of adipic acid increased the ratio of residual Tp-CH$_2$-Tp connections in the depolymerization products (Figure 3.11). Thus, certain segments of the random copolyester have higher thermal stability than the butane-1,4-diol ester rich segments.

Figure 3.15 DSC curves of the PET:EG:AdAc reaction series (2$^{nd}$ heating)

Figure 3.16 The glass transition temperature of the PET:But:AdAc+MA reaction series (determined with DSC). The triangle represents the one-pot reaction product.
The AdAc0 and AdAc0.1 depolymerization products in both series showed low crystallinity with a relatively fast crystallization rate. All the depolymerization products above 0.2 adipic acid ratio showed almost no or minor melt peaks that could be detected with our DSC instrument (Figure 3.15). The AdAc0 and AdAc0.1 depolymerization products in both series showed low crystallinity with a relatively fast crystallization rate. All the depolymerization products above 0.2 adipic acid ratio showed almost no or minor melt peaks that could be detected with our DSC instrument (Figure 3.16). Since the intrinsic viscosity of these samples was found to be similar to the decrease in $T_g$, it should be related to the amount of used adipic acid. Since butane-1,4-diol and adipic acid have longer saturated aliphatic chains (compared to ethylene-glycol, terephthalic acid and maleic-acid) they act as “soft” components and lower the $T_g$ of the polymer.

3.3.4. Unsaturated resin characterization

Significant changes can be observed in the FTIR spectra of unsaturated resins in comparison to the depolymerization and polycondensation products (Figure 3.17) The spectra were normalized so the carbonyl vibration related peaks at 1720 cm$^{-1}$ could have a relative intensity of 1. The two new peaks at 797 cm$^{-1}$ and 699 cm$^{-1}$ can be attributed to the breathing vibration of aromatic phenyl groups. Major increases between the 3000-2800 cm$^{-1}$ interval can be attributed to the valence vibration of the phenyl groups. The peaks at the 1300-1000 cm$^{-1}$ interval are mostly related to the vibrations of the C-O-C ester groups. The intensity of the peaks at 1258 cm$^{-1}$,1099 cm$^{-1}$ and 1020 cm$^{-1}$ are present in the depolymerization and the polycondensation product as well. The observed increase in intensity can be explained by the radical reaction of the vinyl group of the styrene and the unsaturation in the ester chain. Due to the cross-linking reaction, the specific vibrations of the carbonyl and C-O-C groups derived originally from the maleic-anhydride may change.

![Figure 3.17 FTIR spectra comparison of the depolymerization, condensation and the final unsaturated resin product](image-url)
The low condensation time was utilized to keep the molecular weight of the unsaturated polyesters relatively low and only allow the terminal hydroxyl groups to react with the anhydride via ring-opening. This way a looser cross-linked network will be produced and the glass transition temperature will sensitively depend on the constitution of the ester chains. \(^{50}\) Since an increase in molecular weight in the function of the adipic acid ratio the cross-link density should decrease in the function the utilized amount of adipic acid. To test this theory the thermomechanical properties of the unsaturated resins were studied with dynamic mechanical analysis (Figure 3.18, Table 3.2). The unsaturated resin samples were found to be rather elastic at room temperature. The glass transition temperature of the samples is relatively low, the onset of the glass transition starts bellow room temperature, thus their properties considerably change in that temperature interval. The measured \(T_g\) values decreased with the increasing amount of adipic acid used during the depolymerization. The maximum of the \(\tan\delta\) functions shifted to lower temperatures with the increasing ratio of the adipic acid. A shoulder could be observed at 100-120 °C temperature range at the 0.4 and 0.5 ratios that might indicate the presence of more densely cross-linked parts in the resins. The higher amount of adipic acid also could have caused segregation of softer (adipic ester rich) and harder (terephthalic ester rich) segments in the copolyester chains. Just as the intrinsic viscosity measurements suggested higher molecular weighed products were gained that, as a result, causes a decrease in glass transition temperature and cross-link density. The cross-link density values were calculated from the storage modulus data at 180 °C, the calculated values proved to be particularly low. The higher amount of adipic acid directly influenced the needed amount of maleic-anhydride and caused a decrease in cross-link density.

**Figure 3.18 A \(\tan\delta\) curves (a) and \(\tan\delta_{\text{max}}\) and glass transition temperature (b) of the unsaturated resin samples**
Table 3.2 Storage modulus, cross-link density of the USR samples

<table>
<thead>
<tr>
<th>Resin type</th>
<th>Storage Modulus (MPa)</th>
<th>Cross-link density (mol m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
<td>180°C</td>
</tr>
<tr>
<td>USR0</td>
<td>2459.7</td>
<td>10.18</td>
</tr>
<tr>
<td>USR0.1</td>
<td>1629.9</td>
<td>7.08</td>
</tr>
<tr>
<td>USR0.2</td>
<td>1483.3</td>
<td>3.13</td>
</tr>
<tr>
<td>USR0.3</td>
<td>1320.4</td>
<td>2.03</td>
</tr>
<tr>
<td>USR0.4</td>
<td>856.6</td>
<td>0.41</td>
</tr>
<tr>
<td>USR0.5</td>
<td>693.3</td>
<td>0.51</td>
</tr>
</tbody>
</table>

3.4. Conclusions

In this study, we have investigated the use of diacid components and their effects on the depolymerization products of PET solvolysis. Our results have shown that diacids can be utilized during PET solvolysis and their use results in the production of oligoesters. The volatile, low molar weighed components are incorporated into the oligomer chains, thus a more uniform product is achieved at the end of the depolymerization. The reaction has no side-products and the produced oligomers could be directly used without any or minimal purification. The molecular structure of the depolymerization product can be finely tuned via selecting the diol and diacid reagents, thus engineering the thermal, mechanical and chemical properties of its final derivative product. The increasing ratio of the diacid results in increasing the molecular weight of the produced oligomers. We have successfully utilized and characterized acido-alcoholysis so it can be used in one-pot type reactions. Compared to traditional chemical recycling (depolymerization, then polycondensation), acido-alcoholysis combines depolymerization and condensation techniques into a single step. Excess chemical use is not necessary, and purification of the end-product is not needed or minimal. Via acido-alcoholysis oligoesters can be produced that can act as hydroxyl and acid functional mid-products. Due to their reactive terminal groups, they could be tailored to be used as polyols in polyurethanes as well. Thus, the most expensive steps of solvolysis, the purification of products can be completely avoided, and the product properties can be fine-tuned. The authors believe that this technique could be applied with a wide range and combination of diol and diacid components. Although the systems must be tested to find the optimal interval of reagent ratios. The reaction process proved to be quite modular and could be utilized in various fields. The practicality of the method considerable depends on the purity of the feed-stock waste material. The effects of contaminants (other polymers, adhesives, metal salts) must be investigated thoroughly in the future. Further enhancements could be made in the depolymerization step with the use of new, heterogeneous, recyclable catalyst.
3.5. References

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Chapter 4

Synthesis and characterization of isophorondiamine based epoxy hardeners from the aminolysis of PET

4.1. Introduction

Plastic recycling is an ever emerging problem in our society. Several methods have been developed to recycle commodity plastics, such as poly(propylene), poly(ethylene), poly(styrene), poly(vinyl-cloride) and poly(ethylene-terephthalate) (PET) [1-6]. With classical remoulding processes like extrusion and injection moulding a significant decrease in mechanical properties cannot be avoided after a certain number of cycles [7-10]. At one point chemical methods should be applied to regain the resources from these materials. Chemical recycling, namely the solvolysis of PET waste is one of the most widely applied and researched methods. The solvolysis reaction, e.g. glycolysis, is a typically slow equilibrium based transesterification reaction that should be carried out at higher temperatures and pressures with higher reagent ratios and a catalyst to obtain pure terephthalic acid derivatives [11-20]. This is not to mention the need for extra purification steps that must be done to regain the ethylene-glycol and to separate the terephthalic acid derivatives. Due to these circumstances, chemical recycling is mostly known as a rather expensive method. Several publications have focused on the catalytic enhancement of bis(2-hydroxyethyl) terephthale (BHET) production [11,13-15,21]. The aminolysis of PET can occur in less demanding conditions and could be used to gain new value added chemicals and polymeric materials and resins [18,20,22-29]. Epoxy curing with PET aminolysis products is still an expanding field that only a few studies have focused on [19,30]. Most of these utilized aliphatic diamines and applied several cleaning steps to gain pure terephthalic-amides and remove the ethylene-glycol side products. In several early publications the catalytic effects of hydroxyl groups in epoxy curing reactions with amine cross-linkers were tested and proved [31-33]. Thus if, ethylene-glycol (EG) is not removed from the raw aminolysis product it could serve as a catalyst via hydrogen bond formation for the cross-linking reactions. Since a hydrogen bond is required for this kind of catalytic effect [33,34], the amide groups of the terephthal-amide-diamines could also provide a catalytic acceleration as well. Up to this point no research groups have attempted to use the raw aminolysis products of PET for epoxy curing and exploring their catalytic effects.

In this study our goal was to investigate the use of raw aminolysis products of PET as epoxy curing agents, characterize the cross-linked resins, and develop an industrially easily applicable method for diamine curing agent production.

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Figure 4.1 The aminolysis reaction of PET with isophoron-diamine

In this study a widely used cycloaliphatic epoxy hardener, isophoron-diamine (IPD) was used in PET aminolysis to produce terephthalic-amide-diamines (Figure 4.1). The aminolysis was carried out without excess IPD (1:2 ester- to amine group mol ratio). The chemical structure was identified, with $^1$H, $^{13}$C, DEPT), $^1$H-$^{13}$C HSQC, $^1$H-$^{13}$C HMBC, $^1$H-$^{15}$N HMBC, $^1$H-$^1$H COSY, and $^1$H-$^1$H NOESY NMR measurements. The raw reaction product was dissolved in IPD (0-50 m/m%) to gain an easy to handle, low temperature curing epoxy hardener system. The effect of the terephthal-amide-diamine concentration was investigated on the cross-linking reaction (Figure 4.2), gelation, thermomechanical, and mechanical properties of the cured epoxy resins.

4.2. Experimental

4.2.1. Materials

PET granules made by DSM Arnite® D00 301 (DSM, Heerlen Neatherlands) were used for the aminolysis reactions (28.5±1.5 % crystallinity). Bisphenol A-diglicidil-ether IPOX® EH 1010 epoxy resin (EE: 180-196 g mol⁻¹, $\eta$: 10000-14000 mPas, $\rho$: 1.17 g cm⁻³) and Isophoron-diamine ER 2943 (IPD) (Amin value: 645-675 mgKOH g⁻¹, $\eta$: 5-25 mPas, $\rho$: 0.92 g cm⁻³, ~90% pure (HPLC)) were purchased from Ipox Chemicals (Budapest, Hungary). Zinc-acetate (Zn(OAc)₂.2H₂O) was purchased from BDH Chemicals (VWR International, Radnor, USA). N,N-dimethyl-formamide (99%, 06120-203-340) (DMF), pyridine (99%, 08160-203-340), potassium hydroxide (99%, 04300-101-190) and hydrochloric acid (37%, 08710-006-340) were purchased from Molar Chemicals (Halásztelek, Hungary). Phthalic anhydride (99%, A14955) was purchased from AlfaAesar. Deuterated dimethylsulfoxide (DMSO-d6) (99.9%, 15874-10X1ML) was purchased from Sigma-Aldrich (Saint Luis, USA).
4.2.2. Aminolysis of PET with IPD

The aminolysis of PET was carried out in a 250 cm³ four-necked round-bottom glass flask equipped with a thermometer, a gas inlet, a reflux condenser, and a mechanical stirrer. The reaction mixture was heated to 200 °C and was kept there for 4 hours in argon atmosphere. 80 g of the PET granules and 0.8 g of zinc-acetate transesterification catalyst (1% of PET) were added. The applied IPD ratio (1:2) was calculated from the ester group content of the PET. At the end of the reactions the homogenous, viscous, green-yellow melt was poured into an aluminum pan. The reaction yields were near 90%.

4.2.3. Reaction product characterization

The amine and hydroxyl functional group content was determined via titration methods. 0.1-0.2 g samples with analytical balance were weighed in an Erlenmeyer flask and dissolved in 15 cm³ of DMF. The 3 samples and a blank sample were titrated with a 0.1 M hydrochloric acid solution in the presence of a bromocresole green indicator to determine the amine content of the samples. The hydroxyl group content was determined with a back-titration method. 3 samples of 1.3 g were weighed in Erlenmeyer flasks with analytical precision. 25 cm³ of 1 M phthalic anhydride solution in pyridine was added to the 3 samples and to the blank sample. The samples were heated to 110 °C in oil-baths and were refluxed for 2 hours. After the samples cooled to room temperature, 50 cm³ pyridine was added through the condenser. The samples were titrated with a 0.5 M NaOH solution in the presence of a phenolphthalein indicator.

Perkin Elmer TGA 6 (PerkinElmer, Waltham, USA) was used to determine the thermal stability of the reaction product, and the cured epoxy specimens in purging nitrogen gas. A 10 mg sample was heated with a 10 °C min⁻¹ heating rate from 30-700 °C, then the sample was kept at 700 °C for 10 minutes in oxygen atmosphere.

A Brucker Tensor 27 FTIR spectrometer (Bruker, Billerica, USA) was used to measure the FTIR spectra of the reaction products in KBr pastilles (28 scans, 4000-400
cm$^{-1}$). $^1$H, $^{13}$C, DEPT, $^1$H-$^1$H COSY, $^1$H-$^1$H NOESY, $^1$H-$^{13}$C HSQC and $^1$H-$^{13}$C HMBC spectra were recorded with a Bruker Avance 300 spectrometer. $^1$H-$^{15}$N HMBC spectrum was recorded with a Bruker Avance 500 spectrometer. The samples were dissolved in DMSO-d$_6$ (99%). The sample concentration was 29 mg cm$^{-3}$ for the IPD and 51 mg cm$^{-3}$ for the reaction product. The temperature of acquisition was 30 °C.

**4.2.4. Test specimen preparation and characterization**

A solution series of the aminolysis product and IPD was prepared to use as the cross-linking agent for epoxy resins. The reaction product was dissolved in IPD in different concentrations (0, 5, 10, 20, 30, 40, and 50 m/m%). The components were weighed with analytical accuracy. The solutions were prepared in round-bottomed flasks equipped with a reflux condenser. The flasks were heated to 100 °C for 30 minutes. The amine value was determined as previously described.

The epoxy content of the ER1010 epoxy resin was measured with a back-titration method. Three samples of 0.2 g were weighed in Erlemeyer flasks with analytical precision. 16 cm$^3$ concentrated hydrochloric acid (37%) was dissolved in pyridine to obtain the pyridine hydrochloride solution in pyridine. The samples were dissolved in 25 cm$^3$ solution of pyridine hydrochloride in pyridine. The solutions were heated and let to reflux for 1 hour. After the samples cooled to room temperature 10 cm$^3$ water was added through the condenser. A 0.1 M sodium hydroxide (in methanol) solution was used to titrate the samples in the presence of a phenolphthalein indicator. The mixing ratios for the ER1010 epoxy resin and the cross-linker were calculated to the stoichiometric ratio.

The epoxy mixture was prepared according to the calculated mixing ratios. The resin and the cross linker were mixed with a glass rod for three minutes in a plastic cup. The plastic cup was placed in a vacuum chamber for 30-40 minutes until the resin was bubble free. 75x4x1.4 mm “dogbone” shaped specimens and 50x10x4 prismatic shaped specimens were moulded for mechanical tests. The specimens were cross-linked for 2 hours at 90 °C in a VWR Venti-Line 115 drying oven (VWR International, Radnor, USA).

