Co-polyesteramides of Different Microstructures: Synthesis, Properties and Fiber Spinning

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Summary

Among synthetic biodegradable polymers, aliphatic polyesteramides (PEAs) are a new class of high performance polymers combining the properties of aliphatic polyesters and polyamide. In this work, aliphatic PEAs of different microstructures have been synthesized via a batch melt polycondensation process as well as continuous reactive extrusion, and their morphology and properties have been investigated.

The first part of this work focuses on the preparation of a series of PEAs, namely poly(ε-caprolactone-co-ε-caprolactam) copolymers, using a reactive extrusion process. The copolymers are prepared by anionic ring opening polymerization of ε-caprolactam in the poly(ε-caprolactone) melt. The process is performed on a twin-screw microcompounder, and a quantitative monomer conversion can be achieved.

Followed by the successful synthesis in a small scale, up-scaling assisted by a simulation program MOREX that allows calculating the residence time of the polymer melt over the entire length of the designed extruder screw has been realized on a lab extruder. With a proper screw configuration, the monomer conversion can reach more than 95%, yielding polymers with significantly high molecular weight.

It is important to study the spinnability of PEAs, since various textile structures are often used for biomedical applications, and it is a big challenge to find proper and stable spinning conditions such as take-up speed, throughput, draw-down ratio, melting temperature and take-up point. In this work PEAs synthesized via the reactive extrusion process based on anionic polymerization of ε-caprolactam in the melt of commercially available polycaprolactone were successfully spun into fibers on a microcompounder equipped with a melt spinning line.

The second part of the thesis deals with the synthesis of high molecular weight poly(esteramideamides) (PEAAs) by melt polycondensation of a tailor-made amide-containing monomer based on 1,4-diaminobutane and ε-caprolactone and different dicarboxylic acid methyl esters with a varied number of methylene groups under catalysis of an organo-titanium catalyst. A series of PEA polymers were synthesized and their fibers were prepared via a melt spinning process. The mechanical and thermal properties
of as spun and conditioned fibers were then evaluated and interpreted regarding the structure property relationship.

This work shows the incorporation of ester and amide groups in a polymer backbone leading to a new class of degradable polymers, PEAs. Both continuous and batch synthetic procedures have been developed for their preparation. PEAs with tailor-made chemical structures have been synthesized, and they can be melt-spun into fibers of good mechanical properties.
Kurzfassung


Der erfolgreichen Synthese im kleinen Maßstab folgte ein Up-Scaling, das in einem Laborextruder durchgeführt wurde und durch Simulationsrechnungen mittels des Programms MOREX unterstützt wurde, das es erlaubt, die Residenzzeit der Polymerschmelze über die gesamte Länge der entworfenen Extruderschnecken zu berechnen. Bei einer geeigneten Schneckenkonfiguration kann der Monomerumsatz 95% erreichen wobei die resultierenden Polymere hohe Molekulargewichte aufweisen.


Der zweite Teil der vorliegenden Arbeit befasst sich mit der Synthese hochmolekularer Poly(esteramidamid)en (PEAA) durch Schmelzpolykondensation von maßgeschneiderten
Amid-haltigen Monomeren basierend auf 1,4-Diaminobutan und ε-Caprolacton und
durch organische Titan-Verbindungen. Es wurde eine Serie
von PEAA Polymeren synthetisiert und daraus Fasern mittels Schmelzspinnprozess
hergestellt. Die mechanischen und thermischen Eigenschaften der gesponnenen und
die Fasern wurden evaluiert und hinsichtlich der Struktur-Eigenschafts-
Beziehungen untersucht.

Diese Arbeit führte durch die Einbettung von Ester- und Amidgruppen in das
Polymerrückgrad zu einer neuen Klasse von abbaubaren Polymeren, den PEA. Es wurde
sowohl ein kontinuierlicher als auch ein diskontinuierlicher Syntheseprozess zur
Darstellung der Polymere entwickelt. Es wurden PEA mit maßgeschneiderten chemischen
Strukturen synthetisiert, die durch einen Schmelzspinnprozesse zu Fasern mit guten
mechanischen Eigenschaften verarbeitet werden konnten.
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Aachen
“Dream the impossible. Know that you are born in this world to do something wonderful and unique; don’t let this opportunity pass by. Give yourself the freedom to dream and think big”

~ Sri Sri Ravi Shankar
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Chapter 1

Introduction

1.1 Introduction

The ever increasing population has created several serious problems such as deficiency of the resources and energy. However, the rapid progress of science and technology after the World War II has made our life more convenient, but at the same time has also led to the problems like global environmental pollution. In present era synthetic polymers have been used in wide variety of applications ranging from packaging to biomedical devices. Natural fibers, woods and rubber have been replaced by synthetic polymers of petroleum origin. These synthetic polymers thus lead to serious environmental pollution because of their non-degradable nature.\(^1\)

The use of biodegradable polymers has become indispensable to solve this severe environmental pollution problem.\(^2\) Among the synthetic bio-degradable polymers, aliphatic polyesters like poly(lactic acid), poly(\(\varepsilon\)-caprolactone) and poly(butylene adipate) are known to be fully biodegradable,\(^6\) but they lack the necessary mechanical strength for broad use. One strategy to solve this problem was to incorporate amide groups in these polyesters. The incorporation of amide groups provides the polymer with desired mechanical strength and ester groups contribute to the hydrolytic degradation of such polymers. This new class of polymers having both ester and amide groups in polymer backbone is known as Poly(esteramide) (PEA). PEA is being a significant research material of interest as it combines good end-use with better processing properties and biodegradability.\(^8\)-\(^13\)

Several research groups have reported synthetic PEAs of different microstructures including random, alternating and blocky/segmentedstructures,\(^14\)-\(^19\) based on different aliphatic or aromatic monomeric building blocks. In addition, the properties of PEAs can be tuned as desired by varying the ratio of ester and amide groups in the polymer backbone. Both the ring opening polymerization\(^19\)-\(^23\) and polycondensation\(^12,16,23-27\) are considered the most suitable and commonly used procedures for the synthesis of PEAs. In spite of the fact that the first derivative of PEA was developed in 1970s, till date the
production of PEA has never become an industrial process. Exception is the PEA from Bayer AG with the commercial name BAK1095.\textsuperscript{[28]} However, its production was abandoned in 2001.

From the ecological and economic point of view, for the production and processing of PEA, emphasis should be given to the development of low-cost and environmentally benign synthetic procedures. The main goal of this work is therefore to develop a reactive extrusion process, i.e. using twin-screw extruders as polymerization reactors, for the continuous synthesis of PEAs.

1.2 Objectives

The objectives of this thesis are as following:

- To synthesize PEAs of different micro-structures via two different methods-
  - i. By reactive extrusion for the continuous synthesis of PEAs
  - ii. By melt polycondensation to synthesize PEAs in batch
- To investigate the structure-property relationship of these synthesized PEAs using various physico-chemical analytical techniques.
- To analyze the spinnability of the resulting PEAs for producing fibers for different textile structures.

1.3 Contents of this thesis

After a brief introduction to PEA and on the objectives of this thesis, the next chapters will focus on the synthesis, characterization and fiber spinning of PEAs synthesized on twin screw extruder via reactive extrusion process as well as by melt polycondensation in batch process. The outline of the contents of this thesis is as following:

Chapter 2 gives a brief bibliography on the PEAs of different micro-structures and their synthetic procedures. An overview of the twin screw extruder as polymerization reactor as well as of spinning processes is then presented. The last part focuses on the different types of applications of PEAs.

Chapter 3 deals with the anionic ring opening polymerization of $\varepsilon$-caprolactam (CA) in the melt of poly(caprolactone) (PCL) in a twin-screw mini-extruder and thereafter,
focuses on analyzing these synthesized PEAs by different physico-chemical techniques in order to draw the conclusion on the feasibility of this process. The influence of different initiator and activator concentrations as well as the ratio of CA:CL on material properties were also studied and evaluated.

