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

Thesis book

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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). 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 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[1]. 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, then 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 application[1,2]
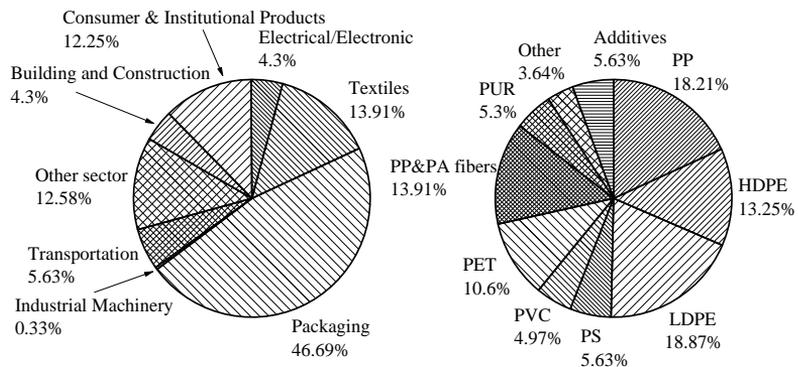

Figure 1 The global plastic waste generation by industrial fields and type in 2015. Total waste production was 302 million tons. Data was published by Geyer et al.[2]

Poly(ethylene terephthalate) (PET) has become one of the most recycled polymers among the commodity and engineering polymeric materials.[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 more environmentally friendly chemical recycling methods and find uses for the raw reaction products in cross-linked systems.

2. Background

2.1. Plastic Recycling

Plastic recycling is one of the several waste management strategies to deal with the emerging problem of plastic waste[11]. Landfilling is one of the conventional approaches that does not deal with sustainability. Well-maintained it could minimize 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 can be used to gain energy 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[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

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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 – expect 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.[1,12]

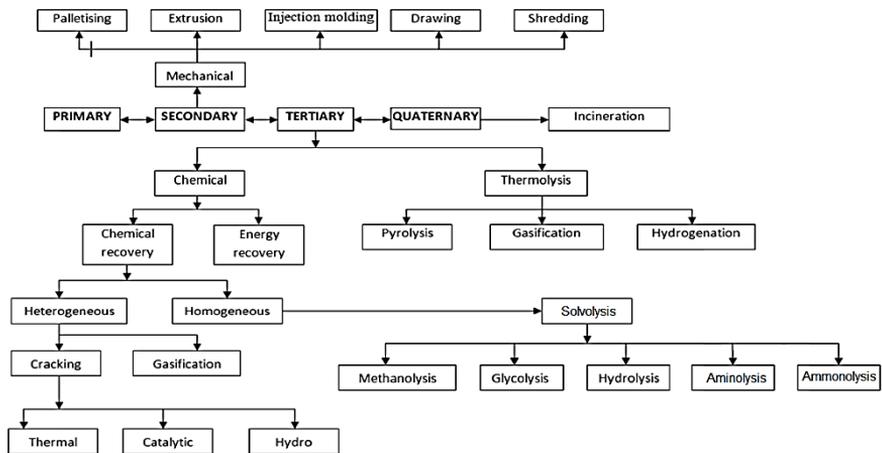

Figure 2 The recycling technologies of solid plastic waste based on the classification of Singh et al.[13]

Plastic recycling methods can be sorted into four categories: primary, secondary, tertiary and quaternary (Figure 2).[13–15] *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 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.[16,17] The miscibility of the plastic components is governed by the interaction forces between the components and it could be tailored by using compatibilizers.[18] 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.

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. The following technologies were developed in this regard: *pyrolysis*, *fluid catalytic cracking*, *hydrocracking* and *hydro-pyrolysis*, *KDV process*, *gasification*, and *solvolysis*.[12] All these processes, except for 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 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. 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.

2.2. The solvolysis of PET

Several studies 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 and purification steps must be introduced into the production line. High volumes of chemicals are needed to reach high levels of yield and conversion due to its equilibrial nature (Figure 3). In addition the reaction products must be separated from the reaction medium. As a result, the solvolysis of PET is an expensive technology.