PerkinElmer DSC7 (PerkinElmer, Waltham, USA) was used to measure the exothermic enthalpy of the cross-linking and the glass transition temperature (Tg) of the mixtures. The 10 mg of the freshly mixed resin samples were weighed with analytical accuracy. The samples were kept at 30 °C for 0.5 min, then they were heated to 90 °C with 200 °C min$^{-1}$ heating rate. The samples were cross-linked at 90 °C for 2 hours, then the samples were cooled to 0 °C with 20 °C min$^{-1}$ cooling rate. The reaction heat was calculated from the integration of the isothermal segment between 0 and 30 min. To determine the glass transition temperature (Tg), the samples were further heated from 0 °C to 250 °C with 20 °C min$^{-1}$, kept at 250 °C for 1 minute, then cooled to 0 °C with 20 °C min$^{-1}$ and kept there for 1 minute. Then the samples were heated with 20 °C min$^{-1}$ heating rate to 250 °C. The Tg was determined from the last heating period. All the calculations and evaluations were carried out in Pyris Software.

PerkinElmer Diamond DMA (PerkinElmer, Waltham, USA) was used to characterize the glass transition temperature and viscoelastic behavior of the epoxy specimens. A tension
test method was used from 20 to 200 °C with 2 °C min⁻¹ heating rate, 1 Hz frequency and 10 μm amplitude. The T_g was determined from the peak of tanδ. The dogbone shaped specimens were cut to a prismatic shape before the DMA measurements.

Rheological measurements for gel point determination were carried out using an Anton-Paar Physica MCR 301 (Anton Paar GmbH, Graz, Austria) apparatus at 40 °C in continuous rotation mode with a plate-plate system (plate distance 1 mm).

Standard tensile tests were conducted on an Instron 5566 type equipment (Instron Co., Canton, USA) with 5 mm min⁻¹ rate to determine the Young’s modulus, tensile strength, and elongation at break. Instrumented impact testing was used to investigate the impact resistance. The measurements were carried out with a Ceast Resil 5.5 instrument (CEAST spa, Pianezza, Italy) with a 4 J hammer (2.9 m s⁻¹). The impact test specimens were V-notch type samples. All the mechanical tests were done at 23 °C in an air-conditioned laboratory with 50% air humidity.

4.3. Results and discussion

4.3.1. Aminolysis product characterization

Functional group analysis was used to characterize the raw reaction product (Table 4.1). The measured amine value approximates the theoretical amine value (4.24 mmol g⁻¹, calculated from the theorized molecular structure of the product). It suggests the presence of longer terephthalic-acid and isophorondiamine derivative oligoamides. The hydroxyl value was determined to measure the amount of ethylene-glycol in the raw product. It was found to be near 100% based on the PET repeating units. This indicated the complete amidation of the ester groups.

Table 4.1 Functional group content of IPD and the aminolysis product

<table>
<thead>
<tr>
<th>Material</th>
<th>Amine value (mmol g⁻¹)</th>
<th>Hydroxyl value (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPD</td>
<td>11.57±0.041</td>
<td>-</td>
</tr>
<tr>
<td>PET:IPD 1:2</td>
<td>3.89±0.009</td>
<td>3.98±0.407</td>
</tr>
</tbody>
</table>

Thermo-gravimetric analysis (TGA) was used to investigate the mass composition and thermal stability of the reaction product (Figure 4.3). A two-step weight loss process was observed. At the first step the ethylene-glycol content evaporated out of the product resulting in over 30% weight loss. The thermal degradation of the main reaction product started above 400 °C.
FTIR spectroscopy was used to determine the general molecular structure of the reaction product (Figure 4.4). The spectra of PET and IPD were added as a reference. The wide peak between 3600-3200 cm\(^{-1}\) are attributed to the valence vibration of the N-H (amine and amide) and O-H groups. The shoulder/peak at 3100-3080 cm\(^{-1}\) is attributed to the aromatic, the peaks at 2951 and 2921 cm\(^{-1}\) are attributed to aliphatic/cyclo-aliphatic C-H valence vibrations. The peaks at 1638 and 1550 cm\(^{-1}\) are attributed to the amide carbonyl vibrations. Most of the peaks between 1500-1000 cm\(^{-1}\) can be attributed to the bending and skeletal vibrations of the aliphatic and the aromatic hydrocarbon groups. No peaks were found that could be attributed to the ester type vibration (~1740-1720 carbonyl vibration, ~1240 cm\(^{-1}\) for C-O-C vibrations). Thus, the amidation of PET was complete and no ester linkages are present in the product.
**Figure 4.4** The FTIR spectrum of PET:IPD 1:2

**Figure 4.5** The $^1$H spectrum and atom numbering of IPD (IPOX EH2293). $^1$H (numbers) and $^{13}$C (alphabet)
4.3.2. IPD and Product characterization with NMR

Full assignation was carried out on both the IPD and the reaction product. The NMR spectra of the IPD served as a reference for the reaction product assignation (Figure 4.5, Figure 4.6). The used IPD is about 90% pure, thus impurity attributed peaks and peak widening were expected to be observed in the spectra. Several peaks attributed to the contaminant were identified in the $^{13}$C spectra. Based on the DEPT and the HSQC spectra the main contaminant is similar to IPD and was identified as 5-(aminomethyl)-3,3-dimethylcyclohexanamine. IPD has two different groups: an aliphatic and a cyclo-aliphatic type amine group that can react during the aminolysis reaction. The results indicate that due to the steric hindrance of the cyclo-aliphatic connection the reactivity of these groups differ. Thus, aliphatic connected amide groups are expected to form. Amide and aromatic related peaks appeared in the $^1$H and $^{13}$C spectra that signaled the success of the amidation (Figure 4.7, Figure 4.8). Several low intensity peaks can be observed between the 60-20 ppm interval in the $^{13}$C NMR spectrum. These peaks can be attributed to the chemical shift differences between aliphatic or cycloaliphatic connected amides. The most illustrative example is the peaks attributed to the $4_{\text{ax}}$, $5_{\text{ekv}}$ and $7_{\text{h}}$ methyl groups in both the $^{13}$C and $^1$H spectra. In the $^{13}$C spectra new peaks appeared close to the high intensity peaks, in the $^1$H spectra secondary peaks appeared between the 1.2-0.8 ppm interval.

![Figure 4.6 The $^{13}$C spectrum of IPD (EH 2293)](image_url)
4.3.3. Cross-linker system design, solubility calculations

The aminolysis reactions yielded a green-yellow coloured, amorphous, brittle material that slowly softened and melted between 100-150 °C. Thus, the produced terephthalic-amides could not be used directly as hardeners in conventional low cure-temperature epoxy resin systems. Our purpose was to gain a cross-linker system that could be
processed at room temperature. Therefore, solubility parameters were calculated using the Fedors group contribution calculation method to find possible solvents for the cross-linking agent (Table 4.2). The raw terephthalic-amides were found to dissolve in DMF, DMSO, ethanol, isopropanol and IPD.

Table 4.2 Calculated solubility parameters and Cohesion energy density data

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( V_m ) (mol cm(^{-3}))</th>
<th>CED (J cm(^{-3}))</th>
<th>( \delta ) (Fedors) (MPa(^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPD</td>
<td>163.9</td>
<td>65 380</td>
<td>20.0</td>
</tr>
<tr>
<td>PET:IPD 1:2</td>
<td>328.6</td>
<td>194 680</td>
<td>24.3</td>
</tr>
<tr>
<td>DMF</td>
<td>70.9</td>
<td>37 050</td>
<td>22.8</td>
</tr>
<tr>
<td>DMSO</td>
<td>77.8</td>
<td>48 560</td>
<td>25.0</td>
</tr>
<tr>
<td>EtOH</td>
<td>58.4</td>
<td>39 450</td>
<td>26.0</td>
</tr>
<tr>
<td>iPrOH</td>
<td>76.34</td>
<td>42 650</td>
<td>23.6</td>
</tr>
</tbody>
</table>

The major problem (except IPD) with these solvents was that most of them could only be used as a non-reactive solvent. During the hardening process these solvents could only act as a viscosity reducing agent and could not react with the epoxy resin. Due to the low amine value of the reaction product, the high amount of unreactive solvents would swell the cross-linked resin to an “organo-gel” like state. These solvents would only act as a reaction medium, and would need to be removed from the final product. IPD is a widely used epoxy cross-linker, it can react with epoxy groups and become part of the resin structure.

Table 4.3 Measured amine and calculated EG content of the cross-linker solutions

<table>
<thead>
<tr>
<th>PET:IPD 1:2 solution concentration (%)</th>
<th>Amine value (mmol g(^{-1}))</th>
<th>OH value (mmol g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.67±0.034</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>11.05±0.027</td>
<td>9.95</td>
</tr>
<tr>
<td>10</td>
<td>10.80±0.035</td>
<td>19.9</td>
</tr>
<tr>
<td>20</td>
<td>9.98±0.014</td>
<td>39.8</td>
</tr>
<tr>
<td>30</td>
<td>9.19±0.005</td>
<td>59.7</td>
</tr>
<tr>
<td>40</td>
<td>8.47±0.022</td>
<td>79.6</td>
</tr>
<tr>
<td>50</td>
<td>7.67±0.020</td>
<td>99.5</td>
</tr>
</tbody>
</table>
In addition, the cross-linker solutions with IPD could be easily prepared by introducing excess IPD at the end of the aminolysis process. Thus, the reaction product was dissolved in IPD and was utilized as a co-curing agent. Due to its chemical structure (longer molecule), the usage of the terephthal-amide-diamines could lower the cross-link density in the final epoxy resins. A cross-linker solution sequence of 0 to 50 weight % was prepared and was used in this study to characterize our reaction product as a cross-linker. The amine value of the solutions followed a linear declining tendency with increasing concentration (Table 4.3). The EG concentration of the cross-linker solutions was calculated based on the hydroxyl group content of the raw product. The mixing ratios were calculated, and several samples were prepared to study the thermal, thermomechanical, and mechanical properties of the epoxy resin systems.

4.3.4. Cross-linking characterization

Calorimetric and rheological measurements were carried out to characterize the cross-linker solution during curing reactions. The exothermic reaction heat was calculated from the integration of isothermal curing curves. Due to the similarity of the amine groups on IPD and the reaction product, a similar reaction rate is expected. Any differences in the reaction rate, compared to IPD, must be the result of the amidation and the catalytic effect of the EG and the terephthal-amide content. Several reaction processes can take place during the curing of epoxy resins with diamines. In our case these are the uncatalyzed reaction—the auto-catalyzed reaction by secondary hydroxyl groups; the catalyzed reaction by hydroxyl (EG) or amide groups; and the reaction of hydroxyl and epoxy groups 33,34. Inasmuch as the reaction catalyzed by ethylene-glycol and the terephthal-amide-diamines should be significantly faster and more dominant than the rest of the reaction processes.

Figure 4.9 Isothermal curing curves registered with DSC (a), the reaction enthalphy and the time belonging to the maximum (peak) of the isothermal curves.
A clear increasing tendency in the reaction heat, and the peak time was observed as a function of the concentration of the cross-linker solution (Figure 4.9 b). The initial peak during the isothermal step became well-defined. The time to reach the maximum of the heatflow curve decreased with a near linear tendency from 90 to 30 seconds. The heatflow curve reached a plateau sooner (Figure 4.9 a). These observations indicated the intensification of the reaction process with increasing concentration.

Rheological studies were conducted at 50 °C to measure and characterize the reaction kinetics and determine the gelation point of the resins. The curing reaction was slower at 50 °C and allowed a more precise measurement. Measuring the gelation at 90 °C was attempted (~2 min for 20% solution), but the fast reaction rate (near complete curing) endangered the instrument. The increased concentration of the cross-linker solutions resulted in faster cure rates, shift of the gelation (Figure 4.10), and the increase in the initial viscosity (Figure 4.11 a). The gel time was attributed to the cross point of fitted linears on the initial and precipitous parts of the curve. The gel time showed a significant 20 min decrease from 0% to 5% solution concentration, then it was followed by a linear decreasing tendency with the increasing solution concentration (Figure 4.11 b). The significant decrease between the 0-5 % points clearly demonstrates the catalytic effect of the aminolysis product. Even 5% of the product accelerates the reaction. To demonstrate, and model the catalytic effect of EG, three cross-linker solutions of EG in IPD were prepared and their gelation point was measured. The concentration of EG in these was based on the calculated amine/hydroxyl mol-ratio of the PET:IPD 1:2 solutions. Equivalents to the 10%, 30% and 50% solutions were prepared. The gelation of these samples was faster than the 0% (IPD) as expected, but only the 50% equivalent solution reached the reaction rate of the 5% PET:IPD 1:2 solution (Figure 4.10 and Figure 4.11 b). Since a strong hydrogen bond is needed between a glycidyl-ether and the catalyst, not just the EG, but the amide groups of the terephthal-amide-diamines act as catalysts during the curing reaction.
The catalytic effect of terephthal-amide-diamines gives significant, additional acceleration to the curing reaction. Even at small amounts terephthal-amide-diamines could act as modifiers for cycloaliphatic curing agents to accelerate the curing. Due to the faster curing rate of these systems a more perfect cross-linked structure is expected to form at the same conditions. This was further inspected with dynamic mechanical analysis (DMA).

![Graph](image)

**Figure 4.11** The initial viscosity of the resin mixtures (a) and the calculated gel times for PET:IPD 1:2 and IPD-EG model solutions (b).

**4.3.5. Dynamic mechanical analysis**

![Graph](image)

**Figure 4.12** The Storage (a) and Loss modulus (b) of epoxy specimen.
Figure 4.13 The tanδ curves of epoxy specimen before (a) and after post-curing (b).

Thermomechanical measurements were conducted via dynamic mechanical analysis (DMA). The dogbone shaped test specimens were moulded, cross-linked at 90°C for two hours. The specimens were cut to prismatic shape before measurements. 3-3 parallel specimen were tested. The storage modulus varied between 2.5-3.5 MPa at 30 °C for every sample (Figure 4.13 a). The differences of the specimens must come from the sample preparation. The storage modulus continuously decreased by increasing the measuring temperature. A major change in slope occurred above 100 °C that indicated the approximation of the glass transition temperature. Another change of slope around 130 °C occurred that indicated that a not perfect cross-linked structure formed during the curing of the specimens. Both the loss modulus and the tanδ curves indicated this (Figure 4.13 b, Figure 4.14 a). In both cases peaks with shoulders can be observed in the 100-160 °C interval. The peak of a tanδ curve is associated with the glass transition temperature of a sample. The registered peaks shifted to lower temperatures with the concentration of the PET:IPD 1:2 in the cross-linker solutions, thus the glass transition temperature decreased. The main peak shifted at a greater extent than the shoulder peak, the shoulder peak became less-well defined. Both the storage-, loss modulus and their ratio, the tanδ indicated a more uniform structure with higher PET:IPD 1:2 concentrations. As we have assumed, the cross-linked structure improved, became more perfect at the same curing conditions due to the catalytic effect of the raw aminolysis product.
Figure 4.14 The glass transition temperature determined with DMA and DSC measurements.