In Chapter 4, an attempt was made for up-scaling the process of PEA synthesis established on the mini-extruder on a lab extruder. The screw configuration was designed and optimized by means of computer simulation. The residence time of the polymer melt over the entire length of different screw configurations was determined. The synthesis of PEAs was then carried on the lab extruder with different screw configurations. The PEA samples were then analyzed for their chemical composition, thermal, mechanical and rheological properties. It was shown that at a constant screw rotating rate the screw configuration with a longer residence time resulted in a significantly improved conversion and molecular weight of the products.

Chapter 5 deals with the attempt to spin fibers from PEA synthesized via reactive extrusion process. The challenge was to find proper and stable spinning conditions such as take-up speed, throughput, draw-down ratio, melting temperature and take-up point. The effect of chemical composition of PEAs on spinning conditions as well as thermal and mechanical properties of the resulting filaments was analyzed.

Chapter 6 deals with the synthesis of high molecular weight poly(esteramideamides) (PEAAs) by melt polycondensation using tailor-made \(\alpha,\omega\)-amino alcohol and dicarboxylic acid methyl esters of different alkylene chain lengths under the catalysis of an organo-titanium catalyst. \(\alpha,\omega\)-Amino alcohol was prepared by ring opening of \(\varepsilon\)-caprolactam with tetramethylene diamine. The chemical structure of the resulting PEAAs was analyzed by NMR and FT-IR spectroscopy. The effect of polymer composition on the thermal and physical properties was evaluated. It was found that the alkylene chain length of dicarboxylic acid methyl esters has a significant effect on physical properties of the PEAAs.

In Chapter 7, the spinnability of PEAAs synthesized in Chapter 6 was tested on a twin screw micro-compounder combined with a winding unit and conditioning unit. The fibers were spun by drawing from the polymer melt through a spinning dye of 1mm diameter.
The as spun fibers were then conditioned at room temperature. The thermal and mechanical properties of these PEAA fibers were evaluated.

1.4 References


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Chapter 2

Literature Review: Polyesteramides

Biodegradable polymers have emerged as a solution for the global environmental pollution problem caused by the non-degradable waste products. Nowadays, biodegradable polymers are increasingly used in different fields ranging from packaging to biomedical applications. Aliphatic polyesters like poly(lactic acid) (PLA), poly(glycolic acid) (PGA) and their copolymers are typical examples among the synthetic biodegradable polymers. However, they suffer from limitations in terms of mechanical strength and dimensional stability. In addition these are quite expensive, and have poor processability. Aliphatic polyamides on other side have good mechanical and processing properties, but have poor biodegradability. This leads to the emergence of a new class of synthetic polymers known as polyesteramides (PEAs). The fundamental idea behind the development of PEAs is to combine the favourable properties of both polyester and polyamide. Furthermore, the physico-chemical properties of PEAs can easily be tuned by varying the ratio of amide to ester groups in the polymer chain. The PEAs can be classified as random, alternating or segmented (blocky) PEAs depending on their synthetic methodologies and monomers used in their preparation. These different microstructures of PEAs, their synthetic routes, fiber spinning and potential applications are discussed in this literature review.

2.1 Microstructures of polyesteramides

2.1.1 Random polyesteramides

When ester and amide groups are randomly distributed in a polymer backbone including the different numbers of adjacent ester or amide groups, such PEAs are said to have a random microstructure. Both ring opening polymerization (ROP) and polycondensation methods can be used to synthesize random PEAs.\(^{[1-16]}\) For example, the commercial product BAK\(^\text{®}\) 1095 of Bayer was a random semi-crystalline PEA prepared from \(\varepsilon\)-caprolactam, 1,4-butanediol and adipic acid.\(^{[7-8]}\)
2.1.2 Alternating polyesteramides

Alternating PEAs can be further classified as strictly alternating and regular PEAs. When the ester and amide groups alternate with one another in a polymer backbone, such PEAs are called strictly alternating PEAs. Their microstructure can be represented as follows.

\[
\begin{array}{c}
\text{E} \quad \text{E} \quad \text{A} \quad \text{E} \\
\text{A} = \text{Amide} \quad \text{E} = \text{Ester}
\end{array}
\]

Here varying number of methylene groups separate the amide and ester bonds. For instance, strictly alternating PEAs are obtained by ROP of morpholine-2,5-diones.\(^{[17-28]}\)

When the two consecutive ester and amide group alternate with one another in a polymer chain, such PEAs are said to be regular PEAs. Their microstructure can be depicted as follows.

\[
\begin{array}{c}
\text{A} \quad \text{E} \quad \text{A} \quad \text{E} \quad \text{A} \quad \text{E} \\
\end{array}
\]

For instance, the condensation of preformed monomers (bisamide diols or bisester diamines) with diacids or diacids chlorides results in regular PEAs.\(^{[29-33]}\)

2.1.3 Segmented or blocky polyesteramides

When the ester and amide blocks of similar or varying lengths are statistically placed in the polymer chain, such PEAs are said to have a blocky microstructure. Their microstructures can be represented as below.

\[
\begin{array}{c}
\text{A(A)} \quad \text{E(E)} \quad \text{A(A)} \quad \text{E(E)} \quad \text{A(A)} \quad \text{E(E)} \\
\end{array}
\]

where, \(x \neq y\)

For instance, the reaction of tailor made or preformed monomers like bisamide diols or bisamide diesters with diols and dimethyl adipate leads to the formation of segmented PEAs.\(^{[34-41]}\)
Segmented PEAs or block copolymers belong to the class of thermoplastic elastomers. They have a micro-phase separated structure at room temperature, i.e., they consist of hard and soft domains which are formed by the self-organization of polymer segments. Amide segments form the hard domains as they can crystallize and give mechanical strength to the polymers while ester segments constitute the soft domains.

2.2 Methods to prepare polyesteramides

PEAs can be prepared by catalyst assisted polycondensation, ROP or by the combination of both methods.[42-43]

2.2.1 Polycondensation

PEAs by polycondensation method can be prepared by using preformed monomers like diamide diol, diester diamine, ester diamines or diamide diester monomers. Condensation of these monomers with dicarboxylic acid derivatives or diols leads to the formation of PEAs. PEAs can also be synthesized by reacting α,ω-amino alcohols with acid anhydride or dicarboxylic acid derivatives.

Polycondensation can be performed by several methods:

2.2.1.1 Melt polycondensation

Melt polycondensation is generally carried out in two steps using a catalyst. In the first step, the conditions used for reactions are milder and a prepolymer is obtained while the second step involves higher temperatures and reduced pressure to accelerate the condensation process and to achieve high molecular weight polymers.

For industry, the melt polycondensation method is advantageous as no post treatment, e.g. removal of solvents, is needed after the polymerization reaction. However, there is a disadvantage that undesirable side reactions might take place at high temperatures used in this method resulting in the lowering of molecular weight of the synthesized polymers.

For instance as shown in Figure 2.1, melt polycondensation has been successfully employed to synthesize PEAs by reacting preformed monomers like α,ω-amino alcohols,
α,ω-diamines or α,ω-diols containing an built-in amide bond with 1,4-butaneediol and dimethyl adipate.\textsuperscript{[44]}

![Figure 2.1. Polyesteramide prepared by polycondensation reaction of α,ω-amino alcohol with 1,4-butaneediol and dimethyl adipate.](image)

2.2.1.2 Interfacial polycondensation

Interfacial polymerization can be done by reacting organic solvent soluble diacid chloride with water soluble diol or diamine. Surface active agents are used to increase the interfacial area to faciliate the reaction by increasing the contact between the reactants. Phase transfer catalysts like quarternary ammonium cation can be added as they favor the interfacial nucleophilic displacement reactions, an important characteristic of interfacial polymerization.\textsuperscript{[45]} Therefore, the reaction is strongly influenced by the choice of solvents, catalytic additives and surface active agents.\textsuperscript{[46]}

Interfacial polymerization can be done at low temperature; however, this method also has disadvantages of undesirable side reactions, which lead to the chain termination resulting in low molecular weight polymers.