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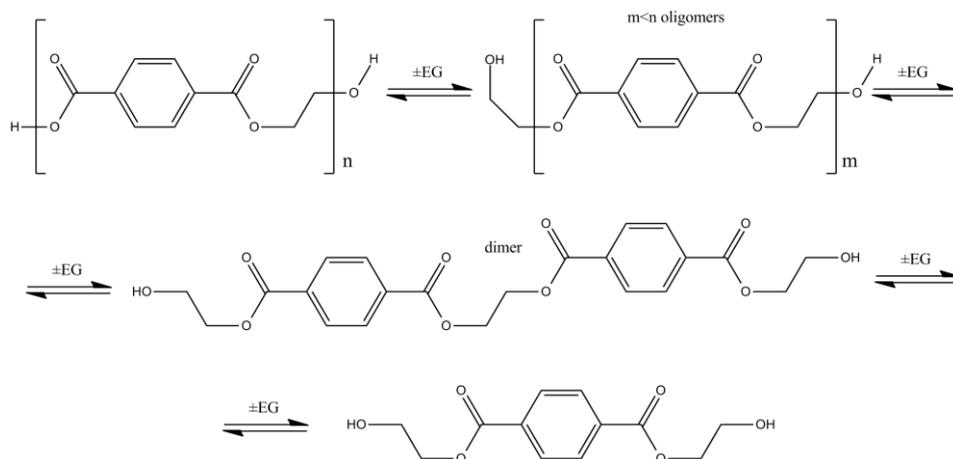
Figure 3 The equilibrial reaction steps of PET glycolysis

Solvolysis of waste plastics especially PET has become one of the main focuses of green chemistry. Over 30 years of research and development led to the discovery of exceptional solvolysis catalyst and engineering new, highly valued specialized products.[14,19-30] 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 to be in the case of other products such as cross-linked systems. In our investigations represented in this thesis, we examined the use of raw solvolysis products. Our goal was to engineer reactive systems where there is no need, or it might even be 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 and minimize the volume of needed chemicals.

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3. Experimental

In our studies commercially available PET granules (DSM Arnite® D00 301) were used for solvolysis reactions. The applied reactant diol and diamine components were used in ratios near the theoretical minimum needed for complete depolymerization at high temperatures (200-220 °C) in inert gas atmosphere. The reaction products were directly used in later steps without any purification to minimalize the chemical use and promote sustainability. The solvolysis products were used to produce polymeric and resinous materials. In this thesis we investigated two different solvolysis techniques, a newly developed technique called acido-alcoholysis, and aminolysis.

The solvolysis products and the soluble polymeric products were thoroughly characterized with functional group analysis, FTIR (ATR) and NMR (^{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) and TGA. These measurements were used to investigate the fine molecular structure of the solvolysis and polymeric products. Chain lengthening of the solvolysis products was attempted with diglycidyl-ethers to gain polyesters.

In our first study we made a comparison between the classical glycolysis, acidolysis and our new technique acido-alcoholysis to depolymerize bottle derived PET scrap. The applied total reagent ratio was kept at 1:1 calculated to the repeating units of the weighed in PET. The reaction products were compared with functional group analysis, GPC and FTIR. The solvolysis products and the polyesters were tested for biodegradability in compost.

As a second step acido-alcoholysis was used as a new technique to produce oligo and polyesters via combining the depolymerization and polycondensation reaction steps into a single reaction. The ratio of the PET derived ester groups and the applied hydroxyl groups were kept at 1:1 ratio while the of the acid groups was changed between 0-0.5 in the ratio interval. The effect of the diacid ratio was investigated on the fine molecular structure of the reaction products. One-pot type depolymerization and polycondensation reactions were engineered to produce saturated and unsaturated polyesters. The unsaturated polyesters were dissolved in styrene and cross-linked resins were produced. The glass transition temperature of the polyesters was measured with DSC, glass transition of the resinous products was determined with DMA. The cross-link density of the resins was calculated from the storage modulus.

The aminolysis products of PET with isophorondiamine (IPD) were directly utilized as cross-linkers in epoxy resin systems. The effect of PET:IPD was investigated in the molecular weight of the aminolysis product. Functional group analysis, solution viscosimetry, NMR measurements, and MALDI-TOF were used to estimate the molecular weight difference of the aminolysis products. Cross-linker solution series were prepared from the PET:IPD 1:1.5 and 1:2 reaction products. Rotational viscosimetry and DSC studies were carried out to investigate the effect of cross-linker solution concentration on the reaction kinetics. Thorough reaction kinetics studies were carried out with DSC to investigate the catalytic effect of the aminolysis product on the curing epoxy systems. DMA measurements were carried out to investigate the effects of the cross-linkers on the glass-transition temperature and cross-link density of the cured epoxy samples.