The presence of longer terephthal-amide-diamines resulted in the decrease of the glass transition temperature. The longer cross-linker molecules decreased the cross-link density of the resins, and as their concentration increased their effect became more dominant. A slight increase in the storage modulus was detected above 150 °C that indicated post-curing during measurements. The effect of post-curing was investigated with DMA on post-cured specimens (170-180 °C for 1 hour) (Figure 4.14). The glass transition temperature followed a near-linear decreasing tendency in all cases (Figure 4.14). The glass transition temperature as expected increased with post-curing. The glass transition temperature of the post-cured specimen correlated with T_g values determined by DSC measurements. The calculated cross-link density (ν) of the samples scattered with the increasing concentration of the reaction product due to post-curing during the measurement. The post-cured specimens showed a clear decreasing tendency in cross-link density with the concentration of the solutions. The tanδ values decreased with post-curing (Table 4.4). The cured specimens showed good thermal stability. The thermal degradation occurred near 350-360 °C.
Table 4.4 Storage modulus, tanδ and cross-link density of the epoxy specimens determined with DMA

<table>
<thead>
<tr>
<th></th>
<th>Cured</th>
<th>Post-cured</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Storage Modulus</td>
<td>Storage Modulus</td>
</tr>
<tr>
<td></td>
<td>(GPa) [40 °C]</td>
<td>(GPa) [40 °C]</td>
</tr>
<tr>
<td></td>
<td>(MPa) [200 °C]</td>
<td>(MPa) [200 °C]</td>
</tr>
<tr>
<td>tanδ</td>
<td>(mol m⁻³)</td>
<td>tanδ</td>
</tr>
<tr>
<td>υ</td>
<td>(mol m⁻³)</td>
<td>υ</td>
</tr>
<tr>
<td>0%</td>
<td>3.52 36.35</td>
<td>2.89 31.81</td>
</tr>
<tr>
<td></td>
<td>1.204 9240.5</td>
<td>0.997 8086.4</td>
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<tr>
<td>5%</td>
<td>2.76 25.21</td>
<td>2.72 29.49</td>
</tr>
<tr>
<td></td>
<td>1.199 6408.6</td>
<td>0.985 7496.6</td>
</tr>
<tr>
<td>10%</td>
<td>2.85 27.52</td>
<td>2.43 27.06</td>
</tr>
<tr>
<td></td>
<td>1.090 6995.8</td>
<td>0.922 6878.9</td>
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<tr>
<td>20%</td>
<td>1.79 26.43</td>
<td>2.50 26.17</td>
</tr>
<tr>
<td></td>
<td>1.199 6718.7</td>
<td>0.938 6652.7</td>
</tr>
<tr>
<td>30%</td>
<td>3.04 25.56</td>
<td>2.67 24.96</td>
</tr>
<tr>
<td></td>
<td>1.230 6497.6</td>
<td>0.924 6345.1</td>
</tr>
<tr>
<td>40%</td>
<td>1.89 26.05</td>
<td>2.59 23.64</td>
</tr>
<tr>
<td></td>
<td>1.140 6622.1</td>
<td>0.840 6009.5</td>
</tr>
<tr>
<td>50%</td>
<td>2.61 16.80</td>
<td>2.56 16.91</td>
</tr>
<tr>
<td></td>
<td>0.826 4270.7</td>
<td>0.837 4298.7</td>
</tr>
</tbody>
</table>

4.3.5. Mechanical properties

The standard tensile tests and instrumented impact resistance measurements were conducted to characterize the mechanical properties of the moulded epoxy specimens (Table 4.5). The test temperature was far below the \( T_g \) of the specimens. Thus, the data were expected to scatter and mostly depend on the flaws of the moulding. Due to the increasing initial viscosity of the resin systems the degassing became less-effective. The more concentrated the cross-linker solution was the more bubbles remained within the resin mixture. In the case of the 40% and 50% specimens near flawless specimens could not be obtained. These bubbles acted as flaws during mechanical testing and decreased the mechanical properties. In future studies and applications, low molecular weight reactive diglycidyl-ether diluents will be needed to lower the initial viscosity of the resin mixture to insure flawless moulding. In this study no reactive diglycidyl-ether diluents were used to consistently report the properties of the cross-linked resins. As expected from an epoxy resin the specimen showed rigid behavior. The impact test showed no significant difference between the different resin mixtures (Figure 4.15). The pure IPD cross-linked samples had the highest impact resistance due to the lack of bubbles in the specimens.
Figure 4.15 The impact resistance, maximum registered force at failure (a) and fractographs (b) of the epoxy specimens

Table 4.5 Tensile test data of the epoxy specimen

<table>
<thead>
<tr>
<th>PET:IPD 1:2 solution concentration (%)</th>
<th>Young’s Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.58±0.04</td>
<td>67.56±15.77</td>
<td>2.64±0.58</td>
</tr>
<tr>
<td>5</td>
<td>3.42±0.14</td>
<td>68.45±4.49</td>
<td>3.13±1.82</td>
</tr>
<tr>
<td>10</td>
<td>3.56±0.11</td>
<td>67.65±4.49</td>
<td>2.51±1.19</td>
</tr>
<tr>
<td>20</td>
<td>3.55±0.12</td>
<td>67.86±5.15</td>
<td>2.46±0.60</td>
</tr>
<tr>
<td>30</td>
<td>3.29±0.21</td>
<td>45.37±4.50</td>
<td>1.60±0.25</td>
</tr>
<tr>
<td>40</td>
<td>3.67±0.10</td>
<td>63.75±1.74</td>
<td>2.31±0.11</td>
</tr>
<tr>
<td>50</td>
<td>3.02±0.12</td>
<td>27.47±17.45</td>
<td>3.21±3.68</td>
</tr>
</tbody>
</table>
4.4. Conclusions

The purpose of this study was to investigate the use of raw aminolysis products as cross-linking agents for epoxy resins. The authors proposed the accelerative nature of the EG side product, and the terephthal-amide-diamine main products during the epoxy curing reaction.

The aminolysis of PET was carried out with an epoxy hardener, isophoron-diamine. The raw reaction product was further used without any purification steps. The chemical structure of the produced terephthalic-amide-diamines was identified with NMR measurements. Full assignment of the spectra was done based on the correlative 2D-NMR spectra ($^1$H-$^1$H COSY, $^1$H-$^1$H NOESY, $^1$H-$^{13}$C HSQC, $^1$H-$^{13}$C HMBC and $^1$H-$^{15}$N HMBC). Cross-linker solutions of the aminolysis product with IPD were prepared (0-50 weight %) and used for the curing of the epoxy resins. The solutions were easy to prepare with additional IPD during or right after the aminolysis process. The curing of the epoxy resin was characterized with isothermal DSC (at 90 °C) and rotational viscosimetry (at 50 °C) measurements. The reaction heat was found to increase with the concentration of the cross-linker solution. The rotational viscosimetry measurements showed a significant acceleration effect of the aminolysis product on cross-linking. The catalytic effect of the terephthal-amide-diamines was demonstrated using model IPD-EG solutions. The results clearly proved the catalytic behavior amides, it clearly exceeded the model IPD-EG solutions. The results of the thermomechanical measurements showed decrease in the glass transition temperature of the epoxy resins. The longer terephthal-amide molecules, compared to IPD formed longer links between the polymeric chains. The concentration of the aminolysis product increased the number of longer cross-links, thus the cross-link density decreased. The mechanical properties at room temperature showed no significant change with the concentration of the cross-linker solutions. The resins showed rigid behavior, any loss in mechanical properties can be attributed to the flaws (bubbles) from the preparation and curing processes.

The findings of this study showed a simpler, greener way to process and use PET aminolysis products. The lack of expensive purification steps even proved to be advantageous during the epoxy curing reaction, and provided a faster curing for IPD based epoxy systems.
4.5. References

Chapter 5

Synthesis and characterisation of isphorondiamine based oligoamides: catalytic effect of amides during the curing of epoxy resins

5.1. Introduction

Epoxy resins are versatile materials, they have excellent physical and chemical properties that make them perfect for various uses. Their properties can be fine-tuned by changing their precursor components and their cure circumstances. Usually various amines, anhydrides and acids are used to cross-link the epoxy (diglycidyl-ether) components. During the curing reaction the glycidyl-ether reacts with the cross-linker via a ring-opening addition reaction. The reactivity of the cross-linking agent determines the processing and curing of the resins. Several publications have shown and studied the curing, reactivity, and reaction mechanism of epoxy systems. The ring-opening of the glycidyl-ethers can be enhanced with catalyst that can form hydrogen bonds with the glycidyl-ether ring. Without any additional catalyst, the curing reaction produces secondary hydroxyl groups from the ring-opening of the glycidyl-ether groups. Thus, the curing of the epoxy resins is autocatalytic, and it could be further enhanced by introducing additional catalytic compounds, accelerators into the resins system. The following hydrogen bond donors were found to accelerate the reaction of epoxy compounds and amines (listed from the most effective to the least effective): \(\text{-OH (Ph-}>\text{PhCH}_2\text{-}>\text{RCH}_2\text{-}>\text{H})\), \(-\text{COOH}, -\text{SO}_3\text{H}, -\text{CONH}_2, -\text{SO}_2\text{NH}_2\). These hydrogen bond donors are mostly considered accelerators by the literature, not catalyst (tertiary amines, imidazols and ureas) since they could react with the epoxy derivatives.

In our previous study we have synthesized terephthal-amides via the aminolysis of PET with isophorondiamine (IPD). These terephthal-amides were proven to have a considerably accelerative effect on the curing of epoxy resins. So far there has been little discussion about the use of PET aminolysis products in epoxy curing, and there is no record on their catalytic, accelerative effect nor on its quantitative description. Nevertheless their hydrogen donor capabilities are well described and has a decisive role in polyamides and their derivatives. Most of the aminolysis related articles focused on the catalysis of the solvolysis reaction; or various uses such as PVC plasticizer, dyes and anticorrosive components of paints, drugs with anti-bacterial and anti-inflammation effects; and alkyd resin components. Almost all of these studies utilized high ratio of amines (1:3 – 1:7 ester-amine ratio) and various purification steps to gain their final product. This concept has recently been challenged in our recent studies and we have tried to make use of raw solvolysis products and apply as low amount of reagents as possible.
In this study we have further attempted to reduce the used amount of diamine in an aminolysis reaction to obtain higher molecular weighed oligoamides. Three different ratios of PET and isophorondiamine were used (1:1, 1:1.5 and 1:2) (Figure 5.1). The produced aminolysis products were characterized with functional group analysis, thermal gravimetric analysis (TGA), Fourier transformation infrared spectroscopy (FTIR), solution capillary viscosimetry, nuclear magnetic resonance spectroscopy (NMR), and matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF) measurements.

Figure 5.1 Terephthal-amide production from the aminolysis reaction of PET without excess IPD

The main focus of this study was to quantitively characterize the accelerative effect of the produced terephthal-amides during epoxy curing. Two solutions series in IPD were prepared of the 1:1.5 and 1:2 reaction products and were used as amine cross-linkers in the curing of epoxy resins. The accelerative effect of the cross-linker solutions was studied with rotational viscosimetry and differential scanning calorimetry (DSC). The reaction kinetics of the curing was studied at 40 °C, 60 °C, 80 °C, 90 °C and 100 °C. Kamal-Sourour and its revised forms were used to determine the reaction rate and activation energy of the curing reaction. Density functional theory (DFT) and local coupled cluster (CC) quantum chemical methods were used to calculate and compare the accelerative effect of the terephthal-amides to other accelerators, catalyst.

5.2. Experimental

5.2.1. Materials

DSM Arnite® D00 301 PET granules were used for PET aminolysis (28.5±1.5 % crystallinity). Isophorondiamine IPOX® ER 2943 (IPD) (η: 5-25 mPas, ρ: 0.92 g cm⁻³, Amine value: 645-675 mgKOH g⁻¹), and bisphenol-A-diglycidyl-ether IPOX® EH1010 (η: 10000-14000 mPas, ρ: 1.17 g cm⁻³, EE: 180-196 g mol⁻¹) were purchased from Ipox Chemicals. Zink-acetate (Zn(OAc)₂·2H₂O) was purchased from BDH Chemicals. Pyridine (99%), N,N-dimethyl-formamide (99%)(DMF), potassium hydroxide (99%), hydrochloric acid (37%) and phthalic anhydride (99%) were purchased from Molar Chemicals. DMSO-d6 (99,9%) was purchased from Sigma Aldrich.
5.2.2. Aminolysis of PET with IPD

Aminolysis of PET was carried out in a 100 cm$^3$ round bottom four-necked glass flask equipped with a mechanical stirrer, thermometer, gas inlet (Ar gas), and reflux condenser. 50 g PET and 0.5 g zinc-acetate were weighed in the glass flask. The amount of IPD was calculated to the ester groups of the weighed in PET granules to 1:1, 1:1.5, and 1:2 ratios. No excess IPD was used during the aminolysis reaction. The reaction mixture was heated to 200 °C and was kept there for 4 hours. The viscous yellowy melt at the end of the reaction was poured into an alumina pan. The reactions’ products were used without any purification.

5.2.3. Characterization of oligo-terephthalamides

Amine and hydroxyl functionality were determined with titration methods. 3-3 parallel samples of 0.1-0.2 g weighed with analytical accuracy, were dissolved in DMF. The 3-3 and the blank samples were titrated with 0.1 M hydrochloric acid to determine the amine content. Three drops of bromocresole-green solution were added and used as an indicator. The hydroxyl content was determined with a back-titration method. 3-3 parallel samples of 1.8-2.0 g weighed with analytical accuracy were dissolved in 25 cm$^3$ 1 M phthalic-anhydride solution in pyridine. The 3-3 parallel and a blank sample were refluxed at 110 °C in oil baths for 2 hours. As the samples cooled down 50 cm$^3$ pyridine was added through the condenser. The samples were titrated with 0.5 M aqueous NaOH solution. Phenolphthalein was used as an indicator.

Solution viscosimetry was used to compare the molecular weight of the aminolysis products. A 5-point solution series was used (0.02, 0.04, 0.06, 0.08 and 0.10 g cm$^{-3}$) to determine the intrinsic viscosity of the 1:1.5 and 1:2 ratio samples. The samples were weighed in Erlenmeyer flasks with analytical precision and were dissolved in ethanol. The samples were refluxed for 30 minutes to dissolve the reaction products. The samples were measured at 40 °C in an Ubbelohde type capillary viscosimeter. The intrinsic viscosity of the samples was calculated from the reduced and relative viscosity of the concentration series.

A Brucker Tensor 27 FTIR spectrometer was used to measure the FTIR spectra. The products were measured in KBr pastilles. 28 parallel scans were made between 4000-400 cm$^{-1}$ interval. $^1$H, $^{13}$C, $^1$H-$^1$H COSY, $^1$H-$^1$H NOESY, $^1$H-$^{13}$C HSQC and $^1$H-$^{13}$C HMBC NMR spectra were recorded with a Bruker Avance 300 spectrometer. The 50 mg samples were dissolved in 1 cm$^3$ of DMSO-d6.

The mass spectrometric measurements were carried out with a Bruker Autoflex Speed MALDI-TOF instrument. Ion source voltage 1, ion source voltage 2, reflector voltage 1, and reflector voltage 2 were 19 kV, 16.65 kV, 21 kV and 9.55 kV, respectively. The instrument was equipped with a solid phase laser (355 nm) operating at 1000 Hz. For each measurement 5000 shots were summed. The MALDI spectra were calibrated with PEG standards. The samples, the matrix (2,5-dihydroxybenzoic acid), and the ionizing agent (sodium trifluoroacetate) were solved at a concentration of 5 mg cm$^{-3}$, 20 mg cm$^{-3}$ and 5 mg cm$^{-3}$ in THF, respectively. The mixing ratio was 2:10:1 (sample, matrix, ionizing agent). A volume of 0.2 mm$^3$ of the solutions was deposited onto a MALDI target plate and allowed to air-dry.
The reaction products were purified before the NMR measurements. The reaction products were first dissolved in ethanol, then the solution was dropwise added to distilled water to precipitate the terephthal-amides. The precipitate was washed thoroughly with water to remove the EG. The precipitate was dissolved in ethanol, the solvent was removed with a vacuum apparatus. At the end of the purification steps amorphous, yellowy powder was obtained.