For instance, interfacial polymerization method has been successfully employed for the synthesis of PEAs with varying L-alanine contents by reacting the mixtures of 1,6-hexanediol diesters of L-\&-D alanine with sebacoyl chloride.\textsuperscript{[47]} Being a fast and simple procedure, interfacial polymerization has also been used by several research groups to synthesize α-amino acid based PEAs. Preformed monomers were synthesized by condensing α-amino acids with diols in presence of p-toluenesulfonic acid to form diester-diamine salts, which were then reacted with diacids or diacid chlorides to give α-amino acid based PEAs.\textsuperscript{[47-51]}

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2.2.1.3 Solution polycondensation

The key features of the solution polycondensation involve mild reaction conditions, high polymerization rates and minimal side reactions resulting in high molecular weight polymers. In the solution polycondensation, the reaction of dicarboxylic acids with diamines is facilitated by the use of condensing agents or by the activation of carboxylic acid groups.\[^{[51]}\]

However, drawbacks of solution polycondensation inspite of its many attractive features are that it requires very pure monomers to maintain the stoichiometric balance necessary for the production of high molecular weight polymers.\[^{[52]}\] Furthermore, the polymer obtained by this method needs a purification step to remove the solvent and toxic by-products.\[^{[53]}\]

Katasarva et al. in 1980s proposed the synthesis of \(\alpha\)-amino acid based PEAs by solution polycondensation which is still one of the most used methods.\[^{[53-55]}\] They synthesized high molecular weight PEAs with narrow polydispersity index by reacting di-p-toluenesulfonic acid salts of bis(\(\alpha\)-amino acid), \(\alpha,\omega\)-alkylene diesters and di-p-nitrophenyl esters of diacids in chloroform or N-methyl-2-pyrolidone in the presence of triethylamine as an acceptor for p-toluene sulfonic acid at room temperature.\[^{[43]}\]

2.2.2 Ring opening polymerization

PEAs can be prepared by ROP of cyclic depsipeptides (morpholine-2,5-dione derivatives). By reacting morpholine-2,5-dione derivatives having \(\alpha\)-amino acid residues with other lactones, a wide range of biodegradable PEAs can be synthesized.\[^{[56]}\]

Enzyme catalyzed ROP was applied on several morpholine-2,5-dione derivatives by Höcker et al.\[^{[24-26]}\] to give PEAs with Mn ranging from \(6.9 \times 10^3\) to \(1.5 \times 10^4\), using Porcine pancreas as a catalyst.

PEAs of different microstructures can be synthesized by ROP. Random copolymers were synthesized by the copolymerization of morpholine-2,5-dione derivatives with D,L-lactide. Similarly alternating copolymers (poly-\(\alpha\)-amino acid-alt-D,L-lactic acids) was synthesized by ROP of the corresponding morpholine-2,5-dione derivatives.\[^{[43]}\] Lactam-
caprolactone based PEAs with a blocky microstructure were also prepared by ROP through a reactive extrusion process.\textsuperscript{[57-58]}

2.3 Reactive extrusion process for preparation of PEAs

Reactive extrusion is a cost effective, very attractive polymer processing method carried out on extruder for not only melt blending but also for carrying out polymerization reactions including branching, grafting and functionalization of polymers.\textsuperscript{[59-60]} The reactive extrusion process involves the introduction of reactants in a proper reaction sequence, their complete homogenization and maintaining sufficient residence time to achieve the completion of the reaction.

2.3.1 Twin screw extruder as polymerization reactor

In the reactive extrusion either single screw or twin-screw extruders are used. However, twin-screw extruders (TSEs) are more preferred over single screw-extruders because of better mixing and dispersion, control of residence time distribution as well as their better capabilities in respect of heat and mass transfer. The single screw and twin-screw extruders differ mainly in their conveying mechanism. In a single screw extruder it depends on the frictional and viscous forces developed in conveying and melt pumping zone while in a TSE it depends mainly on the screw configuration. The single screw extruders are used mostly for simple tasks employing melting and plaststicizing for making films, pipes etc., while more complex tasks can be performed on TSE like reacting compounding, polymerization, etc.\textsuperscript{[61]}

TSE are of two types depending on the direction of the two screw rotations: counter rotating TSE and co-rotating TSE. Figure 2.2 illustrates the classical intermeshing counter-rotating and co-rotating screws.

![Figure 2.2. Classical intermeshing counter-rotating and co-rotating screws.][62-63]
It has been demonstrated that the co-rotating intermeshing TSE is more suitable for the reactive extrusion because of following reasons:\textsuperscript{[61, 64-65]}

- Self-cleaning property to prevent stagnation of material
- Favorable and effective degassing conditions
- Homogeneous rapid mixing at high speeds and thus low residence time

2.3.1.1 Screw elements

TSE provide a high degree of flexibility for reactive extrusion because of their modular construction. In addition, specific arrangements and variation of the screw elements on the screw shaft is possible to carry out specific processing tasks. The most commonly used screw elements in co-rotating intermeshing TSE are discussed below.

2.3.1.1.1 Conveying elements

Conveying elements are used to forward the material from feed opening towards kneading and mixing elements or to discharge the material from die in an extrusion process. Conveying elements could be distinguished by the number of flights, length or pitch of the elements. An element with a longer pitch offers more volume and thus conveys more material, while an element with a shorter pitch is used to pressurize the die. Similarly an element with reverse flight can be used for retaining the material for a longer duration in the extruder. Figure 2.3 shows the conveying elements of 90mm length with different pitches.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{conveying_elements.png}
\caption{Conveying elements of 90mm length with different pitch.\textsuperscript{[62]}}
\end{figure}
2.3.1.2 Kneading elements

Kneading elements are used for effective shearing and dispersive mixing of materials. Kneading elements are made up of several kneading discs which determine its element length and have different advance angle which determines its conveying ability.\cite{62-63} The advance angle of 90° has a neutral character i.e. it pushes the material neither forward nor backward, while 30°, 60° etc. convey the material forwarding; and a reverse flight kneading element has a retaining character. As the advance angle increases, the mixing and shearing capability also increases. Figure 2.4 shows the kneading blocks of 30mm length with different advance angles.

![Kneading blocks with different advance angles](image)

**Figure 2.4.** Kneading blocks of 30mm length with different advance angles.\cite{62}

2.3.1.2 Process zones of the extruder

There are different zones in the TSE, which perform specific functions in a series. These different zones of TSE (Figure 2.5) along with their functions are discussed below.

![Different zones of a twin screw extruder](image)

**Figure 2.5.** Different zones of a twin screw extruder.\cite{66}
2.3.1.2.1 Feed zone

The material is introduced into the extruder through a feed zone with the help of a hopper. The feed zone is made up of active conveying screw elements to promote the solid and liquid reactants to the next zone of the extruder. The two well-known ways of feeding are force-feeding and starve-feeding. In the force-feeding, there is the reserve material maintained in the hopper and is positively forced in the extruder while in the starve feeding, the hopper remains empty, i.e. the extruder is fed at a less rate than its capacity. Out of these two methods, the starve feeding is mostly used because of an important advantage that the feeding can be split in it.

2.3.1.2.2 Melting or plasticizing zone

After the feed zone is the melting or plasticizing zone, in which primarily melting of reactants and therefore the beginning of reaction takes place as well as the pre-dispersion of fillers also starts in this zone. This mixing along with melting is achieved by the use of kneading elements. A rapid and uniform plasticization of reactants is important to avoid undesirable reactions and to achieve a better product quality. In addition, for many reactions, care must be taken to avoid the presence of oxygen and moisture which may terminate the reaction by providing a vent if possible after the melting stage.