The last section of this thesis is a stand-alone study concerning the fine structure and characterization of aliphatic poly(esters amide)s. This study worked as a cornerstone for us in the fine structure characterization of polymers and oligomers. Four differently substituted amino-alcohols were used to react with adipic-acid. The polymeric products were thoroughly characterized with functional group analysis, FTIR (ATR) and NMR (^{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) and TGA. Based on our studies on the fine structure of the polymers a sequential structure was proposed. DSC crystallization studies and WAXS measurements were carried out to provide proof for our theory on different sequences in the fine molecular structure of the poly(ester amide)s.
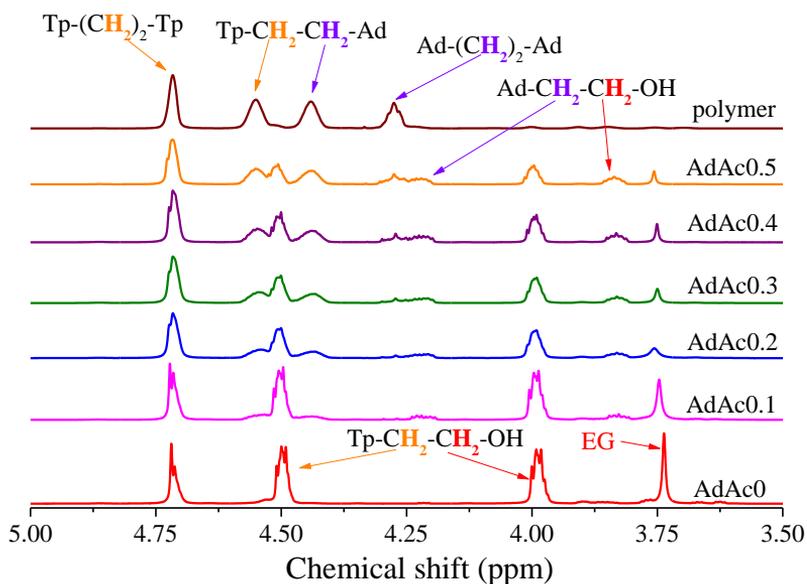
4. Results

4.1. The acido-alcoholysy of PET

Figure 4 ^{1}H NMR spectra of the PET:EG:AdAc depolymerization reaction series**.**

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 (Figure 4). The oligoesters/polyesters show reasonable level of fragmentation and weight loss after a 6 week period in compost.

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 or in unsaturated polyester resins as well. The thermomechanical properties of the unsaturated polyester resins proved to be tunable by the structure of produced oligoesters. The glass transition temperature and cross-link density decreased with increasing the ratio of adipic acid in the acido-alcoholysis reaction. (Figure 5)
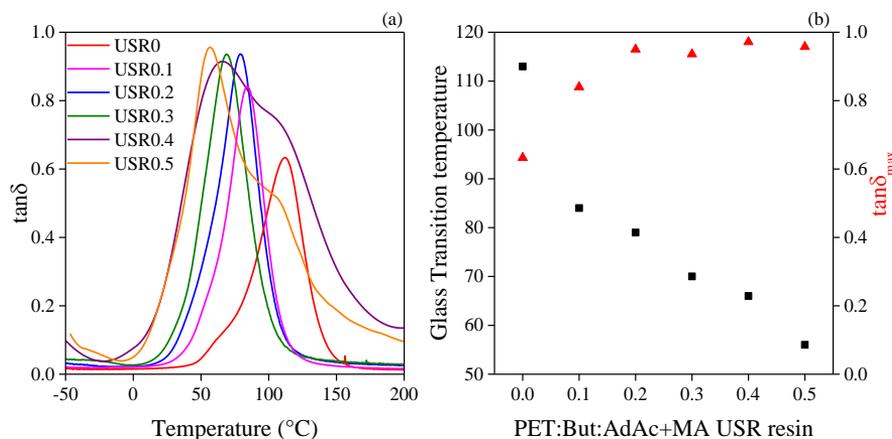

Figure 5 A $\tan\delta$ curves (a) and $\tan\delta_{max}$ and glass transition temperature (b) of the unsaturated resin samples

Thus, the most expensive steps of solvolysis, the purification of products can be completely avoided, and the product properties can be fine-tuned. 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 considerably 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.