5.2.3. Epoxi preparation and characterization

A solution series of the 1:1.5 and 1:2 ratio aminolysis products were prepared to use as cross-linking agents. The 1:1.5 reaction product was dissolved in the commercial IPD to gain 5, 10, 15, 20, and 30 % solutions. The 1:1.5 15% and 30% solutions were used for the reaction kinetics study. The 1:2 ratio reaction product was used to produce 30% and 50% solutions with IPD for reaction kinetics measurements. The reaction products and the IPD were weighed in with analytical accuracy in Erlenmeyer flasks. The flasks were equipped on reflux condensers and were heated with an oil bath to 110-120 °C. The solutions were heated, stirred with a magnetic stirrer, and let to reflux until no solid residue remained in the flasks. The 1:1.5 solutions took 3-4 hours to completely dissolve, while the 1:2 solution took only 1 hour. The amine content of the solutions was measured as previously described. It must be noted that, since the aminolysis products were used without any purification steps the residual zinc-acetate catalyst from the aminolysis reaction might influence the curing of the epoxy specimen. The effect of zinc-acetate was not investigated in this thesis. The theoretical concentration of the salt in the cross-linker solutions is between 0.02-0.2 m/m% interval.

The epoxy value of the base resin was measured with a back-titration method. Pyridine-hydrochloride reagent solution in pyridine was prepared by dissolving 16 cm$^3$ concentrated hydrochloric acid in 1 dm$^3$ pyridine. 0.1-0.2 g samples of the epoxy resin were weighed in Erlenmeyer flasks and were dissolved in 25 cm$^3$ of pyridine-hydrochloride solution in pyridine. The samples were let to reflux for 1 hour, then after they cooled down, 10 cm$^3$ distilled water was added through the condenser. 0.1 M sodium hydroxide solution (in methanol) was used to titrate the samples in the presence of phenolphthalein indicator. The stoichiometric ratios of the epoxy resin and the amine cross-linkers were calculated based on the measured functionality. All the prepared resin samples were mixed according to the calculated 1:1 stoichiometric ratios. The epoxy samples were prepared in plastic cups. The epoxy base resin was weighed in a cup and the stoichiometric amount of the cross-linker solution was weighed with analytical precision. The epoxy resin was vigorously mixed with a glass rod for 3 minutes.

PerkinElmer DSC7 was used for the reaction kinetics study. After the 3 minutes long mixing period, an 8-10 mg sample was weighed in an alumina sample pan. Reaction kinetics studies were conducted on the commercial IPD (0 %); the 15 % and 30 % 1:1.5 solutions; and the 30 % and 50 % 1:2 solutions. The epoxy curing reaction was studied at 5 different reaction temperatures, respectively at 40 °C, 60 °C, 80 °C, 90 °C and 100 °C with the following heat cycle. The samples were kept at 30 °C for 0.5 min than it was heated to the cross-linking temperature with 200 °C min$^{-1}$ heating rate and were kept there for 2 hours. Then the samples were cooled down to 0 °C with 20 °C min$^{-1}$ heating rate.
and were kept there for 1 minute. Then the samples were heated up to 250 °C with 20 °C min⁻¹ and kept there for 1 minute. The $T_g$-onset value and the residual reaction heat was determined from this heating period. The samples cooled down to 0°C with 20 °C min⁻¹ heating rate, then they were kept there for 1 minute and were heated back to 250 °C with 20 °C min⁻¹ heating rate. The residual ($\Delta H_{\text{res}}$) and total ($\Delta H_{\text{total}}$) reaction heat (see below) were used to calculate the conversion ($\alpha$) of the curing. The $d\alpha/dt$ function was calculated from the numerical derivate of the isothermal heatwave-time curve. The $T_g$ of the 1:1.5 0-30% series was determined from the last heating period (the isothermal step was at 90 °C).

The total reaction heat of the cross-linking reaction was determined via a screening method. The samples (3-5 mg) were kept at 30 °C for 0.5 mins then were cooled down to 0 °C. Then the samples were heated with 20 °C min⁻¹ heating rate to 250 °C and were kept there for 1 minute. The total reaction heat was determined from the exothermal peak located at this period. Then the samples cooled to 0 °C with 20 °C min⁻¹ and were kept there for 1 minute. The cooling curves were checked for any residual reaction heat. The samples were then heated up to 250 °C with 20 °C min⁻¹.

5.2.4. Quantum chemical computation

The geometry optimizations, transition state searches, and frequency calculations were carried out using the B3LYP functional 55 with the 6-31G(d,p) basis set 56 utilizing the Gaussian 09 quantum chemistry program 57. The Gibbs free energy barrier ($\Delta G(298K)$) of the reactions were calculated as $\Delta G(298K) = \Delta E_e + \Delta E_{ZPE} + \Delta G_{0\rightarrow298}$, where $\Delta E_e$ is the difference of electronic energies, $\Delta E_{ZPE}$ is the difference of zero-point vibrational energies, while $\Delta G_{0\rightarrow298}$ is the difference of thermal corrections to free energy between the initial and transition states. To improve the accuracy of the results single-point calculations were performed for the preferred reaction path using the local natural orbital coupled-cluster singles, doubles, and perturbative triples [LNO-CCSD(T)] method 58 with the aug-cc-pVTZ basis set 59 using of the MRCC program suite 60. Then, the B3LYP/6-31G(d,p) electronic energy was replaced with the obtained LNO-CCSD(T)/aug-cc-pVTZ electronic energy to get the improved free energy barrier.

5.3. Results and discussion

5.3.1. Oligo-terephthalamides characterization

Functional group analysis, FTIR and TGA measurements were used to determine the success of the aminolysis reaction. The measured amine values decreasing with the ratio of IPD. This suggests that different molecular weighed terephthal-amides were produced (Table 5.1). Based on the measured amine values the main components of the 1:1.5 and 1:2 reaction should be the monomer (4.26 mmol g⁻¹, 470.69 g mol⁻¹) and dimer (2.60 mmol g⁻¹; 771.09 g mol⁻¹) terephthal-amil derivates. The molecular weight difference between the two products was also confirmed with solution viscometry. The intrinsic viscosity of the 1:1.5 product was found to be significantly higher than the 1:2 ratios
products. The hydroxyl content of the reaction products comes from ethylene-glycol. The OH content of the 1:2 and 1:1.5 ratio reaction products were 80-90% of the theoretical maximum that derives from the weighed in PET granules. The hydroxyl content of the 1:1 ratio product was 43%.

Table 5.1 Functional group content and intrinsic viscosity of the aminolysis products

<table>
<thead>
<tr>
<th>PET: Amine ratio</th>
<th>Amine content (mmol g⁻¹)</th>
<th>OH content (mmol g⁻¹)</th>
<th>Intrinsic viscosity (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>1.12±0.74</td>
<td>2.39±0.398</td>
<td>-</td>
</tr>
<tr>
<td>1:1.5</td>
<td>2.38±0.05</td>
<td>3.49±0.019</td>
<td>0.0437</td>
</tr>
<tr>
<td>1:2</td>
<td>3.65±0.26</td>
<td>3.89±0.013</td>
<td>0.0119</td>
</tr>
</tbody>
</table>

Figure 5.2 FTIR spectra of the aminolysis products and the PET granules

In the cases of 1:1.5 and 1:2 no residual ester groups were present, the total amidation was achieved (1640 cm⁻¹ amide carbonyl valence vibration, 1549 cm⁻¹ N-H plain bending deformation). The ester attributed peaks (1720 cm⁻¹ ester carbonyl valence vibration, 1530 cm⁻¹ ester C-O-C bending vibration) were absent from their FTIR spectra. The characteristic end-group (-Ph-COO-CH₂-CH₂-OH) rocking vibrations of PET at 720 cm⁻¹ disappeared in the aminolysis products. The 1:1 reaction mixture was highly viscous at the reaction temperature, and the reaction was hard to manage. This ratio probably resulted in even longer oligomer chains, that had residual ester linkages as its FTIR spectrum suggested (Figure 5.2). The ratio of the used IPD was too low for any practical use. Due to the presence of residual ester groups the 1:1 ratio was not studied further. Only functional group analysis, FTIR and TGA measurements were done on the 1:1 ratio product. The
TGA measurements of the aminolysis products further supported the success of the aminolysis reactions (Figure 5.3). The 1:1.5 and 1:2 reaction products showed two distinct peaks in their DTG curves. The terephthal-amides showed high thermal stability (~460 °C), only the evaporation of the ethylene-glycol could be observed in their TGA curves below their thermal degradation. On the contrary, the 1:1 ratio product showed a shoulder at lower temperatures (~410 °C) that suggested the presence of less thermally stable components or segments, probably esters in the reaction product. The volatile component content of the aminolysis products increased (15.2 %, 20.8 % and 34.7 % weight loss at 350 °C) respectively with the increasing IPD ratio. Below 200 °C the aminolysis products had a similar behavior.

**Figure 5.3 TGA and DTG curves of the aminolysis products**

### 5.3.2. Molecular structure characterization of the aminolysis products

NMR spectrometry was used to compare the 1:1.5 and 1:2 ratio reaction products. 2D correlative NMR spectroscopy measurements ($^1$H-$^1$H COSY, $^1$H-$^1$H NOESY, $^1$H-$^{13}$C HSQC, $^1$H-$^{13}$C HMBC) were done to fully assign the spectra of the 1:1.5 ratio product. The 1:2 ratio reaction was thoroughly studied and fully assigned in our previous work. For the 2D correlative spectra of the 1:1.5 reaction product see the supplementary information. The hydrogen and carbon atoms were numbered as shown in Figure 5.4. In both cases, we looked for traces of the amidation in the NMR spectra in comparison of the reagent IPD. The chemical shift of the IPD related hydrogen and carbon atoms changes due to the amidation. Slight changes in chemical shifts and peak duplication appeared in the case of the methyl groups (4i$_{ekv}$, 5j$_{ax}$ and 7h).
Figure 5.4 The $^1$H NMR spectrum of PET:IPD 1:1.5 and the used numbering (numbers for H, alphabet for C) on the theorized reaction product.

Figure 5.5 $^{13}$C spectrum of the 1:1.5 depolymerization product.

Low intensity peaks around the a, c, e, i, j, and h main peaks can be observed in the $^{13}$C spectra of both reaction products (Figure 5.5). These low intensity peaks indicate the slight chemical shift changes of the carbon atoms due to the amide group formation on one or both amine groups. The carbon and hydrogen atoms near the amide groups (2b, 8g) showed the most significant change in their chemical shifts in the $^1$H and $^{13}$C spectra. The 2, 2’, 8, and 8’ peaks in the $^1$H were integrated for quantitative analysis. An amine/amide ratio was calculated for both groups to compare the reactivity of the different amines, the average amidation percentage and the number average molar masses of the aminolysis products. As Table 5.2 shows the amide ratio changed with the initial ratio of PET and IPD. The cycloaliphatic connected amine groups (2) showed – as expected –
lower amine/amide ratio than the aliphatic connected amine groups (8). Overall the higher aspect of amide ratio in 1:1.5 reaction product suggests a higher molecular weight as well. The 1:1.5 product showed worse solubility in both ethanol and IPD than the 1:2 ratio product. The specific viscosity of the samples measured in ethanol at 40°C further supported this observable difference (Table 5.1). The calculated number average molar masses suggest that the 1:1.5 reaction product is mostly a mixture of the dimer (771.09 g mol⁻¹) and trimer (1071 g mol⁻¹), and the 1:2 reaction product is mostly a mixture of monomer (470.69 g mol⁻¹) and dimer. Due to their rather high molecular weight we will refer to the dimers, trimers or any longer chained species collectively as oligomers.

As seen in Figure 5.6, one main series appeared in both MALDI-TOF spectra (PET:IPD, 1:1.5 and 1:2). Those series were identified as terephthal-amide oligomers where the composition of the monomer unit is the following ((C₁₀H₁₉N)(C₈H₅O₂N) (arrows in Figure 5.6 a and b). The end groups are hydrogen and isophorondiamine as it is presented in Figure 5.6. The measured m/z values are in good agreement with the simulated ones. For example, the m/z of the oligomer with polymerization degree of 3 is 1093.719 (simulated) while the measured mass is 1093.731. Beside the accurate mass, the isotopic distribution supports the chemical composition of [C₁₀H₂₁N₂((C₁₀H₁₉N)(C₈H₅O₂N))₃H+Na]⁺ for that adduct ion. As a minor series, the terephthal-amide oligomers appeared with hydroxyl and hydrogen end groups indicated by red color in Figure 5.6 a and b. As it turns out from Figure 5.6, the higher PET:IPD ratio (Figure 5.6b) results in higher molecular weight products up to m/z 3000. The number and weight average molecular weights were determined based on the main series. The number average molecular weights are 1040 g mol⁻¹ and 860 g mol⁻¹ for PET:IPD 1:1.5 and 1:2, respectively (Table 5.2.).
Table 5.2 Quantitative characterization of the $^1$H spectra of the reaction products and calculated number average molecular weights (NMR and MALDI-TOF)

<table>
<thead>
<tr>
<th>PET:IPD</th>
<th>$^1$H integral</th>
<th>$2/2'$ amine/amide ratio</th>
<th>$8/8'$ amine/amide ratio</th>
<th>$\overline{M}_n$ ($g , mol^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1.5</td>
<td>1.07 1.43 0.45 4.13</td>
<td>42.8/57.2</td>
<td>9.8/90.2</td>
<td>980.29 1040</td>
</tr>
<tr>
<td>1:2</td>
<td>0.82 1.10 1.22 2.91</td>
<td>57.3/42.7</td>
<td>29.5/70.5</td>
<td>569.53 860</td>
</tr>
</tbody>
</table>

5.3.3. Cross-linkers effect on gelation and glass transition

Table 5.3 Amine content of the cross-linking agents

<table>
<thead>
<tr>
<th>Cross-linker</th>
<th>Concentration (%)</th>
<th>Amine content (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPD</td>
<td>0</td>
<td>11.58±0.033</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>11.09±0.204</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10.62±0.065</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>10.16±0.056</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>9.85±0.115</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8.77±0.072</td>
</tr>
</tbody>
</table>
| PET:IPD solution series | 1:1.5 | 30 9.19±0.050  
|              | 50                | 7.67±0.020                    |

The amine values of the cross-linker solution series can be found in Table 5.3. The 1:1.5 solution series followed a linear decreasing trend with the increasing concentration of the dissolved reaction product. In our previous work we tested the catalytic effect of the terephthal-amides with gel time measurements and reaction heat measurements with DSC. A solution series of a PET:IPD 1:2 ratio reaction product and a model IPD-EG solution series were studied. We found that the terephthal-amides solutions have a significant accelerative effect on the curing of epoxy resins. Since the amide group cannot react with the glycidyl-ether groups these molecules should be considered catalysts beside their role as a cross-linker.

The gel point data of the 1:2 and IPD-EG solution series were added to Figure 5.7 as reference 37. The gel time of the 1:1.5 solution series followed a near linear, declining tendency but compared to 1:2 series from our previous study higher gel time was achieved. This result may be explained by the fact that the 1:1.5 reaction product has higher molecular weight than the 1:2 ratio product. The higher molecular weight of the 1:1.5 product probably slowed down the diffusion of the amide groups and restricted their availability in the system. Since the amide groups are connected (oligomers) their distribution in the reaction medium is not as homogenous as the lower $M_w$ amides. It can therefore be assumed that the longer oligoamides should have lower catalytic activity. Both reaction solution series had faster gelation time than the IPD-EG model solution series.
The IPD-EG solution were designed to have an equivalent concentration of EG as a PET:IPD 1:2 solution \(^{37}\). This clearly demonstrates the catalytic effect of the amides. To thoroughly characterize this effect isothermal kinetic studies were carried out with DSC. The conversion \(\alpha\) of the isothermal curing was determined with the following equation:

\[
\alpha = \frac{(\Delta H_{total} - \Delta H_{res})}{\Delta H_{total}}
\]

The isothermal heatwave-time functions were calculated to conversion-time \(\alpha(t)\) functions. Numerical derivates were calculated to determine the \(d\alpha/dt (\alpha)\) functions to characterize the reaction kinetics.