2.3.1.2.3 Mixing zone

Mixing is very essential to increase the uniformity of the composition to obtain a homogeneous product. Mixing can be of two types – distributive or dispersive mixing. In the distributive mixing, there is an uniform distribution of the mix, whereas in the dispersive mixing, crushing of the solid agglomerates or liquid droplets takes place.

2.3.1.2.4 Polymerization zone

The polymerization reaction i.e. the synthesis or modification of polymers takes place in this zone after the plasticizing and mixing of reactants. For polymerization different reactions require different conditions and corresponding screw design. For instance, for some reactions a minimum barrel temperature is required to initiate the reaction. Excess temperatures may lead to fast decomposition reactions. Also, if the reaction is exothermic, it may result in the increase of barrel temperature.
2.3.1.2.5 Venting zone

This zone is optional and is required in many reaction processes with the need to remove residual monomers (volatiles) or moisture and air. For instance, removal of moisture is very essential in condensation polymers such as nylon and PET to prevent their hydrolysis.\textsuperscript{67} Also, the reaction kinetics is influenced and the conversion rate can be increased by removing the low molecular weight components during venting. Additionally the venting also helps in controlling temperature in highly exothermic reactions.

2.3.1.2.6 Metering zone and die

Metering zone which is the final processing zone in an extruder is also known as pumping zone. The screws in this zone are designed to build optimum pressure required to pump the homogeneously compounded polymer melt at the die for a continuous output. Here the design of the die determines the optimum pressure required and thus, the screw design. Excessive cooling of this zone should be avoided for optimum performance of the designed screws used in this zone.\textsuperscript{67}

2.3.1.3 Screw configuration

Configuration of screws of an extruder depends on the process to be performed on it. The flexibility due to the modular design of the barrel and screw in twin screw extruder is another advantage to design the extruder for reactive extrusion processes. The screw designing involves a number of estimates and calculations; and interpretation of information and knowledge for example heat flow, temperature profiles, kinetics of reaction etc., related to the course of reaction.\textsuperscript{61, 64, 68-70} The sequence of the screw elements is very important in designing screws as it determines the residence time distribution, filling level and pressure build-up in that particular screw configuration.

2.3.2 Polyesteramide via reactive extrusion in a twin screw extruder

Attempts have been made by several researchers to prepare PEAs by reactive extrusion in a twin screw extruder. Kim et al prepared lactam-caprolactone block copolymers in a modular intermeshing co-rotating twin screw extruder using sodium hydride and N-acetyl caprolactam as cointiators.\textsuperscript{57-58} They found that the sequence of feeding of monomers
played an important role in defining the chemical structure of the final products. When both caprolactam and caprolactone along with co-initiators are simultaneously fed into the first hopper, then a mixture of homopolymers was obtained, while a sequential feeding of \( \omega \)-lauryl lactam (LLA) and \( \varepsilon \)-caprolactam (CLA) along with cinitiators in first hopper and \( \varepsilon \)-caprolactone (CLO) into the second hopper resulted in high molecular weight block copolymers. Also by controlling the feed ratio of the monomers during the reactive extrusion process, the block length of the copolymers could be adjusted. Terpolymers with block and random polylactam structure, i.e P(LLL-b-CLA-b-CLO) and P(LLL/CLA-b-CLO), were prepared through the reactive extrusion process in a similar way.

2.4 Spinning of polyesteramide fibers

2.4.1 Fiber spinning

In the fiber spinning either molten polymer or its solution is forced through the barrel from a spinning die to get long thin filaments of relatively constant cross-sectional area. The main types of spinning techniques are discussed below.

2.4.1.1 Melt spinning

When the polymer melt is thermally stable, melt spinning process is used to spin fibers. The polymer melt is extruded through a spinning die which gets cool and solidifies as it exits. A tensile force is then applied on this polymer melt to draw the filaments which wound onto a bobbin. According to the fiber application, mono or multifilament fibers can be produced depending on the used die.\[^{71-73}\]

So far, only few research groups were successful in making PEA fibers via the melt spinning process. Z. Qian, et al. prepared PEA fibers via melt spinning using a melt flow rate instrument equipped with a single nozzle circular spinning die. The PEAs used in melt spinning were based on \( \varepsilon \)-caprolactam and 11-aminoundecanoic acid and were synthesized via a melt polycondensation process. C. Liu, et al. prepared melt spun fibers of PEAs based on 6-aminocaproic acid, adipic acid and 1,6-hexane diol. They both studied the tensile and degradation properties of the obtained fibers thereafter.\[^{74-75}\] Melt spun fibers from PEAs based on phenylalanine were also known in the literature.\[^{76}\]
2.4.1.2 Solution spinning

When the polymer melt is thermally unstable, solution spinning is employed provided that the polymer must dissolve in an appropriate solvent in a high concentration to get 5-30% of polymer content.[77] In a solution wet spinning process, a non-volatile solvent is used to dissolve the polymer and the solution is extruded into a bath containing a compatible non-solvent for the polymer, while in dry spinning, the spinning solvent used is volatile and is removed by thermal evaporation during draw down.[71,78]

It was attempted to spin fibers of PEA based on phenylalanine by solution wet spinning. The solvents n,n-dimethyl formamide and chloroform were used to create PEA solutions, and ethyl acetate was used in the coagulation bath. However, it was unsuccessful to make fibers by this technique.[76]

2.4.1.3 Electrospinning

This technique is used to prepare fibers with submicron diameters. This method was first patented by Formhals in the 1930’s and afterwards applied on several polymers because of its technical simplicity, versatility and reproducibility. Electrospinning involves the charging of polymer solution using a high voltage supplier resulting in development of a potential gradient between the collector and the charged solution. The strong electrostatic repulsions develops between the similar charges in solution and when the electric field strength exceeds the surface tension of this liquid, then a polymer jet is released from the polymer solution droplet. The solvent of the polymer jet so released gets evaporated in atmosphere resulting in the deposition of polymer fibers on the collector.

P. Garg et al. have successfully electrospun PEA fibers from solution. These PEAs were based on 1,4-butanediol, dimethyladipate and preformed α,ω-amino alcohol (based on ε-caprolctone and 1,4-diamino butane) and synthesized via melt polycondensation. They studied the influence of different electrospinning parameters on the diameter of nanofibers and concluded that the conditions like 20kV voltage and solvents like CHCl3/HCOOH (9:1 v/v) are optimum for producing fibers in the nanometer range from those PEAs.[44]
2.4.2 Fiber drawing

Fiber drawing or orientation is a process in which fiber samples obtained are generally drawn at a temperature above their glass transition temperature (T_g) by applying uniaxial tensile stress to induce the orientation of polymer chains. This process results in the fibers which are stronger in the draw direction but weaker in the transverse direction. In case of crystalline polymer fibers, drawing sets in rapid crystallization due to molecular orientation of the chains.[78] Cicero et al.[79] proposed the molecular structure of PLA during drawing (Figure 2.6) in which the stacks of crystalline and amorphous regions are formed within the microfibrils and microfibrils get aligned along the fiber axis.

![Figure 2.6. Supramorphological model for melt spun PLA.][79]

2.5 Polyesteramide: A potential biodegradable polymer

The need for environmental protection has triggered the research for development of environmental friendly polymers i.e. biodegradable polymers. PEAs due to the presence of both ester and amide group ensure degradability and has emerged as one of the promising class of biodegradable polymers.[51,61]

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Previously, the use of PEAs was restricted mainly to applications involving low molar mass for example in hot melt adhesives, as the various possibilities for higher-molecular PEAs were at the research stage. Use of PEAs as an additive for blends[80-81] and as a coating material was reported.[82-84] However because of its good biocompatibility and degradation behavior, PEAs offer a large potential for other applications, too. A large number of applications ranging from packaging to biomedical applications like controlled delivery systems,[85-95] tissue engineering[96-104] etc. have been studied by many research groups in the last years.