4.2. PET derived aminolysis products in epoxy curing

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 (Table 1). Our findings suggested that the molecular weight of the produced terephthalamides can be tuned with the ratio of isophorondiamine while no residual ester groups remain. Terephalamides with two distinct molecular weights were used to produce cross-linker solutions with isophorondiamine.

Table 1 The amine content, molecular weight of the aminolysis products, and the intrinsic viscosity of their solutions in pyridine

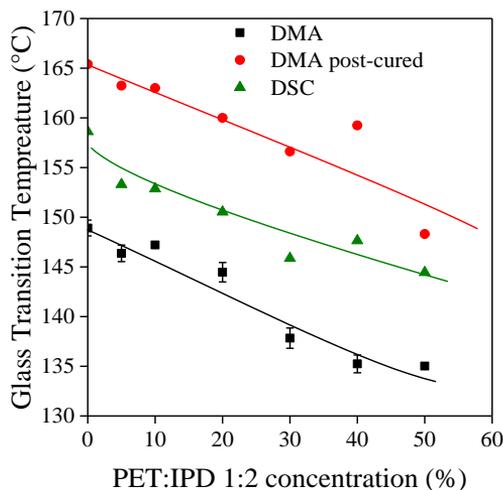| PET:IPD	Amine content (mmol g^{-1})	Intrinsic viscosity (cm^3 g^{-1})	$\overline{\mathrm{M}}_n$ (g mol^{-1})	
			NMR	MALDI-TOF
1:1.5	2.38±0.05	0.0437	980.29	1040
1:2	3.65±0.26	0.0119	569.53	860

Figure 6 The glass transition temperature of epoxy resin specimens cross-linked with the PET:IPD 1:2 solution series

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 (Figure **6**). 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 mol (Figure **7** (a)). The reaction kinetics studies supported these findings. Three models, the Kamal-Sourour, and two revised Kamal models were used to quantitatively describe the kinetics of curing. The Cole factor and the Fournier factor modified models assured a better fit at lower cure temperatures. 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 tem-perature. The k_2 values of the solutions series ranked as the following at all cure temper-atures: *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 activation energy of the autocatalitic curing could decrease with 20-30 kJ/mol (Figure **7** (b)).
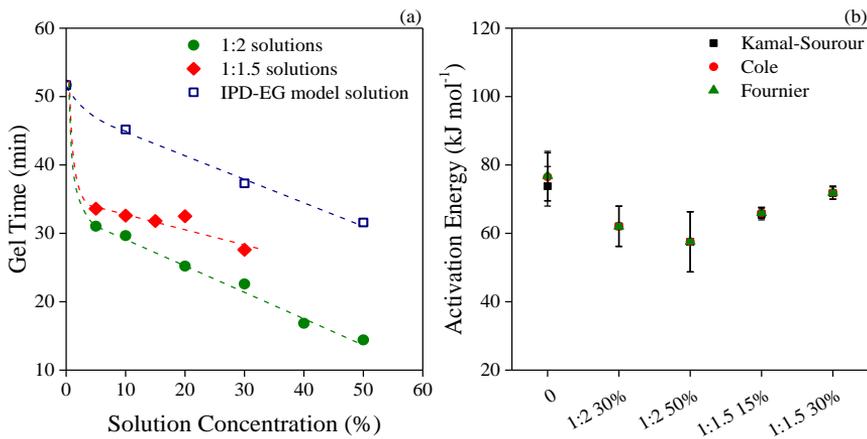

Figure 7 The effect of PET:IPD solution series concentration on the gel time (a) and the activation energy fn the actocatalytic curing reaction (b).

4.3. The sequenced structure of random aliphatic poly(ester amide)s

      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 chapter we have given a possible explanation of the sequenced organisation of random poly(ester amides) and the formation of separate crystalline phases.