![Figure 5.7 Gel time of epoxy resins cross-linked with the PET:IPD and the IPD-EG model solution series. The hollow points are used as a reference from our previous study\(^{37}\) (see chapter 4).](image)

The conversion dependence of the glass transition temperature in cross-linked systems is generally agreed on. The glass transition of a curing system approximates the equilibrial \(T_g\) with the increasing conversion. The \(T_g\) onset of the studied systems was measured and an increasing tendency was found with the conversion level (Figure 5.8 (a)). In our previous study we showed that terephthal-amides have a decreasing effect on the glass transition in IPD based epoxy systems. Due to the higher molecular weight of the cross-linking agent (compared to IPD) the cross-link density decreases, and as a result the \(T_g\) decreases as well \(^{37}\). In this study a five-point concentration series was prepared of the 1:1.5 reaction product to study the effect of longer crosslinker molecules on the \(T_g\) (Figure 5.8 (b)). Due to the even higher molecular weight of the 1:1.5 reaction product the glass transition temperature considerably decreased at a narrower concentration interval. The \(T_g\) values of the 1:2 reaction series of our previous work was added as reference \(^{37}\).
5.3.4. Epoxy crosslinking kinetics characterization

Five different cross-linkers were compared in our kinetics study at five different curing temperatures. Commercial IPD (IPOX® ER 2943) was used as a reference. 1:2 30 % and 50 % solutions and 1:1.5 15% and 30% solutions were used to quantitatively compare the reaction products and the reference material. Figure 5.9 demonstrates the differences between the IPD and the terephthal-amide solutions((a) IPD, (b) 1:1.5 solutions, (c) 1:2 solutions). Just as the gelation measurements suggested the terephthal-amide solutions proved to be more active during cross-linking than the IPD. The reaction rate increased with the cross-linking temperature and in almost all cases the IPD < 1:1.5 < 1:2 trend can be observed.
Isophorondiamine base oligoamides: catalytic effect during epoxy curing

Figure 5.10 The \( \frac{d\alpha}{dt} (\alpha) \) functions plotted at different curing temperatures.

Figure 5.10 is used to compare the cross-linkers at different curing temperatures. The commercial IPD was the least active and the 1:2 50 % solutions were the most active at all the curing temperatures. The 1:1.5 15 % solution was the least active among the terephthal-amide solutions. The 1:1.5 30 % and 1:2 30% solutions “competed”, at the early stages of the reaction (\( \alpha = 0-0.4 \)). The 1:2 30% solution showed higher activity at 60 °C, 80 °C and 90 °C. 1:1.5 30% and 1:2 30% solutions had similar reactivity at 100 °C. These trends and activity ranking were completely disrupted at 40 °C because the curing reaction was substantially governed by diffusion. The amide catalytic effect kick-started the reactions even at this low temperature, but the high molecular weighed components significantly increased the viscosity and diffusion rates. Thus, almost none of the samples except 1:2 30 % could achieve higher than 60 % conversion. Since the viscosity of this sample is lower than any of the used terephthal-amide solutions (see supplementary information) the amide catalytic effect might have been able to push the reaction further to a higher conversion rate.\(^{37}\). The conversion rate increased with the curing temperature and approximated 100 %. The \( \frac{d\alpha}{dt} (\alpha) \) functions of the least active cross-linkers showed a plateau like behavior. This indicates a decrease in the activity of the reaction and the increasing influence of diffusion during curing. The slope of the \( \frac{d\alpha}{dt} (\alpha) \) functions started to follow a near linear declining trend around a 40% conversion rate. At higher temperatures (80 °C, 90 °C and 100 °C) a second change of slope can be observed around 60% conversion rate that indicated the slowing down of the reaction.

Three kinetic models, the Kamal-Sourour (eq. 1)\(^{26,27}\), a revised Kamal model by Cole diffusion factor (\( f_d(\alpha) \)) (eq. 2)\(^ {29} \) and revised Kamal model by Fournier diffusion factor (eq. 3)\(^ {31} \) were used to fit to the \( \frac{d\alpha}{dt} (\alpha) \) functions. The revisions on the Kamal-Sourour model serve as a way to consider the diffusion-controlled regime of the curing
reaction with a $f_\alpha(\alpha)$ function. The $k_1$ and $k_2$ are the kinetic rate constants of the uncatalyzed and autocatalyzed reaction respectively. The $n$ and $m$ are fitting parameters thought to be connected to the order of the reaction $(n+m)$, they allow a more precise fitting. As the reaction progresses the increase in molecular weight slows down the reaction. The $\alpha_c$ parameter in eq. 2 is defined as the critical conversion point where the diffusion control becomes dominant over chemically controlled regime. The $C$ is a fit parameter. The $\alpha_f$ in eq. 3 is not a fit parameter, it is the maximal conversion that was achieved during the isothermal curing. The $b$ parameter is a fit parameter. Since eq. 2 and eq. 3 are quite similar the $C\approx b^{-1}$ relationship is expected.

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n$$ (1)

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \left(1 + \exp(C(\alpha - \alpha_c))\right)^{-1}$$ (2)

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \left(2 \left(1 + \exp\left(\frac{\alpha - \alpha_f}{b}\right)\right)^{-1} - 1\right)$$ (3)

The three models resulted in similar $k_1$ and $k_2$ reaction rate constants. The revised models resulted in better fits at lower (40 ºC and 60 ºC) curing temperatures. At higher cure temperatures (80 ºC, 90 ºC and 100 ºC) the three models resulted in almost identical $k_1$ and $k_2$ values. The Arrhenius plot of both $k_1$ and $k_2$ showed declining tendency indicating that the reactions became more active at higher temperatures, although $k_1$ scattered considerably (Figure 5.11). The autocatalytic $k_2$ rate constant followed an almost linear tendency in the Arrhenius plot and is several magnitudes higher than $k_1$. The calculated $k_2$ values allowed us to rank the autocatalytic activity of the cross-linking agents. The following rank was found at all curing temperature with all the applied models: commercial IPD $< 1:1.5$ 15% $< 1:1.5$ 30% $< 1:2$ 30% $< 1:2$ 50%. The 40 ºC and 60 ºC $k_2$ values diverged from the linear determined by $k_2$ values determined at higher cure temperatures. This could be explained by the stronger effect of the diffusion-controlled regime at lower temperatures. The higher diffusion rate causes the reaction to diverge from the classical Arrhenius type behavior. Thus, the calculated values will shift. Due to these reasons only the higher cure temperature data (80 ºC, 90 ºC and 100 ºC) were used to calculate the activation energy of the auto-catalytic reactions.
Isophprondiamine base oligoamides: catalytic effect during epoxy curing

The $n$ and $m$ fit parameters both showed an increasing tendency with the cure temperature (Figure 5.12). The $m$ parameter showed almost no dependence on the cross-linking agent, a clear monotone increasing tendency was found between the 0-0.4 interval. The $m$ parameter is almost independent on the used model and it clearly resembled the dependence of $k_2$ on temperature. On the other hand, just as $k_1$ the $n$ parameter strongly coherently changed with the temperature, the cross-linking agent, and the applied model. The $n$ parameter value scattered between a wide interval. The $n$ and $m$ parameters calculated from the revised Kamal models (eq. 2 and eq. 3) shifted to lower values at the lower cure temperatures (40 °C and 60 °C). $n+m$ is thought to be the overall reaction order and it is usually between the 2-3 interval. In our case $n+m$ scattered around 2 in the 1.5-2.5 interval. Although in some cases with the revised Kamal models even $n+m<1$ was observed at 40 °C and 60 °C; that probably results from the mistakes of the fitting process. There is no general agreement about the value and temperature dependence of these parameters.

Figure 5.12 The $n$ and $m$ fit parameters calculated from the Kamal-Sourour, Cole and Fournier models.
Figure 5.13 shows the fit parameters of the revised Kamal models (eq. 2 and eq. 3). Eq. 2 and eq. 3 are similarly built models, but their principals differ. Eq. 2 utilizes $\alpha_c$ as a fit parameter and defines it as the critical conversion point where the diffusion-controlled regime becomes dominant over the chemically controlled regime. On the contrary the $\alpha_f$ in eq. 3 is the maximum conversion reached during the isothermal curing. In our case $\alpha_c$ approximated the value of $\alpha_f$ and both parameters increased and approximated $\alpha=1$ value. All things considered, $\alpha_c$ might not fulfill its original definition and purpose. The $C$ parameter (eq. 2), just as $b$ (eq. 3) acts as a way to consider the restraining effect of diffusion. The authors believe eq. 3 is the better one of the used revised models. As we have stated earlier a $C\sim b^1$ connection is expected, and that is roughly fulfilled. At higher cure temperatures both parameters had taken extreme values and as a result the eq. 2 and eq. 3 approximated the values given by the original Kamal-Sourour equation (eq. 1). The $R^2$ values increased at lower cure temperatures (40 °C and 60 °C) due to the use of revised models and a better fit was achieved.

The Arrhenius equation was used to calculate the activation energy and preexponential factors of the non-catalytic ($k_1$) and catalytic ($k_2$) reactions (Figure 5.14, Figure 5.15). The non-catalytic reaction rate value heavily scattered with the curing temperature and the used cross-linking agent. Therefore, one or two points had to be left out of the fitting process to determine the activation energy values. Due to these reasons, the calculated activation energy of the non-catalytic reaction is ambiguous, unreliable.
Isophprondiamine base oligoamides: catalytic effect during epoxy curing

Figure 5.14 The calculated activation energy and preexponential factors for the non-catalyzed reaction

Figure 5.15 The calculated activation energy and preexponential factors for the auto-catalyzed reaction

The activation energy of the auto-catalytic reaction in the terephthal-amide solution series was compared to the commercial IPD (Figure 5.15). In the case the of the samples cured with only commercial IPD only the secondary hydroxyl groups formed during the curing can act as a catalyst. The activation energy of the catalyzed reaction decreased due to the terephthal-amides. The 1:2 30% and 50% solutions caused the most significant decrease of 10-15 kJ mol\(^{-1}\) in the activation energy. The activation energy of the reaction decreased with the concentration with the 1:2 series. In comparison 1:1.5 15% and 30% solutions could only achieve a 5-10 kJ mol\(^{-1}\) decrease. Surprisingly the activation energy of the 30% solution was found to be higher than the 15% solution. These relationships may partly be explained by the molecular weight difference between the 1:2 and 1:1.5 reaction products. There are similarities between the attitudes expressed by this...
phenomenon, those described by the rotational viscosity measurements. The 1:1.5 solution series proved to be slightly less effective in enhancing the curing in comparison of the 1:2 series. Thus, it can be concluded that the produced terephthal-amides can act as a catalyst in epoxy systems and their catalytic activity can be influenced by their molecular weight.

5.3.5. Catalytic effect of amides studied with computational chemistry

Figure 5.16 The scheme of the studied epoxy curing reactions.

Figure 5.17 The general structure of the possible transition states in the studied reactions.

Figure 5.16 shows the computationally studied reactions, i.e., the reaction of epoxy with the possible amine-derivatives. The studied epoxy-amine curing reaction according to Ehlers et al can follow a direct or an indirect mechanism. The corresponding general transition states shown in Figure 5.17. On the direct path the epoxy ring breaks up, the amine connects to the free CH2 of the epoxy, and the O of the epoxy ring is hydrogenated by the catalyst (or the reactant, if there is no catalyst), which regenerates instantly with a H from the reactant amine group. In contrast, during the indirect path, the catalyst only stabilize the free O group of the epoxy after the ring breaking, and its hydrogenation happens later in the process. The investigation of whole polymer chains with the chosen method would be impracticable, therefore the reduced size epoxy and amines used to model the reaction are shown on Figure 5.16 (the wavy line represents that the chain would continue from there). As catalyst/accelerator glycol, phenol, and the self-catalysis of the possible amine and amide groups of the two amine reactants were studied.
Table 5.4 Free energy barriers of the epoxy curing reaction with different reactants, catalysts, and pathways. All values are in kJ/mol. c-NH₂/c-NH: amine/amide group connected to cycloaliphatic group (2b/2'b'), R-CH₂-NH/R-CH₂-NH₂, amine/amide group connected to aliphatic group (8g/8'g').

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Reaction path</th>
<th>Calculation method</th>
<th>Direct</th>
<th>Indirect</th>
<th>Direct</th>
<th>Indirect</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>B3LYP/6-31G(d,p)</td>
<td></td>
<td>B3LYP/6-31G(d,p)</td>
<td></td>
<td>LNO-CCSD(T)/aug-cc-pVTZ</td>
</tr>
<tr>
<td>No catalyst</td>
<td></td>
<td></td>
<td>209.3</td>
<td>166.5</td>
<td>157.9</td>
<td>198.9</td>
</tr>
<tr>
<td>zHOCH₂-CH₃OH</td>
<td></td>
<td></td>
<td>175.0</td>
<td>94.7</td>
<td>106.4</td>
<td>175.9</td>
</tr>
<tr>
<td>PhOH</td>
<td></td>
<td></td>
<td>175.1</td>
<td>89.3</td>
<td>92.1</td>
<td>171.7</td>
</tr>
<tr>
<td>c-NH₂</td>
<td></td>
<td></td>
<td>196.6</td>
<td>123.6</td>
<td>123.0</td>
<td>194.0</td>
</tr>
<tr>
<td>R-CH₂-NH₂</td>
<td></td>
<td></td>
<td>196.6</td>
<td>125.6</td>
<td>126.4</td>
<td>202.6</td>
</tr>
<tr>
<td>c-NH</td>
<td></td>
<td></td>
<td>189.6</td>
<td>94.2</td>
<td>90.8</td>
<td>178.6</td>
</tr>
<tr>
<td>R-CH₂-NH</td>
<td></td>
<td></td>
<td>184.6</td>
<td>94.5</td>
<td>96.8</td>
<td>170.9</td>
</tr>
</tbody>
</table>

Table 5.4 summarizes the energy barriers of the possible settings. The coordinates and energies of the structures are presented in the Supplementary Material. The transition states of direct path have an imaginary frequency of 370.3-441.4 cm⁻¹, while the TSs of the indirect path have 375.4-406.2 cm⁻¹. It can be seen that in every case the energy barrier of the indirect path is lower with 30-95 kJ mol⁻¹ than the direct path, i.e. the indirect path is favored. Therefore, the more accurate LNO-CCSD(T) calculations were performed only for the indirect path. The difference between DFT and LNO-CCSD(T) results can reach 11.7 kJ mol⁻¹, however the trends are similar, therefore the results of the more reliable LNO-CCSD(T) results are discussed here. Also, there is no notable difference in the reactivity of the c-NH₂ and R-CH₂-NH₂ groups.