Among synthetic methodologies as discussed before both polycondensation and POM appear to be the suitable procedures for obtaining PEAs with sufficient molecular weight required for the end use.[51] However, compared to other commodity plastics, the use of PEAs is still restricted due to high cost of production and limited thermo-mechanical properties. For the commercial viability, an inexpensive, easy and appropriate process is required to manufacture PEAs.

In the present work, we have developed a reactive extrusion process for the preparation of PEAs on a micro-compounder (a batch-wise operating screw machine) and transferred the synthetic procedure to a continuous production on a laboratory co-rotating twin-screw extruder. For the successful transfer, a computer simulation program MOREX was used to optimize the screw design/configuration by comparing different screw configurations in respect of the melt residence time. This work could be interesting from an economic point of view for industrial production of PEAs.

Furthermore, we have also prepared new PEAs by batch melt polycondensation technique. High molecular weight polymers obtained from both batch synthesis and reactive extrusion were further processed and spun into fibers, which can be used further for making various textile structures.

2.6 References

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Chapter 3

Development of Reactive Extrusion Process for Synthesis of Polyesteramides on Microcompounder

The part of this work was done in collaboration with group of Prof. Dr.-Ing. Edmund Haberstroh, Chair of Lehr- und Forschungsgebiet Kautschuktechnologie, RWTH Aachen University, Eilfschornsteinstr. 18, 52062 Aachen, Germany, and was partially published in Macromolecular Materials and Engineering (Manisha Gupta, Felixine Siegmund, Edmund Haberstroh, Martin Rosenthal, Dimitri A. Ivanov, Martin W.M. Fijten, Xiaomin Zhu, Martin Möller. Preparation of Polyesteramides in a Reactive Extrusion Process, Macromolecular Materials and Engineering, 2014, 299, 1343-1351.)

Abstract

In this work the synthesis of a series of polyesteramides, namely poly(ε-caprolactone-co-ε-caprolactam) (P(CLO-co-CLA)) copolymers, using a reactive extrusion process is reported. The copolymers are prepared by anionic ring opening polymerization of ε-caprolactam in the PCLO melt, and the process is performed in a twin-screw microcompounder. For a fast reaction the masterbatches of sodium caprolactamate and hexamethylene-1,6-dicarbamoylcaprolactam in ε-caprolactam are employed as initiator and activator, respectively. Remarkably, the monomer conversion is found to be almost quantitative. By means of gel-permeation chromatography, thermal analysis and wide-angle X-ray diffraction, the extruded products are proved to be polyesteramide copolymers with short polyamide fragments integrated into the polyester backbones. All copolymers form co-existing PCLA and PCLO crystalline domains. The crystallinity index of PCLO is found to be quite low and rather constant, whereas the amount of the α- and γ-phases of PCLA varies noticeably with the copolymer composition and initiator/activator concentration. The fraction of the metastable PCLA γ-phase reaches the
maximum at the lowest content of PCLA, signifying that the formation of the γ-phase is preferred, when the crystallization conditions are not favorable for PCLA.

3.1 Introduction

Due to the increasing environmental pollution caused by non-degradable plastic wastes worldwide, there is an urgent need for the development of new biodegradable and compostable polymers with low production costs but at the same time satisfactory material properties.[1] Even though, aliphatic polyesters are the most common biodegradable polymers, they suffer from low thermal, mechanical and processing properties that restrict their practical applications.[2] Polyesteramides (PEAs), which comprise both ester and amide bonds in the polymer backbone, are among biodegradable polymers from petroleum sources.[3] In contrast to pure polyesters, PEAs combine the good mechanical and processing properties of polyamides with biodegradability of aliphatic polyesters, thus resulting in a high potential in various application fields ranging from packages up to biomedical devices.

Using different synthetic methods PEAs of various chain microstructures can be obtained, including random,[4] alternating,[5] segmented block copolymers,[6] and even blends of polyester and polyamide[7] with a broad property profile. Random PEAs are statistical co-polycondensation products of monomers of polyamides and polyesters. A well-known example is thermoplastic PEA from Bayer AG under commercial name BAK® 1095 that was synthesized via polycondensation of ε-caprolactam, adipic acid and 1,4-butanediol.[8] The behavior of regularly alternating PEAs usually resembles that of a homopolymer. For example, poly(3(S)-sec-butylmorpholine-2,5-dione) prepared by ring-opening polymerization of the corresponding monomer exhibited a single glass transition at 50 °C and melting at 74 °C.[5a] Segmented PEAs with a defined short amide sequence in the backbone can be obtained via co-polycondensation of a tailor-made monomer containing a short amide segment and monomers of a polyester.[6a-c] Thermal analyses revealed that the length and content of the amide segment affected significantly the phase behavior of the PEAs. For the PEAs with a triple amide segment, only the amide groups can crystallize, and the melting temperature increases with the increase of the amide content. However, in the case of PEAs with a double amide segment, both ester and amide
fragments can crystallize, showing multiple crystallization/melting processes. PEAs with long polyamide segments can be prepared by sequential copolymerization.\cite{6d-f}

Poly(ε-caprolactam-co-ε-caprolactone) (P(CLA-co-CLO)) copolymers can be considered as one of the most promising classes of biodegradable polymers\cite{9} due to the availability of both CLA and CLO monomers. Random and block P(CLA-co-CLO) copolymers can be synthesized either by hydrolytic or anionic ring-opening copolymerization of these monomers\cite{6d-f,10}, and the mechanism of copolymerization of CLA and CLO was also studied in detail. The use of extruders as polymerization reactors, so called reactive extrusion, has been the focus of increasing interest in the industry because of a number of obvious advantages including environmental benignity, handling of very high viscosity, decrease of processing steps, etc.\cite{11}, and reactive extrusion is also used to prepare biodegradable polymers.\cite{12} It was reported that the copolymerization of CLA and CLO was carried out in a modular intermeshing co-rotating twin-screw extruder using sodium hydride as initiator and N-acetylcaprolactam as activator\cite{6d,e}, and random or block P(CLA-co-CLO) copolymers formed by simultaneous or sequential feeding of monomers, respectively. It is known that due to enhanced polymerization activity of CLO, PCLO is preferentially formed in the initial stage of anionic copolymerization. It was further shown that polymerization of CLA performed in the presence of PCLO and initiated with ε-caprolactam magnesium bromide gave high yield of copolymer.\cite{10c} This reaction seems to be more suitable to be transferred to a reactive extrusion process, since the melt viscosity does not change as significantly as in the case of direct copolymerization of monomers. So in this work we attempt to carry out the polymerization of CLA in the PCLO melt in a twin-screw microcompounder and analyze the products by different physico-chemical techniques in order to draw the conclusion on the feasibility of this process.

3.2 Experimental section

3.2.1 Materials

CLA (99%) and PCLO (Mn 80000) were purchased from Aldrich and dried at 45°C in vacuum for 12 h before use. Masterbatches of sodium caprolactamate in CLA (C10) and
hexamethylene-1,6-dicarbamoylcaprolactam in CLA (C20), which contain 2 mol/kg sodium caprolactamate and 1.4 mol/kg hexamethylene-1,6-dicarbamoylcaprolactam (Figure 3.1), respectively, were obtained from Brüggemann Chemical (Germany) and used as anionic initiator and activator, correspondingly.

![Figure 3.1: Structures of initiator and activator used in this study: a) sodium caprolactamate (C10) and b) hexamethylene-1,6-dicarbamoylcaprolactam (C20 P).](image)

3.2.2 Reactive extrusion

![Figure 3.2: Schematic representation of the microcompounder with corotating conic screws (DSM Xplore).](image)

A co-rotating twin-screw microcompounder with conic screws and a volume of 15 mL (DSM Xplore, The Netherlands, cf. Figure 3.2) was used as a chemical reactor for the reactive extrusion of PEA. Monomer, polymer, initiator and activator were fed together
into the microcompounder at the barrel temperature of 120 °C. Afterwards the
temperature of the barrel was raised to 180 °C and the processing was conducted at this
temperature with a screw rotation rate of 100 rpm for 10 min. The whole process was
carried out in a nitrogen atmosphere. Afterwards, the resulting copolymers were extruded
out in the form of a strand and granulated.