      We have concluded from the functional group analysis and the SEC measurements 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 [1]H-^{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 influenced 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 (Figure 8). The two major crystalline phases were identified on the WAXS diffractograms.
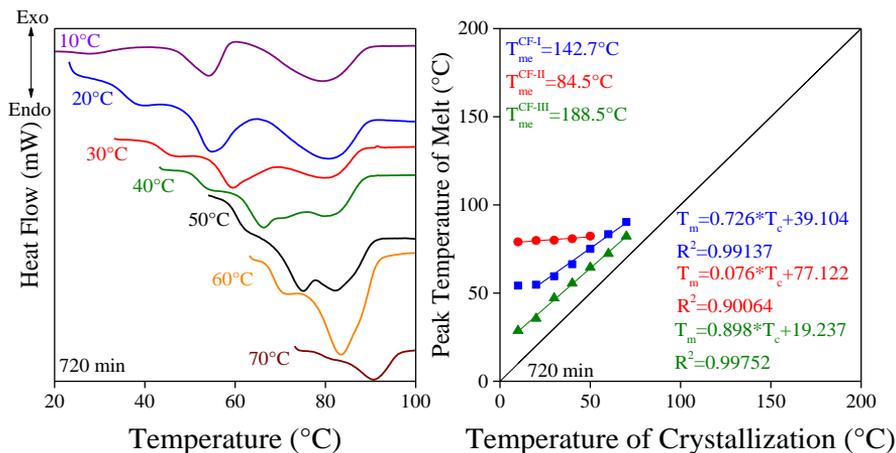

Figure 8 Melting curves of PEA after 12 hours of crystallization (a) and the shift of peak temperatures of the 3 crystalline phases(b)

5. New scientific results

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 oligo-meric 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. [1, 2]

2. One-pot type acido-alcoholysis reactions were engineered to combine depoly-merization and polycondensation into a single technological step. Acido-alco-holysis proved to be a modulable technique that allowed us to finely tune the thermal and mechanical properties of the produced polyesters. Increasing the ra-tio 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 pol-yester resins. [2]

3. Decreasing the ratio of utilized amine reagent during PET aminolysis could be used to deliberately increase the molecular weight of the produced tereph-thalamides. 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 decreases with increasing the molecular weight and the concentration of the terephthalamides. [3, 4]

4. The aminolysis products, acting as multipurposed crosslinkers can accelerate the curing 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 prod-ucts have a higher catalytic activity than the ethylene glycol. Their catalytic ac-tivity decreases with increasing the molecular weight of the terephthalamides. The DSC reaction kinetics studies further supported these observations. Compu-tational chemistry studies indicated that the accelerative activity of the tereph-thalamides is in the same order of magnitude as phenols. [4]

5. Random aliphatic poly(ester amide)s derived from adipic acid and substituted amino-alcohols were synthesized and thoroughly characterized with NMR meas-urements. 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) lead to the for-mation of different crystalline phases. DSC measurements have proven the for-mation two major and a minor crystalline phase with different equilibrium melt-ing temperature and crystallization rate. The major phases were identified with WAXS. [5]

6 Future applications

The results presented in this thesis focus on engineering a greener, more sustainable way of chemical recycling, solvolysis of PET. We have chosen to reduce the reagent ratios to the theoretical minimum and evade the use of purification methods on the final reaction products. Such solvolysis products could be used in various cross-linked systems. We have shown that such systems can be finely tuned to obtain the desired thermomechanical properties.

The one-pot type polyester depolymerisation and polycondensation technique has a considerable potential, since it is quite versatile and modular. Thus, this technique could be finely tuned for the production for any PET based polyester. These oligo- or polyester could be utilized in polyols, or polyester based plastics or unsaturated polyester resin production.

The terephthal-amide derivates could serve as a special-grade, double purposed co-cross-linker and accelerator components for epoxy resins. The cross-linker solutions could be easily prepared with adjusting the excess amount of diamine reagent during the depolymerisation reaction. Consequently the aminolysis products could be directly used in epoxy systems.

7 Publications

Papers used for the preparation of the Thesis

1. Kárpáti, L.; Szarka, G.; Hartman, M.; Vargha, V. Oligoester and polyester production via acido-alcoholysis of PET waste. *Period. Polytech. Chem. Eng.* **2018**, *62* (3), 336–344. IF (2019): 1.382 https://doi.org/10.3311/PPch.11513.

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