Comparing the effects of the catalysts, it can be seen that PhOH is the best performing with the lowest barrier, 86.6-92.1 kJ mol⁻¹. Amide groups have almost the same catalytic effect, regardless of type, with barrier of 90.8-98.8 kJ mol⁻¹. Glycol is also effective to catalyze the curing reaction with a slightly higher barrier, 103.2-106.4 kJ mol⁻¹. The catalytic effect of the amine groups results in barriers of 123.0-123.1 kJ mol⁻¹, meaning that they are worse than the -OH and -NH groups but still better than if there was no catalyst (barriers of 157.4-157.9 kJ mol⁻¹). The notable difference between experimental and calculated activation energies can be attributed to the approximations of the calculations, i.e.
Chapter 5

gas-phase calculations with the relevant part of the species. Nevertheless, the applied model is able to reveal the differences in activity between the possible catalysts. In summary, according to the calculations, the curing reaction occurs with the indirect mechanism, and the amide groups of the reactants are as good as the phenol as a catalyst of this reaction.

5.4. Conclusions

In our previous study we observed the catalytic effect of amides during the curing of epoxy resins and we showed that raw aminolysis products of PET can be applied as epoxy cross-linkers. The main purpose of this study was to quantitatively characterize the catalytic effect of therephthal-amides. We have further decreased the required amount of diamine compound during PET aminolysis to produce oligoamides. The aminolysis products were used as co-cross-linkers with isophorondiamine to study their effect on the curing reaction and glass transition temperature.

The aminolysis of PET was carried out with different PET:IPD ratios (1:1, 1:1.5 and 1:2). Based on the functional group analysis, FTIR and TGA measurements total amidation was achieved in the case of the 1:1.5 and 1:2 ratios. The 1:1 ratio was found to be too low to achieve total amidation, traces of residual ester groups were found in the reaction product. Based on the functional group analysis and the capillary viscosity measurements the molecular weight of the 1:1.5 and 1:2 ratio products differ. The 1:1.5 and 1:2 ratio reaction products were compared with NMR. The quantitative analysis of the $^1$H and MALDI-TOF spectra further supported that the 1:1.5 ratio reaction product has higher molecular weight than the 1:2 ratio product. Further lowering of the used amine ratio resulted in increasing the molecular weight of the therephthal-amides. Thus, the aminolysis of PET can be also used to produce oligoamides. The 1:1.5 reaction product was shown to more effective in decreasing the glass transition temperature of epoxy systems than the 1:2 ratio product.

The rotational viscosimetry and DSC reaction kinetics measurements confirmed the catalytic effects of the raw aminolysis products during curing. The therephthal-amides are double-purposed components that can also acts as cross-linkers and capable catalysts that can kickstart the curing reaction. Their higher molecular weight can also decrease the diffusion rates in the system, that could set back the reaction at lower cure temperatures. This effect can be completely negated at higher cure temperatures ($T_{\text{cure}} > 60 \, ^\circ\text{C}$). Three models, the Kamal-Sourour, and two revised Kamal models were used to quantitatively describe the kinetics of curing. Our calculations show that at 40 °C and 60 °C the revised models result in a better fit. At higher cure temperatures the revised models gave almost the same results as the Kamal-Sourour equation and high $R^2$ values were achieved. The non-catalytic related reaction rate $k_1$ and the fit parameter $n$ significantly scattered, while the autocatalytic related reaction rate $k_2$ and fit parameter $m$ increased with the cure temperature. The $k_2$ values of the solutions series ranked as the following at all cure temperatures: commercial IPD < 1:1.5 15 % < 1:1.5 30 % < 1:2 30 % < 1:2 50 %. Thus, these experiments confirmed that the increase in molecular weight of therephthal-amides results in decreased catalytic activity during epoxy curing. The activation energies of the auto-catalytic reaction were found to decrease with the presence of aminolysis product in
the cross-linking agent.

The quantum chemical calculations show that the indirect pathway is preferred compared to the direct one in the epoxy curing reaction. Even though the phenol catalyzed reaction has the lowest barrier, amide groups have almost the same catalytic activity, better than the glycol and amine groups. Thus these calculations supported our theory on amides being utilized as accelerators in epoxy curing.

Nevertheless it must be noted that the effects of the residual zinc-acetate on the curing of epoxy resins is undetermined. Additional measurements must be carried out to determine the exact efficiency and order of magnitude compared to the terephthalamides. The catalytic effects of metal salts is currently undiscussed in the curing of epoxy resins with amines. These studies exceeded the previously set time limitations of this thesis.

In conclusion we have shown that PET derived oligoamides can be used to cure epoxy resins. They can be used as double-purpose components in epoxy systems as cross-linkers and catalysts. Their effects on the curing reaction and properties of the cured resin can be tailored with their molecular weight.
5.5. References

Isophorondiamine base oligoamides: catalytic effect during epoxy curing

Chapter 5


Chapter 6

The sequenced structure of amino-alcohol based random poly(ester amide)s

6.1. Introduction

Several studies focus on engineering new polymeric materials suitable for a wide range of uses. Poly(ester amide)s have a great potential as biocompatible/biodegradable materials due to their unique molecular structure. A wide range of applications from implants, microfluidical systems to common plastic bags and other products were investigated since Carothers produced the first poly(ester amide)s in 1932. Ester linkage provides a relatively easier scission of the backbone that enhances biodegradability. Amide linkages provide good mechanical properties due to the strong inter- and intramolecular bonds between the chains. The properties of these materials can be finely tuned. The backbone structure, the ratio and distribution of the ester and amide linkages (alternating, block, random) determine the thermal, chemical and mechanical properties. Just like with polyesters, several methods such as ring-opening polymerization, chain lengthening, direct polycondensation or two-step polycondensation based on diacid derivatives have been utilized in poly(ester amide) synthesis.

The amide/ester ratio and distribution substantially influence the thermal properties. At lower amide ratios the amide linkages disrupt the organized ester rich structure that mostly causes lower crystallinity. As the amide ratio is raised, amorphous phase separation can occur, and two glass transition temperatures can be observed. At higher amide to ester ratios the highly crystalline amide rich segments dominate the crystalline structure. In the case of random poly(ester amide)s the linkages are statistically distributed along the backbone. The crystallinity of random poly(ester amide)s was observed in several studies, but only a few focused on it in detail. P. Garg and his co-workers produced poly(ester amide)s with isolated, two and three adjacent amide groups. They have shown that in segmented poly(ester amide)s the thermal properties and crystallinity changes with the total content and type of amide linkages along the backbone. Higher amide content resulted in higher melt temperatures and at certain amide intervals multiple melting peaks. The authors have attributed these separate peaks to different number of ester-amide sequences along the chains.

Amino-alcohol based poly(ester amide)s produced without any prepolymerisation steps tend to form randomly structured polymers. Without any prepolymerisation steps the distribution of ester-ester (EE), amide-amide (AA) and amid-ester (AE/EA) linkages is statistically determined. Despite this, crystallinity was observed in these seemingly random polymers, clearly indicating a certain degree of order along the polymer backbone.

In this study we investigated the molecular structure of amino-alcohol based poly(ester amide)s with nuclear magnetic resonance spectroscopy (NMR) in order to study the ordered nature of the backbone. Substituted amino-alcohols were used to change the reactivity of the amine and hydroxyl groups, thus the number of AA, AE and EE type linkages. Residual functional group analysis and size exclusion chromatography was used to study the blocking effect of the small aliphatic substituent. Differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS) were used to investigate the crystallinity of poly(ester amide)s. Adipic acid and 4 different amino-alcohols (2-amino-1-ethanole, 1-amino-propan-2-ol, 2-amino-butan-1-ol and 2-amino-2-methyl-propan-1-ol) were used to produce aliphatic poly(ester amide)s via two-step direct polycondensation. The produced polymers were named according to the amino-alcohol used in their production, consecutively PEA, PEA-Me, PEA-Et and PEA-MeMe (Figure 6.1 a). No steps were done during the polycondensation to influence the backbone structure (Figure 6.1 b).

![Chemical structure of the used monomers and the adipic units](image)

**Figure 6.1** Chemical structure of the used monomers (a) and the adipic units in the backbone (b)

### 6.2. Experimental

#### 6.2.1. Materials

Adipic acid (99 %) was purchased from Tokyo Chemicals Industry. 2-amino-1-ethanole (ethanol amine) (99%), 1-amino-propan-2-ol (93 %), 2-amino-butan-1-ol (97 %), 2-amino-2-methyl-propan-1-ol (90%) and dimethyl sulfoxide-d6 (99.9%) were purchased from Sigma Aldrich. Hydrochloric acid (cc), sulfuric acid (cc), potassium hydroxide, N,N-dimethylformamide (DMF) (99.96 %), methanol (99.98 %), potassium dichromate (100 %) were purchased from Molar chemicals. Zirconium dioxide (99 %) and Polyethylene glycol 1000 (PEG1000) were purchased from Alpha Aesar. All reagents were used as received.
6.2.2. Synthesis of Poly(ester amide)s

Aliphatic poly(ester amide)s were prepared in a 250 cm$^3$ 4-necked round bottom flask equipped with a gas inlet, a thermometer, a mechanical stirrer and a reflux condenser. The reactions were carried out in two steps. In the first step 1 mol adipic acid and 1 mol amino-alcohol were weighed in and reacted without catalyst in inert argon atmosphere. A distillation apparatus was used to remove the water from the system. The reaction temperature was held near the boiling point of the used amino-alcohol (160-170 °C) for 4 hours, then it was raised with 10 °C (to 175-180 °C) and was held there for 2 hours. Before the second step 0.02 mol catalyst ($\text{ZrO}_2$) was added and the reactor was equipped with a vacuum apparatus. The reactions were kept at 175-180 °C for 5 hours under vacuum (10-30 mbar). The viscous melt at the end of the reaction was poured into an aluminium pan. The reactions yields were over 90 %.

6.2.3. Characterization

A standard titration method was used to measure the acid and the amine content of the produced poly(ester amide)s. 0.2 g were weighed in Erlenmeyer flasks with analytical accuracy and dissolved in 15 cm$^3$ DMF. 3 parallel and one blank sample were titrated with 0.1 M NaOH solution in methanol in the presence of phenolphthalein indicator to determine the acid content. 3 parallel and one blank sample were titrated with 0.1 M HCl solution in the presence of methyl orange to determine the amine content. The hydroxyl content was determined by a colorimetric method introduced by Padilha de Paula 26. 3 samples of 0.1 g were weighed in with analytical accuracy and dissolved in 5 cm$^3$ of DMF. 300 mm$^3$ of Jones reagent was added to the samples and stirred vigorously. After 1 minute 2 cm$^3$ of 3 M HCl solution was added. The samples were tested with UNICAM UV500 spectrophotometer at 600 nm wavelength. A calibration curve of PEG1000 was used to determine the hydroxyl values of the poly(ester amide)s.

Molecular mass distribution was determined with a SEC TSK gel 901B (Tosoh Bioscience Corporation, Ltd., Japan) column using HPLC grade DMF. An evaporative light scattering detector (ELS-1000 Polymer Laboratories) was used with PS molar mass equal calibration.

FTIR ATR measurements (28 scans) were done with Bruker Tensor 27 FTIR. $^1$H and $^1$H-$^15$N NMR measurements were done with Bruker Avance 500 in DMSO-$d_6$. $^{13}$C, DEPT, $^1$H-$^{13}$C HSQC and HMBC were done with Bruker Avance 300 in DMSO-$d_6$. The NMR sample concentration was approximately 60 mg cm$^{-3}$. The temperature of acquisition was 30 °C. Spectral with of 30030 Hz with 0.45 Hz resolution, 1.09 s acquisition time and 2 s recycle delay were used for the $^{13}$C measurements.

Perkin Elmer TGA 6 was used to determine the thermal stability of the poly(ester amide)s on 9-10 mg samples in purging nitrogen. The beginning of thermal degradation was determined at 95 m/m% of the measured sample. A 10 °C min$^{-1}$ heating rate was used from 30-700 °C, then the sample was kept at 700 °C for 10 minutes. Perkin Elmer DSC7 was used to measure the glass transition temperature ($T_g$) and the crystallinity on 3-4 mg samples in purging nitrogen. The $T_g$ was measured with a dynamic method from -40 to 150 °C with a 10 °C min$^{-1}$ heating rate. Crystallinity was investigated after removing the
thermal history (3 min at 150 °C). Then the sample was cooled (10 °C min\(^{-1}\)) to the crystallization temperature (10-75 °C) and kept at the given temperature for a given time (50, 180, 300 and 720 min). Philips PW 1830/PW 1050 equipment with CuK\(\alpha\) radiation (0.154 nm) at 40 kV and 35 mA anode excitation with 0.04 step size and 4 s counting time was used for Wide-angle X-ray scattering (WAXS). 100x100x2 mm sheets were pressed at 150 °C with 140 kN for WAXS.

6.3. Results and discussion

6.3.1. Functional group analysis, molecular weight and degradation

![Figure 6.2 Residual functional group content of poly(ester amide)s](image)

Functional group analysis on amine, hydroxyl and acid content was used to compare the four poly(ester amide)s. The substituents were expected to partially block the access to hydroxyl and amine functions on the amino-alcohols. Regardless of the position of the substituent amino-alcohol (closer to the hydroxyl or the amine group) caused an increase in residual functional group content in the poly(ester amide)s. The hydroxyl group content indicated this sensitively. Its value more than doubled with substitution. In the case of PEA-Me the methyl group had a major effect on the accessibility of the hydroxyl group (Figure 6.2). PEA-Et and PEA-MeMe had a similar OH content since the substituents were closer to the amine groups. The acid content slightly changed with substitution, in the case of PEA-MeMe a major increase was observed. The blocking effect on polycondensation showed also in the size exclusion chromatography results, and it correlated with functional group analysis. The average molecular weight decreased with the number of substituents. The PEA-Me and PEA-Et showed similar results as it was expected from the close amine and acid values. The high residual acid and hydroxyl content of PEA-MeMe indicated a lower conversion rate, that was confirmed by SEC.
The sequenced structure of amino-alcohol based random poly(ester amide) 

Table 6.1 Molecular mass data from SEC and thermal degradation temperatures

<table>
<thead>
<tr>
<th>Poly(ester amide)</th>
<th>PEA</th>
<th>PEA-Me</th>
<th>PEA-Et</th>
<th>PEA-MeMe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$ [g mol$^{-1}$]</td>
<td>4588</td>
<td>2948</td>
<td>3552</td>
<td>2199</td>
</tr>
<tr>
<td>$M_w$ [g mol$^{-1}$]</td>
<td>7461</td>
<td>4640</td>
<td>5876</td>
<td>3260</td>
</tr>
<tr>
<td>Polydispersity</td>
<td>1.62</td>
<td>1.57</td>
<td>1.65</td>
<td>1.48</td>
</tr>
<tr>
<td>Degradation temperature (°C)</td>
<td>302.0</td>
<td>295.0</td>
<td>295.7</td>
<td>244.8</td>
</tr>
</tbody>
</table>

Thermal degradation was tested on the poly(ester amide)s. The beginning of thermal degradation was determined at 5 m/m% mass loss of the measured sample on the TGA curve. The thermal degradation temperature decreased with decreasing molecular weight. Except for PEA only one degradation step can be observed on the TGA and DTG curves (Figure 6.3). For PEA a change of slope on the TGA curve (~30-33% at 360 °C) can be observed. This change of slope indicates a thermally more stable structure. Poly(ester amide)s tend to have higher degradation temperatures than similarly structured polyesters\textsuperscript{19,27,28}. Thus amide rich segments of the polymers should have higher heat stability. The exceptional properties of polyamides and poly(ester amide)s – including thermal stability - depend on the strong bonds between the chains. The lack of this shoulder in case of the substituted PEA can be explained by the steric effect of the substituents. This means that due to the steric hindrance less hydrogen bonds can form. Hydrogen bonds can enhance the stability of the amide bonds\textsuperscript{29}, thus if these sites are blocked the thermal stability is reduced.