3.2.3 Analytical techniques

3.2.3.1 Determination of conversion

The degree of conversion (\( \chi \)) was determined as follows. PEA samples were ground into
powder, weighed (\( m_{\text{tot}} \)) and stirred in deionized water 3 times for 2 h at room temperature
to remove the residual monomer.\(^{[13]}\) After drying at 50 °C in vacuum for 24 h the polymer
samples were weighed again (\( m_{\text{pol}} \)). The conversion (\( \chi \)) was calculated according to (1):

\[
\chi = \frac{m_{\text{pol}}}{m_{\text{tot}}} \times 100 \%
\]  

(1)

3.2.3.2. Elementary analysis

Elementary analysis (EA) of carbon, hydrogen and nitrogen was performed on a Carlo
Erba MOD 1106 instrument in order to determine the chemical composition of
synthesized PEA.

3.2.3.3. Gel permeation chromatography (GPC)

GPC measurements were performed on a GPC system equipped with a Waters 1515
Isocratic HPLC pump, a Viscotek 250 model refractive index detector, a Waters 2707
autosampler, a PSS PFG guard column followed by 2 PFG-linear-XL (7 \( \mu \)m, 8\*300 mm)
columns in series at 40 °C. Hexafluoroisopropanol (HFIP, Biosolve) containing
potassium trifluoroacetate (3 g/L) and toluene (2.5 mL/L) was used as eluent at a flow
rate of 0.8 mL/min. The molecular weights were calculated against polymethylmethacrylate (PMMA) standards (Polymer Laboratories, \( M_p = 580 \) up to \( M_p = 7100000 \)).
3.2.3.4. Thermal analysis

A TG-209 thermal gravimetric analysis (TGA) instrument (Netzsch, Germany) was used to study the thermal stability of synthesized polymers. 10-15 mg of the sample were placed in standard Netzsch 85 µL alumina crucibles and were heated in nitrogen flow from 30 °C to 600 °C at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) measurements were carried out on a DSC-204 (Netzsch, Germany). 5-8 mg of sample were placed in standard Netzsch alumina crucibles and were heated from 0 °C to 220 °C at a heating rate of 10 °C/min. The flow rate of nitrogen was 10 cm³/min.

3.2.3.5. Wide-angle X-ray diffraction (WAXD)

The WAXD measurements were conducted at the BM26 beamline of the ESRF (Grenoble, France). The samples were hot-molded into discs of 1 mm thickness by non-isothermal crystallization from the melt at a cooling rate of 10 °C/min. The discs were measured in transmission geometry. X-ray photons with energy of 12keV were used in the experiments. The 2D diffractograms were recorded using a FreLon CCD camera. The norm of the scattering vector \( s = 2\sin(\theta)/\lambda \) was calibrated using corundum standard. The patterns were corrected for parasitic scattering and empty cell background. The data reduction and analysis including background and geometrical correction were performed using a home-built routine procedure designed within the IgorPro® software (Wavemetrics Ltd.).

To quantify the phase composition of the extruded compounds, the 1D WAXD curves were decomposed into sets of peaks representing crystalline reflections of different crystalline phases \( I_i(s) \). The peaks were approximated with a set of Gaussian functions:

\[
I_c(s) = \sum I_i(s) = \sum A_i \exp \left[-\frac{(s_0 - s_i)^2}{2\sigma_i^2}\right]
\]  

(2)

where \( A_i \) is the peak amplitude of the \( i^{th} \) reflection of one phase, \( s_i \) is its center and \( \sigma_i^2 \) - its variance. Due to the powder-like nature of the samples the relative intensities of the
different crystalline reflections within one phase are proportional to the corresponding structure factors, and, therefore, can be kept constant during the fitting procedure to minimize the number of independent fit parameters.

To represent the amorphous halo, a combination of two Pearson type VII functions\textsuperscript{14} were used as follows:

\[ I_a(s) = \frac{A_a}{(1 + k_1 (s - s_a)^2)^n} \text{ for } s \leq s_a \quad (3a) \]

\[ I_a(s) = \frac{A_a}{(1 + k_2 (s - s_a)^2)^n} \text{ for } s \geq s_a \quad (3b) \]

Here \( s_a \) corresponds to the maximum of the peak while \( A_a \) stands for its amplitude. The crystallinity index \( X_C \) was calculated using the following equation:

\[ X_C = \frac{\sum I_c(s)}{I_a(s) + \sum I_c(s)} \quad (4) \]

where \( I_c(s) \) and \( I_a(s) \) correspond to the integral intensities of the different crystalline and amorphous fractions, respectively.

The relative crystalline fractions \( \Phi_c \) of the different phases were calculated as:

\[ \Phi_c = \frac{I_c(s)}{\sum I_c(s)} \quad (5) \]

3.2.3.6 Mechanical analysis

To determine the mechanical properties of the synthesized PEA, tensile tests were performed on tensile testing machine Zwick / Roell Z010 at room temperature. For this, first the synthesized PEA melt from the micro compounder is directly transferred in a 5.5 mL injection molding (DSM Xplore, Geleen, NL) machine consisting of a cylinder with a plunger. Through this process, standard tensile test specimens with a gauge length of 20
mm, a width of 4 mm and a thickness of 2 mm were prepared. Tensile tests were performed according to DIN EN ISO 527-2 5A on these standard dumble shaped tensile test bars. Modulus of elasticity (Young's modulus and tensile modulus), maximum nominal strain and maximum voltage reached before a significant drop in force (tensile strength) were determined. The test conditions used are listed in the Appendix of this chapter.

3.3 Results and discussion

Table 3.1: Recipes for the preparation of (P(CLA-co-CLO)) copolymers and monomer conversion determined after water extraction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content of C10 [mol%]</th>
<th>Content of C20P [mol%]</th>
<th>CLA/CLO weight ratio</th>
<th>Conversion [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA 1</td>
<td>1.5</td>
<td>1.5</td>
<td>1/2</td>
<td>85.5</td>
</tr>
<tr>
<td>PEA 2</td>
<td>1.5</td>
<td>3.0</td>
<td>1/2</td>
<td>93.9</td>
</tr>
<tr>
<td>PEA 3</td>
<td>3.0</td>
<td>1.5</td>
<td>1/2</td>
<td>98.0</td>
</tr>
<tr>
<td>PEA 4</td>
<td>3.0</td>
<td>3.0</td>
<td>1/2</td>
<td>98.1</td>
</tr>
<tr>
<td>PEA 5</td>
<td>1.5</td>
<td>1.5</td>
<td>1/1</td>
<td>94.1</td>
</tr>
<tr>
<td>PEA 6</td>
<td>1.5</td>
<td>3.0</td>
<td>1/1</td>
<td>94.8</td>
</tr>
<tr>
<td>PEA 7</td>
<td>3.0</td>
<td>1.5</td>
<td>1/1</td>
<td>97.8</td>
</tr>
<tr>
<td>PEA 8</td>
<td>3.0</td>
<td>3.0</td>
<td>1/1</td>
<td>98.6</td>
</tr>
<tr>
<td>PEA 9</td>
<td>1.5</td>
<td>1.5</td>
<td>2/1</td>
<td>98.3</td>
</tr>
<tr>
<td>PEA 10</td>
<td>1.5</td>
<td>3.0</td>
<td>2/1</td>
<td>92.6</td>
</tr>
<tr>
<td>PEA 11</td>
<td>3.0</td>
<td>1.5</td>
<td>2/1</td>
<td>99.6</td>
</tr>
<tr>
<td>PEA 12</td>
<td>3.0</td>
<td>3.0</td>
<td>2/1</td>
<td>99.9</td>
</tr>
<tr>
<td>PEA 13</td>
<td>3.0</td>
<td>3.0</td>
<td>5/1</td>
<td>99.4</td>
</tr>
</tbody>
</table>

P(CLA-co-CLO) copolymers were synthesized via anionic ring opening polymerization of CLA in the melt of PCL in a co-rotating twin-screw microcompounder with conic screws and a volume of 15 mL. In principle, the polymerization of CLA can be initiated by caprolactamate in the presence of PCLO, since PCLO can act as an activator in this
reaction; however, it takes a long time to reach a high yield.\textsuperscript{[10c]} The reaction can be significantly accelerated by the addition of a low molecular weight activator. The initiator-activator combination C10-C20 offers a fast reaction formulation for CLA, i.e. at 150 °C. A high yield of PCLA polymer (> 95%) can be reached within less than 5 min.\textsuperscript{[13]} Therefore, it can allow the polymerization of CLA in the extruder where a fast reaction is required. The polyamide fragments will be incorporated in the polyester chains via chain transfer reactions as previously demonstrated.\textsuperscript{[10c]} In this study the ratio of CLA and PCLO as well as the initiator-activator content were systematically varied (Table 3.1).

The anionic ring opening polymerization of CLA into high molecular weight polymer is generally a catalyzed reaction performed in the temperature range between 130-170 °C. In this work, the reactants were fed to the extruder at a barrel temperature of 120 °C to prevent significant polymerization during the blending process. After mixing the components for 2 min, the temperature of the barrel was raised to 180 °C to afford a fast reaction in the homogeneous mixture. The polymerization process was monitored by measuring the melt temperature as well as the axial force as an assessment of the viscosity of polymer melts with time (Figure 3.3). It can be seen that the viscosity of the polymer melt increased rapidly in a short induction period of 2 minutes after reaching the desired melt temperature.

![Figure 3.3: Plastogram, i.e. melt temperature and axial force vs. processing time for the synthesis of PEA 12.](image)

The relative amount of initiator and activator has a critical influence on the reaction kinetics and the degree of polymerization. The polymer yield after water extraction is
very high, i.e. above 90 % in most of the cases. At higher initiator contents, i.e. 3.0 mol% related to CLA amount, almost quantitative monomer conversion was observed (Table 3.1).

The chemical structure of the extracted P(CLA-co-CLO) copolymers was verified by elemental analysis (cf. Table 3.2). The elemental composition of the copolymers was found to be close to the theoretical values calculated assuming a qualitative monomer conversion.

**Table 3.2:** Results of elemental analysis of (P(CLA-co-CLO)) copolymers after water extraction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical by 100 % conversion [%]</th>
<th>Experimental [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>PEA 1</td>
<td>63.64</td>
<td>9.09</td>
</tr>
<tr>
<td>PEA 2</td>
<td>63.64</td>
<td>9.09</td>
</tr>
<tr>
<td>PEA 3</td>
<td>63.64</td>
<td>9.09</td>
</tr>
<tr>
<td>PEA 4</td>
<td>63.64</td>
<td>9.09</td>
</tr>
<tr>
<td>PEA 5</td>
<td>63.44</td>
<td>9.25</td>
</tr>
<tr>
<td>PEA 6</td>
<td>63.44</td>
<td>9.25</td>
</tr>
<tr>
<td>PEA 7</td>
<td>63.44</td>
<td>9.25</td>
</tr>
<tr>
<td>PEA 8</td>
<td>63.44</td>
<td>9.25</td>
</tr>
<tr>
<td>PEA 9</td>
<td>63.53</td>
<td>9.41</td>
</tr>
<tr>
<td>PEA 10</td>
<td>63.53</td>
<td>9.41</td>
</tr>
<tr>
<td>PEA 11</td>
<td>63.53</td>
<td>9.41</td>
</tr>
<tr>
<td>PEA 12</td>
<td>63.53</td>
<td>9.41</td>
</tr>
<tr>
<td>PEA 13</td>
<td>63.62</td>
<td>9.57</td>
</tr>
</tbody>
</table>

The molecular weights of the polymers were determined by GPC using hexafluoroisopropanol as an eluent and calibrated by PMMA standards (cf. Table 3.3).
All polymer products obtained exhibit a unimodal molecular weight distribution (cf. Figure 3.4), implying the formation of copolymers, but not blends of two homopolymers. Due to employing the high-molecular-weight PCLO as the base material for the reaction, P(CLA-co-CLO) copolymers with high molecular weight were obtained, which can be further processed by fiber spinning or injection molding. Furthermore, copolymers prepared using a higher concentration of initiator and activator (3 mol%) irrespective of the CLA/CLO weight ratio have a higher molecular weight, most probably due to an increased polymerization rate.

**Table 3.3:** Number average ($M_n$) and weight average ($M_w$) molecular weights of (P(CLA-co-CLO)) copolymers after water extraction measured by GPC in hexafluoroisopropanol as eluent calibrated by PMMA standards.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (kDa)</th>
<th>$M_w$ (kDa)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA 1</td>
<td>35.4</td>
<td>68.9</td>
<td>1.95</td>
</tr>
<tr>
<td>PEA 2</td>
<td>34.5</td>
<td>88.7</td>
<td>2.57</td>
</tr>
<tr>
<td>PEA 3</td>
<td>66.9</td>
<td>171.1</td>
<td>2.55</td>
</tr>
<tr>
<td>PEA 4</td>
<td>72.0</td>
<td>219.5</td>
<td>3.05</td>
</tr>
<tr>
<td>PEA 5</td>
<td>35.2</td>
<td>117.5</td>
<td>3.33</td>
</tr>
<tr>
<td>PEA 6</td>
<td>73.5</td>
<td>136.9</td>
<td>1.86</td>
</tr>
<tr>
<td>PEA 7</td>
<td>40.4</td>
<td>158.9</td>
<td>3.94</td>
</tr>
<tr>
<td>PEA 8</td>
<td>69.6</td>
<td>239.3</td>
<td>3.44</td>
</tr>
<tr>
<td>PEA 9</td>
<td>52.5</td>
<td>109.4</td>
<td>2.08</td>
</tr>
<tr>
<td>PEA 10</td>
<td>28.8</td>
<td>79.4</td>
<td>2.76</td>
</tr>
<tr>
<td>PEA 11</td>
<td>36.5</td>
<td>84.8</td>
<td>2.33</td>
</tr>
<tr>
<td>PEA 12</td>
<td>93.0</td>
<td>279.7</td>
<td>3.00</td>
</tr>
<tr>
<td>PEA 13</td>
<td>68.9</td>
<td>184.2</td>
<td>2.67</td>
</tr>
<tr>
<td>PCLO $^{b)}$</td>
<td>120.1</td>
<td>195.0</td>
<td>1.48</td>
</tr>
</tbody>
</table>

$^{b)}$ measured by GPC in THF as eluent calibrated by PMMA standards
According to the TGA data shown in Figure 3.5, all copolymer samples exhibit a two-step degradation profile with onset degradation temperatures between 250 and 270 °C. The thermal stability of these compounds is slightly lower than that of PCLA and PCLO homopolymers. This is possibly due to the presence of amino end groups in the reaction products, which catalyze the decomposition of the PCLO fragments. The DSC results of the P(CLA-co-CLO) copolymers are given in Table 3.4.

![Molecular weight distribution curve](image)

**Figure 3.4:** Molecular weight distribution curve of a P(CLA-co-CLO) copolymer PEA 12 measured by GPC showing a monomodal distribution of molecular weight.