![Figure 6.3 TGA and DTG curves of poly(ester amide)s](image)

6.3.2. Molecular structure identification

FTIR spectroscopy was used to generally identify the ester-amide structure of the produced polymers. The representative peaks were found in all the polymers for the ester and the amide groups as well (Figure 6.4). $1730$ cm$^{-1}$ for the carbonyl and $1250$ cm$^{-1}$ ester linkage, $1645$ cm$^{-1}$ and $1540$ cm$^{-1}$ for the amide vibrations. The wide peak over $3200$ cm$^{-1}$
is attributed to the N-H and O-H valence vibrations. Minor differences found in the spectra between 1500-1200 cm\(^{-1}\) are attributed to the aliphatic chain. PEA-Me and PEA-Et showed methyl attributed to the C-H deformation vibration at 1381 cm\(^{-1}\). PEA-MeMe showed C-H deformation vibration at 1365 and 1392 cm\(^{-1}\) attributed to C-(CH\(_3\))\(_2\) groups. At 2965 cm\(^{-1}\) a 3\(^{rd}\) peak or shoulder appeared that can be attributed to the valence C-H vibrations of methyl groups.

![Figure 6.4 FTIR ATR spectra of the poly(ester amide)s](image)

Figure 6.4 FTIR ATR spectra of the poly(ester amide)s

![Figure 6.5 The used numbering in the ester-amide unit type in NMR](image)

\(^1\)H, \(^{13}\)C, \(^1\)H-\(^{15}\)N HMBC NMR measurements were done to determine the molecular structure of the poly(ester amide)s. The generally assumed molecular structure was identified with the \(^1\)H and \(^1\)H-\(^{15}\)N HMBC NMR. The carbon and hydrogen atoms in the ester-amide repeating unit were numbered as shown in Figure 6.5. As we compare the \(^1\)H spectra of the polymers it can be seen that the 1-4\(^{th}\) numbered atoms’ chemical shift did not change with the substitution. Surprisingly the chemical shift of the 4\(^{th}\) peak was found to be higher than that of the 1\(^{st}\) peak. One would expect the chemical shift of hydrogen atoms
to be higher when they are closer to the amide group, than the ester group in the acid unit. 
$^1$H-$^{15}$N and $^1$H-$^{13}$C correlation showed this “switch” between these peaks. This spectral behavior is unique to poly(ester amide)s. Major shifts can be observed on the 5-9th atoms. Depending on the substitution the 5th and 6th peaks shifted in the spectra. As expected the 6th peak completely disappeared from the $^1$H spectrum of PEA-MeMe. The 8th and 9th peaks were consistently attributed to the substituent atoms.

Chemical shift differences ($^{13}$C spectra) in the 2nd and 3rd carbon atoms were used to characterize the distribution of amide and ester linkages along the polymer backbone. The chemical shift differs if the adipic-acid formed AA, EE or EA bonds. The EA/AE linkage gives 2 peaks, because the chemical shift changes if the carbon atom is closer to the ester (EA) or amide (AE) bonds. Thus 4 kind of peaks appear in the $^{13}$C spectra between 26.24 ppm (Figure 6.7). $^1$H-$^{13}$C HSQC and HMBC correlation were used to assign the peaks. In the case of PEA-MeMe the peak at 24.46 ppm belongs to the 8th and 9th carbon from methyl substituents, in the case of PEA-Et the peak at 24.16 ppm belongs to the 8th carbon from the ethyl substituent. Molar % fractions were calculated from peak deconvolution and integration based on the publication of Witt et al. The integrated areas of the appointed peaks at Figure 6.7 were divided by the total area of the 4 peaks. This method was further explored and supported by Otte et al. Otte and his coworkers concluded that as long as the differences in NOEs and relaxation times are considered $^{13}$C NMR spectra integration is quantitative. Even standard pulse sequences and short recycle delay times (d1) could result in accurate enough comparison between two compounds. The data showed that the polycondensation reaction wasn’t completely stochastic. In a completely stochastic process 25% AA and EE, and 50% AE/EA linkages would form. The probability of finding an ester group next to an amide (P$_{EA}$) on an adipic acid unit and vica versa (P$_{AE}$) were calculated from the mol% fractions (Table 6.2). As we have
seen on the functional group analysis and the GPC measurements the substituents generally lowered the conversion rate of the reactions, thus lower molecular weight was obtained. Our calculations showed that substitution changed the $P_{AE}$ and $P_{EA}$ values. As expected the amidation was generally favored. PEA-Me showed that the steric effect of the hydroxyl-near methyl group raised the amidation and lowered the esterification probability. The ethyl group balanced the probability of amidation and esterification compared to PEA (closer to stochastic ratios were obtained). The double methyl groups shifted the reaction in favor of the esterification and significantly raised the amount of EA/AE linkages along the backbone. Compared to the PEA an alternating structure was obtained. According to these data we can infer that even small aliphatic substituents can have a major effect on the fine composition of poly(ester amide)s.

Figure 6.7 $^{13}$C spectra showing zones associated with the 2nd and 3rd carbon atoms

Table 6.2 Molar fractions calculated from the relative peak integrals

<table>
<thead>
<tr>
<th></th>
<th>PEA</th>
<th>PEA-Me</th>
<th>PEA-Et</th>
<th>PEA-MeMe</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE</td>
<td>22.70</td>
<td>20.73</td>
<td>23.85</td>
<td>25.62</td>
</tr>
<tr>
<td>AA</td>
<td>28.67</td>
<td>31.46</td>
<td>27.81</td>
<td>19.09</td>
</tr>
<tr>
<td>EE</td>
<td>23.41</td>
<td>22.03</td>
<td>24.53</td>
<td>22.24</td>
</tr>
<tr>
<td>EA</td>
<td>25.23</td>
<td>25.78</td>
<td>23.82</td>
<td>33.07</td>
</tr>
</tbody>
</table>

Molar fractions [%]

<table>
<thead>
<tr>
<th>Probability [%]</th>
<th>$P_{EA}$</th>
<th>$P_{AE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA</td>
<td>53.88</td>
<td>74.34</td>
</tr>
<tr>
<td>PEA-Me</td>
<td>39.59</td>
<td>67.17</td>
</tr>
<tr>
<td>PEA-Et</td>
<td>42.88</td>
<td>58.51</td>
</tr>
<tr>
<td>PEA-MeMe</td>
<td>44.88</td>
<td>56.51</td>
</tr>
</tbody>
</table>
Based on the calculated molar fractions, the polymerization reaction is a near stochastic process. These values can be interpreted as the statistical averages of the polymerization reaction. The molar fractions give us information only on the backbone composition, and not on the fine distribution. One of the key criteria in polymer crystallization is the ordered backbone structure, yet crystalline behavior was observed in the seemingly random aliphatic poly(ester amide)s\(^{10,25}\). Our goal was to find certain sequences that could build up the polymeric backbone with the same stochastic or near stochastic constitution represented in Table 6.2.

The bifunctional ethanol-amine predetermines the possible connections of the adjacent adipic units, thus 2 or 4 “adipic unit” long sequences can be identified as repeating units along the backbone. The possible connections and repeating sequences are represented at Figure 6.8. The theoretical sequences “a” and “b” on their own could form in a near stochastic process and build up the chains with the same total composition. AAEE and AEAE/EAEA linkages can form various sequences. Alternating variations of these linkages result in “b” type of sequences. If AAEE or AEAE/EAEA form longer blocks “c” and “d” appear along the backbone structure. Due to the statistical nature of the reaction any combination of these sequences could appear along the backbone. The “c” and “d” type of sequences together are capable of building backbones with the desired composition.

Therefore it is possible, that this near stochastic process can result in sequenced backbone structure with several kinds of repeating units. Intra- and intermolecular secondary bonds (hydrogen bond) could be a strong enough driving force to initiate crystallization. Sasanuma and coworkers used high-accuracy molecular orbital calculations to study the conformations and inter- and intramolecular forces in poly(ester amide)s and polyurethanes\(^{11}\). In their studies they have shown that both polymers develop strong secondary forces, especially hydrogen bonds (N-H ~ O and C-H ~ O=C). Comparison was made and was concluded that poly(ester amide)s have a more rigid molecular structure.
due to intramolecular forces. Polyurethanes are more likely to behave as elastomers in the same conditions. Thus we can conclude that the sequenced backbone structure in poly(ester amide)s and strong secondary bonds could result in the folding of the polymeric chains and crystal formation. The different sequences could build up separate crystalline phases that resemble the simultaneous crystallization of two or more type of polymers in block copolymers or blends\textsuperscript{32,33}. To test our theory on separate crystalline phases thermal properties were studied on our poly(ester amide)s in DSC and WAXS.

6.3.3. Thermal properties and crystallinity

Table 6.3 Glass transition temperatures and enthalpy changes of the poly(ester amide)s

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Glass Transition Temperature (°C)</th>
<th>dCp (J°C(^{-1})g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA</td>
<td>-11.14</td>
<td>0.483</td>
</tr>
<tr>
<td>PEA-Me</td>
<td>-2.76</td>
<td>0.452</td>
</tr>
<tr>
<td>PEA-Et</td>
<td>-2.73</td>
<td>0.477</td>
</tr>
<tr>
<td>PEA-MeMe</td>
<td>-3.54</td>
<td>0.473</td>
</tr>
</tbody>
</table>

Glass transition temperature (\(T_g\)) was determined via dynamic DSC measurement from \(-40\) °C to \(150\) °C at \(10\) °C min\(^{-1}\) heating rate (Table 6.3). \(T_g\) raised, the specific heat change slightly changed with the incorporation of small aliphatic substituents. Substituents like methyl and ethyl groups change the secondary interaction bonds between the polymer chains. Steric blocking effect of the substituents could significantly decrease the amount of hydrogen bonds between the chains. The lower amount of hydrogen bonds should raise the \(T_g\)\textsuperscript{34,35}. The slightly lower \(T_g\) value of the Me-Me substituted polymer can be attributed to its lower \(M_w\) and symmetric backbone. In lower molecular weighed polymers the \(T_g\) is always lower compared to a similarly structured, but higher \(M_w\) polymer. Asymmetry can cause bipolarity along the backbone that can enhance the intermolecular forces. Attributed to their lower than room temperature \(T_g\) the aliphatic poly(ester amide)s are elastomers, except PEA that showed crystallinity (Figure 6.9 a).
The sequenced structure of amino-alcohol based random poly(ester amide) as our calculations suggested on the possible sequenced structure of random poly(ester amide)s, a wide multi-peaked endothermic melting was observed on the first heating of PEA (Figure 6.9 a). The following cooling step showed no sign of crystallization, since the 10 °C min\(^{-1}\) cooling rate was too fast for the polymer to recrystallize. Three separate peaks were identified from the first heating curve. Hence, we used isothermal crystallization from 15-75 °C for 50 minutes to further study the peaks. After the 50 min isothermal period the sample temperature was raised at 10 °C/min to study the melt curve. Two separate peaks were observed (CF-I, CF-II) on the melting curves (Figure 6.9 b). The CF-I peak is well-defined, symmetric with ~2 °C full width at half maximum value, while CF-II peak is wide, asymmetric with 4-6 °C full width at half value. CF-III didn’t form during 50 minutes of isothermal crystallization. The peak temperatures shifted to higher temperatures following linear functions. Hoffman-Weeks equilibrium melting temperature can be determined from these data\(^{10}\). Yet the occurrence of crystallization at the isothermal period must be proven to enable applicability of this model. No exothermic peaks were found during the 10 °C min\(^{-1}\) cooling, and the 50-minute-long isothermal periods either. Yet endothermic melting peaks appeared at the second heating. Thus, the data suggest a very low rate of crystallization, which cannot be measured with DSC. To prove the isothermal crystallization, longer isothermal steps were used (3h, 5h and 12h) between 10-70 °C. The enthalpy change of melting increases with the longer isothermal step time and reaches a plateau after 12 hours of crystallization (Figure 6.10 a). Thus, the primary crystallization occurs during the first 12 hours of crystallization. Further improvements of the crystal structure occur after 12 hours during the secondary crystallization. The optimal crystallization temperature was found to be near 40 °C (Figure 6.10 b).
Chapter 6

Figure 6.10 The enthalpy change of crystalline peaks melting as a function of crystallization time in PEA samples

Figure 6.11 Melting curves of PEA after 12 hours of crystallization (a) and the shift of peak temperatures of the 3 crystalline phases(b)

The three-peaked melt curves were observed between 10-50 °C after 3-5 hours of crystallization (Figure 6.11 a). At 60-70 °C the CF-I peak shifted over to 80 °C, thus it became indistinguishable from CF-II. The Hoffman-Weeks model was used to determine the equilibrium melting temperature (Figure 6.11 b) of the three phases. Surprisingly the CF-I and CF-III phases were found to have higher equilibrium melting temperatures than CF-II. In regular crystalline polymers higher melting temperature means a wider lamellar width and improved crystalline structure. CF-II proved to be the less stable crystalline phase. The CF-II phase peaks were rather undefined and wide, the peak temperatures barely changed with the crystallization temperature. Partial areas were calculated
based of the deconvolution on the calorimetric curves (Figure 6.12). CF-I and CF-III phases had a clear rising tendency, and CF-II had a declining trend of the crystallization temperature. At lower temperatures CF-II clearly outcompetes the other phases with its faster crystallization rate, even at higher temperatures it still occupies nearly 40% of the total crystalline phase. CF-III has the lowest rate of crystallization; it needs at least 3-5 hours to form depending on the crystallization temperature. The optimal crystallization temperature of CF-III is between 40-50 °C. The three observed phases show different rates of crystallization and stability. Such behavior can be explained by the sequenced structure of the polymer.

**Figure 6.12 Relative area of the crystalline peaks in PEA**

Wide angle X-ray scattering was used to determine the total crystallinity of PEA and to further study the crystalline structure. 6 mm thick pressed plates were made, and kept at 30, 40, 50 and 60 °C (Figure 6.13). The total crystallinity (~30-35 %) was calculated based on a two-phase model from the partial areas of the fitted peaks. All the observed peaks shifted to higher 2θ values with the increase of crystallization temperature. The first peak showed decline in area with higher crystallization temperatures. The intensity of the first peak at 60 °C significantly declined and the half width at half maximum doubled. Thus a less perfect crystalline structure formed. The second peak’s area was observed to be lower than the first at all tested temperatures, its area slightly changed with the temperature. The 3rd and 4th minor peaks are possibly higher diffractions of the first two major phases. Based on our observations from the DSC the 1st peak resamples the CF-II crystalline phase. The intensity drop at 60 °C (where CF-II became indistinguishable from CF-I, Figure 6.11 a) clearly indicates the connection. Thus the 2nd peak must be connected to the other major phase, CF-I. The 1st and 2nd peak area ratios resemble the area ratios (~2:3-1:1) of CF-I and CF-II from the DSC. CF-III phase cannot be identified on the WAXS diffractograms. A small shoulder-like peak appeared at 24.7° on the 60 °C samples diffractogram that might be attributed to it. The DSC data indicated that CF-III takes up to 10-20 % of the crystalline phases that could be too low to detect with WAXS. The calculated Bragg’s crystal lattice distances follow a growing trend in both cases. As we have concluded from the equilibrium melt temperatures the CF-I phase is more stable than CF-II, thus it should have a more defined structure with wider lamellas.
Figure 6.13 WAXS diffractograms of PEA crystallized at 30-60 °C

Table 6.4 Area of the crystalline peaks of PEA

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Total area (%)</th>
<th>Crystalline peak area (%)</th>
<th>Bragg’s crystal lattice distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>30</td>
<td>34.81</td>
<td>18.56</td>
<td>12.69</td>
</tr>
<tr>
<td>40</td>
<td>30.08</td>
<td>15.94</td>
<td>10.42</td>
</tr>
<tr>
<td>50</td>
<td>32.10</td>
<td>17.24</td>
<td>11.34</td>
</tr>
<tr>
<td>60</td>
<td>30.23</td>
<td>14.61</td>
<td>11.86</td>
</tr>
</tbody>
</table>
6.4. Conclusions

Random aliphatic poly(ester amide)s derived from adipic-acid and substituted amino-alcohols were obtained via two-step direct polycondensation. Several characterisation methods were used to compare the effects of substitution on the properties and structure of the poly(ester amide)s. In this paper we have given a possible explanation of the sequenced organisation of random poly(ester amides) and the formation of separate crystalline phases.

From the functional group analysis and the SEC measurements we have concluded that the substitution generally lowered the conversion of the polycondensation. The thermal stability of the poly(ester amide)s declined with lower molecular weight and substitution. The FTIR, $^1$H and $^{15}$N confirmed the ester-amide structure. The $^{13}$C NMR studies revealed that even small aliphatic substituents can have a major steric hindrance effect. The AA, EE, EA and AE molar fractions varied with the size and number of substituents. Consequently they influence the fine structure of the poly(ester amide)s. We proposed 2-4 “adipic unit long” repeating sequences that could appear in and build up the polymeric backbone structure. Thus a sequenced structure was found in random poly(ester amide)s, that could cause the formation of separate crystalline phases. The DSC measurements proved the existence of three separate crystalline phases in PEA (two major, and a third minor) with different heat stability and crystallization rate. The two major crystalline phases were identified on the WAXS diffractograms.

6.5. References

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35 R. G. M. Van Der Sman, .
Chapter 7

Summary

The recycling of waste streams is one of the most emerging problems of our modern society that not just endangers our environment, but all living beings as well. The number of research projects concerning sustainability and treating waste materials has increased substantially in all fields. Over the years not just the leading governments, but the leading companies started to participate and made large investments to maintain sustainability. Dealing with plastic waste has become the center of attention even in communal forums. There are several methods to deal with and recycle plastic waste materials, nevertheless they have certain advantages and disadvantages that must be taken into consideration. Mechanical recycling cannot be used indefinitely due to degradation processes occurring in plastics. Incineration might be the most economically favorable, yet most plants cannot reach the needed high temperatures to inhibit the formation of toxic volatile compounds. Not to mention losing expensive, special materials that could be recuperated from the waste stream. Chemical recycling could be used to regain the building blocks of plastics and repurpose them. Regrettably chemical recycling – and mechanical recycling as well – is restricted by the necessary purification and separation steps, and chemical use. To overcome this issue in the case of PET solvolysis, in this thesis we investigated the use of raw solvolysis products in cross-linked systems.

In the first part of our studies, we attempted to modify the standard glycolysis technique to purposely produce PET derivate oligoesters that could be utilized as mid-products. We introduced diacid components into glycolysis systems to incorporate low molar weight side components into oligomeric chains, thus completely negating any side-products from our system. Acido-alcoholysis was compared to conventional glycolysis and acidoysis. Our results have shown that the molar weight of the depolymerization products considerably increased and all the low molar weight volatile products were incorporated into the depolymerization products. The chain-lengthening of the depolymerization products with epoxy compounds probably resulted in branched or even cross-linked products. To thoroughly characterize acido-alcoholysis reaction series were designed to understand the effects of diacids on glycolysis. Our studies with NMR have shown that the depolymerization of PET and condensation via the diacid components occurs at the same. Thus, the diacid components act as a chain lengthening agent during the depolymerization increasing the molar weight. Based on these results one-pot type depolymerization and polycondensation reactions were designed and carried out. Un satu rated resins were prepared from the butane-1,4-diol and adipic acid reactions series. The viscoelastic properties of the cross-linked resins considerably changed with the amount of adipic acid used during depolymerization. The glass transition temperature shifted to lower temperatures and the cross-link density decreased as the ratio of adipic acid was increased. Thus acido-alcoholysis is capable of yielding functional oligoesters that could be finely tuned to be utilized in various products. It combines depolymerization and polycondensation in the same system and it does not need excessively high volumes of chemicals to work. Since the traditional “side-products” of glycolysis are incorporated into the end product there is no need for purification steps, it can be directly used in syntheses.
In the second part of our studies, we used aminolysis to produce terephthalamides that could be utilized as cross-linkers in epoxy systems. The aminolysis of PET was carried out without excess amine. The aminolysis products were thoroughly characterized with functional group content, FTIR, NMR, and MALDI-TOF. Our findings suggested that the molecular weight of the produced terephthalamides can be tuned with the ratio of isophorondiamine used for the aminolysis while no residual ester groups remain. Terephthalamides with two distinct molecular weights were used to produce cross-linker solutions with isophorondiamine. The viscoelastic properties changed with the concentration of the amide co-cross-linker. The glass transition temperatures shifted to lower temperatures, and the cross-link density decreased substantially with increasing concentrations. The effects of the terephthalamides on the curing was investigated with rotational viscosimetry and DSC reaction kinetics studies. The gelation studies indicated a significant decrease in gel time compared to the model isophorondiamine cure systems. Compared to the model equivalent solutions of ethylene-glycol with isophorondiamine the terephthalamide solutions were significantly faster, decreasing the gelation time with over 10 minutes at 50°C. The higher molar weighed PET:IPD 1:1.5 solutions proved to be less active than the PET:IPD 1:2 solutions. The reaction kinetics studies supported these findings and have shown that the activation energy of the autocatalitic curing could decrease with 20-30 kJ/mol. The reaction rate constants decreased with decreasing the concentration and increasing the molar weight of the terephthalamides in the cross-linker solutions. The three different model equations were used to fit to the curing data. The Cole factor and the Fournier factor modified models assured a better fit at lower cure temperatures. At higher cure temperatures the modified models barely differed for the results of the classic Kamal-Sourour equation. This indicates a decreased effect of diffusion control on the curing.

In the last part of our studies we investigated the effects of small substituents on the polycondensation and fine molecular structure of aliphatic poly(ester amides). The increasing residual functional group content and the decreasing molecular weight of the poly(ester amides) suggested a dampening effect on the polycondensation by the small substituents. Based on the correlational NMR studies a quantitative analysis was carried out to investigate the ratios of amide-amide, amide-ester/ester-amide and ester-ester in the polyester amides. A sequenced structure was proposed that could build up the polymeric chains of the random polyester amides, that could even give an explanation for the crystallinity of these materials. The formation of different sequences suggests the formation of different crystalline phases that were detected with DSC and WAXS. Two major and a minor crystalline phase was found with different equilibrium melting points and crystallization rate.
The most important conclusions of this thesis are briefly summarized in the following points:

1. We have shown that the introduction of diacid components into the glycolysis of PET results in the incorporation of lower molar weight components into oligomeric chains. Thus, eliminating the need for separation and purification steps after the depolymerization reaction with completely annulling side products and yielding a more uniform product.

2. One-pot type acido-alcoholysis reactions were engineered to combine depolymerization and polycondensation into a single technological step. Acido-alcoholysis proved to be a quite modulable technique that allowed us to finely tune the thermal and mechanical properties of the produced polyesters. Increasing the ratio of the diacid components during the depolymerization step resulted in the production of higher molar weighed oligomers. Thus, decreasing the cross-link density and the glass transition temperature of the cross-linked unsaturated polyester resins.

3. Decreasing the ratio of utilized amine reagent during PET aminolysis could be used to shift the molecular weight of the produced terephthalamides. The raw aminolysis products of PET could be utilized as amine co cross-linkers. The glass transition temperature and cross-link density of the epoxy resin specimen could be tuned with the concentration and molecular weight of the terephthalamides.

4. Aminolysis products can influence the cure kinetics of epoxy resins. The eliminated ethylene glycol and the amides can form hydrogen bonds with the epoxy groups, thus catalyzing the addition reactions with amines. The gelation measurements have shown that the aminolysis products have a higher catalytic activity than the ethylene glycol. Their catalytic activity can be tuned with the molecular weight of the terephthalamides. The DSC reaction kinetics studies further supported these observations. Computational chemistry studies indicated that the terephthalamides are in the same order of magnitude in accelerative activity as phenols.

5. Random aliphatic poly(ester amide)s derived from adipic acid and substituted amino-alcohols were synthesized and thoroughly characterized with NMR measurements. Based on our findings a sequenced molecular structure was proposed that consists of repeating sequences of amide-amide, amide-ester and ester-ester connections. Such organized structure in poly(ester amides) could lead to the formation of different crystalline phases. DSC measurements have proven the formation two major and a minor crystalline phase with different equilibrium melting temperature and crystallization rate. The major phases were identified with WAXS.
List of symbols

\[ \eta \] intrinsic viscosity
b fit parameter in the Fournier diffusion factor
C fit parameter in the Cole diffusion factor
CED cohesion energy density
CF crystalline phase
\( C_p \) heat capacity
D diffusion coefficient
\( f_d(\alpha) \) diffusion factor used in the revised Kamal-Sourour models
G’ storage modulus
G” loss modulus
k_1, k_2 reaction rate constant
n, m fit parameters for the Kamal-Sourour equation
T_c crystallization temperature
T_g glass transition temperature
t_gel gelation time
T_m melt temperature
\( \alpha \) conversion
\( \alpha_c \) fit parameter in the Cole diffusion factor, critical conversion where the reaction is dominantly governed by diffusion
\( \delta \) Hildebrand solubility parameter (MPa)^{1/2}
\( \delta \) phase lag between stress and strain
\( \Delta E \) electronic energy difference
\( \Delta G \) Gibbs free energy barrier
\( \Delta H \) enthalpy change
\( \eta \) viscosity
\( \nu \) cross-link density
\( \rho \) density
\( \tau \) relaxation time

Abbreviations

[bmim] 1-butyl-3-methylimidazolium cation
AA amide-amide linkage
AdAc adipic acid
AE/AE ester-amide linkage
APK German plastic recycling and producing company
ATR attenuated total reflectance
aug-cc-pVTZ augmented version of the correlation consistent triple zeta basis set
BASF Badische Anilin- und Soda Fabrik GmbH, German chemical company
BHET bis(2-hydroxyethyl)-terephthalate
But butane-1,4-diol
CC coupled cluster
CCSD couples cluster single double
COSY correlated spectroscopy NMR (\(^1\)H-\(^1\)H)
List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>DEPT</td>
<td>distortionless enhancement by polarization transfer NMR</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMA</td>
<td>dynamic mechanical analysis</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl-sulfoxide</td>
</tr>
<tr>
<td>DMT</td>
<td>dimethyl-terephthalate</td>
</tr>
<tr>
<td>DTG</td>
<td>the first derivative of the TGA curve</td>
</tr>
<tr>
<td>EE</td>
<td>epoxy equivalent ((g \text{ resin})/(1 \text{ mol epoxy functional group}))</td>
</tr>
<tr>
<td>EE</td>
<td>ester-ester linkage (chapter 6)</td>
</tr>
<tr>
<td>FCC</td>
<td>Fluid catalytic cracking</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>HMBC</td>
<td>hetero-nuclear multiple-quantum coherence NMR</td>
</tr>
<tr>
<td>HSQC</td>
<td>heteronuclear single quantum coherence NMR</td>
</tr>
<tr>
<td>IH(^2)</td>
<td>Integrated hydro-pyrolysis and hydro-conversion</td>
</tr>
<tr>
<td>IPD</td>
<td>isophorondiamine</td>
</tr>
<tr>
<td>KDV</td>
<td>Katalytische Drucklose Verölung, depolymerization process developed by Alphakat GmbH</td>
</tr>
<tr>
<td>LNO</td>
<td>local neutral orbital</td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix assisted laser desorption/ionization</td>
</tr>
<tr>
<td>MOL</td>
<td>Magyar Olaj- és Gázipari Nyrt, Hungarian oil and gas company</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>NOESY</td>
<td>nuclear Overhauser effect spectroscopy NMR ((^1\text{H}-^1\text{H}))</td>
</tr>
<tr>
<td>PEA</td>
<td>poly(ester-amide) of 2-Amino-1-ethanol and adipic acid</td>
</tr>
<tr>
<td>PEA.Et</td>
<td>poly(ester-amide) of 2-amino-butan-1-ol and adipic acid</td>
</tr>
<tr>
<td>PEA-Me</td>
<td>poly(ester-amide) of 1-amino-propan-2-ol and adipic acid</td>
</tr>
<tr>
<td>PEA-MeMe</td>
<td>poly(ester-amide) of 2-amino-2-methyl-propan-1-ol and adipic acid</td>
</tr>
<tr>
<td>PET</td>
<td>poly(ethylene-terephthalate)</td>
</tr>
<tr>
<td>PE(_{XY})</td>
<td>the probability of finding a X group (ester, amide) next to an Y group</td>
</tr>
<tr>
<td>PVC</td>
<td>poly(vinyl chloride)</td>
</tr>
<tr>
<td>SebAc</td>
<td>sebacic-acid</td>
</tr>
<tr>
<td>SucAc</td>
<td>succinic acid</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TOF</td>
<td>Time of flight mass spectrometer</td>
</tr>
<tr>
<td>WAXS</td>
<td>wide angle X-ray scattering</td>
</tr>
</tbody>
</table>
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“I am glad you are here with me. Here at the end of all things…”*

* J. R. R Tolkien, The Lord of The Rings Vol. III The Return of the King
List of publications

Papers used for the preparation of the Thesis


Other publications


   a. Bugyi Orsolya, Szarka Györgyi, Kárpáti Levente, Vargha Viktória; Poli(etilén-tereftalát) hulladék kémiai újrahasznosítása és az új, érték-növelt termékek jellemzése; 29-40
   b. Csoknay Tamás, Szarka Györgyi, Kárpáti Levente, Vargha Viktória, Hartman Mátyás; Biológiailag lebomló polimer keverékek előállítása és jellemzése; 61-71
   c. Menyhért Balázs, Szarka Györgyi, Kárpáti Levente, Vargha Viktória, Hartman Mátyás, Biodegradálható Polimerek Szintézise, 153-164
d. Vargha Viktória, Menyhért Balázs, Csoknay Tamás, Kárpáti Levente; Poliolefin fóliák viselkedése talajban és komposztban; 235-242


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Oral presentation


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7. **Kárpáti, L.**; Menyhért, V.; Vargha, V. Biológiailag lebontható poliészterek szintezise és jellemzése, XXIII. Nemzetközi Végysészkonferencia Déva, 27.10.2017


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**Poster presentations**


14. **Bugyi, O.**, Szarka, Gy., Kárpáti, L., Vargha, V.: Value added products by chemical decomposition of PET waste. 3rd Conference of Biobased Polymers and Composites, Szeged, 08. 28 – 09.01 2016 P 372-373 Poster 81

15. Heffner T., Szarka, Gy., **Kárpáti, L.**, Hartmann M., Vargha, V Biodegradable Polymers from PET Waste via Solvolysis 3rd Conference of Biobased Polymers and Composites, Szeged, 08. 28 – 09.01 2016 P 374-375 Poster 82


17. **Kárpáti, L.**, Hamar, G. & Vargha: The effect of substituents on direct polycondensation and properties of aliphatic polyester-amides. 4th Conference of Biobased Polymers and Composites, Balatonfüred, 02-06 09.2018
Nyilatkozat

Alulírott Kárpáti Levente kijelentem, hogy ezt a doktori értekezést magam ké-
színtettem és abban csak a megadott forrásokat használtam fel. Minden olyan részt, ame-
lyet szó szerint, vagy azonos tartalomban, de átfogalmazva más forrásból átvettem, egy-
értelműen, a forrás megadásával megjelöltém.


Kárpáti Levente