![TGA curves](image)

**Figure 3.5:** TGA curves of PCLA, PCLO homopolymers and PEA 9-12 after extraction with deionized water.
Table 3.4: DSC data of water-extracted (P(CLA-co-CLO)) copolymers as well as PCLA and PCLO homopolymers obtained from cooling and second heating runs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling run</th>
<th>Second heating run</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{c1}$ [°C]</td>
<td>$\Delta H_{c1}$ [J/g]</td>
</tr>
<tr>
<td>PEA 1</td>
<td>26</td>
<td>52</td>
</tr>
<tr>
<td>PEA 2</td>
<td>26</td>
<td>44</td>
</tr>
<tr>
<td>PEA 3</td>
<td>26</td>
<td>42</td>
</tr>
<tr>
<td>PEA 4</td>
<td>27</td>
<td>39</td>
</tr>
<tr>
<td>PEA 5</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>PEA 6</td>
<td>26</td>
<td>25</td>
</tr>
<tr>
<td>PEA 7</td>
<td>26</td>
<td>25</td>
</tr>
<tr>
<td>PEA 8</td>
<td>27</td>
<td>28</td>
</tr>
<tr>
<td>PEA 9</td>
<td>30</td>
<td>13</td>
</tr>
<tr>
<td>PEA 10</td>
<td>27</td>
<td>16</td>
</tr>
<tr>
<td>PEA 11</td>
<td>26</td>
<td>14</td>
</tr>
<tr>
<td>PEA 12</td>
<td>26</td>
<td>11</td>
</tr>
<tr>
<td>PEA 13</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>PCLO</td>
<td>30</td>
<td>58</td>
</tr>
<tr>
<td>PCL A</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The curves of the second heating run of samples PEA9-12 with CLA/CLO ratio of 2:1 are shown in Figure 3.6. Upon heating from room temperature most copolymer samples show 2 endothermic peaks corresponding to the melting of PCLO ($T_{m1}$) and PCLA ($T_{m2}$) fragments, respectively. The melting temperature of PCLO units is found to be only slightly decreased as compared to the PCLO homopolymer. The crystalline domains formed by PCLA units, however, melt at a much lower temperature than the PCLA homopolymer. These findings indicate, first of all, the block nature of the copolymers. Furthermore, they also imply that after the reactive extrusion the polymerization degree
of PCLO remains still high, in contrast, PCLA fragments exhibit pretty short chain length. It is further observed that the copolymers obtained with a lower amount of activator C20 show a higher melting temperature independent of the amount of initiator and CLO/CLA ratio. Due to the higher amount of activator, more polymer chains "grow" simultaneously, resulting in the lower final molecular weight by consuming the same amount of monomer.\textsuperscript{[15]}

![Figure 3.6: DSC curves of PEA 9-12 after extraction with deionized water.](image)

A typical 1D WAXD curve recorded on PEA 5 is given in Figure 3.7. It exhibits three main diffraction peaks in the $s$-range from 0.2 to 0.3 Å$^{-1}$. In this case, three crystalline phases can be identified. Thus, the peak at 0.2305 Å$^{-1}$ can be assigned to the 200 reflection of PCLA $\alpha$-phase alone, while the other intense peaks are pertinent to more than one crystalline phase. The 002/202 doublet of the PCLA $\alpha$-phase at 0.2685 Å$^{-1}$ is superimposed on the 200 reflection of the PCLO phase. The peak at 0.2420 Å$^{-1}$ is assigned to a superposition of the 110$_{PCLO}$ reflection and 100/010 reflection of the PCLA $\gamma$-phase, which is located at a slightly higher $s$, i.e. at 0.2434 Å$^{-1}$.\textsuperscript{[16]}
Figure 3.7: Decomposition of the WAXD curve recorded at room temperature for sample PEA 5. The peaks corresponding to the crystalline phase of PCLO and two crystalline phases of polyamide and amorphous halo are indicated.

Selected wide-angle X-ray diffraction curves corresponding to samples PEA 1 through PEA 13 are presented in Figure 3.8. All curves reveal a significant amount of amorphous material, which is in agreement with the DSC data. To better comprehend the relation between crystallinity and composition, a comparative analysis was performed for the case when the concentrations of the initiator and activator were constant while the ratio of the block weights varied (cf. Figure 3.8b) and for the case when the ratio of the blocks was fixed while the relative concentrations of the initiator and activator were variable (cf. Figure 3.8c). The values of the crystallinity index normalized to unity are summarized in Table 3.5. Generally, it can be seen that both sets of parameters, i.e. the contents of the initiator and activator and the relative weights of the blocks are important for the crystallinity values. However, the crystallinity indices of the PCLO and PCLA blocks follow different trends: the one of PCLO is rather constant (except for PEA 13 with the highest fraction of the PCLA block), whereas the amount of the α- and γ-phases of PCLA varies more noticeably with the copolymer composition (cf. Figure 3.8b). Interestingly, the fraction of the PCLA γ-phase becomes higher than that of α-phase when the content of PCLA is the lowest. The same observation can be made for the case when the activator and initiator contents are the lowest (cf. Figure 3.8c).

This signifies that the preferred formation of the metastable crystalline phase (i.e. the γ-phase) is observed when the crystallization conditions are not favorable for PCLA. In the PCLA homopolymer, the polymorphic behavior is reported to depend strongly on the thermal history. When annealed in the melt and subsequently crystallized non-
isothermally, a transition from the thermodynamically stable α-phase to the kinetically favored γ-phase is reported when the cooling rate increases.\textsuperscript{[17]} Another factor favoring the formation of the γ-phase is found to be the presence of interfaces being capable of forming hydrogen bonds with the amide groups of the PCLA segments, as could be the case in the presence of PCLO polymer chains. It is known that this interaction can restrain the chain mobility of the PCLA molecules, thus hindering the formation of the PCLA α-phase with respect to the PCLA γ-phase.\textsuperscript{[18]} Therefore, the relative fraction of the PCLA crystal modifications can be an important indicator revealing the morphology of the copolymers.

Figure 3.8: a) Room-temperature WAXD curves corresponding to samples PEA 1 through PEA 8, PEA 12 and PEA 13. The main crystalline reflections are indicated; b) Crystallinity indices for the PCLA and PCLA crystals as a function of the ratio between the corresponding block weights evaluated at fixed concentrations of initiator and activator (i.e. for samples PEA 4, PEA 8, PEA 12 and PEA 13); c) Crystallinity indices of the crystalline phases of PCLA and PCLA as a function of the ratio between the activator and initiator concentrations evaluated at 1/1 ratio between the PCLA and PCLO blocks (i.e. for samples PEA 5 through PEA 8).
Finally, it is noteworthy that the crystallinity index of the degradable fragments PCLO is all the time rather low at variance with the situation in the PCLO homopolymer, though their polymerization degree remains pretty high after the copolymerization. The PCLA blocks seem to disrupt the crystallization of PCLO due to their high crystallization ability. This observation makes the developed copolymers interesting from the point of view of degradability as the amorphous material can undergo this process much faster than the crystals.\textsuperscript{19}

Table 3.5: Crystallinity index and relative fractions of three different crystalline phases of (P(CLA-co-CLO)) copolymers after water extraction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity index</th>
<th>Fractions of crystalline phases normalized to unity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PCLO</td>
<td>PCLA $\alpha$</td>
</tr>
<tr>
<td>PEA 1</td>
<td>0.286</td>
<td>0.71</td>
<td>0.00</td>
</tr>
<tr>
<td>PEA 2</td>
<td>0.248</td>
<td>0.72</td>
<td>0.00</td>
</tr>
<tr>
<td>PEA 3</td>
<td>0.227</td>
<td>0.49</td>
<td>0.25</td>
</tr>
<tr>
<td>PEA 4</td>
<td>0.229</td>
<td>0.46</td>
<td>0.15</td>
</tr>
<tr>
<td>PEA 5</td>
<td>0.207</td>
<td>0.52</td>
<td>0.16</td>
</tr>
<tr>
<td>PEA 6</td>
<td>0.226</td>
<td>0.37</td>
<td>0.33</td>
</tr>
<tr>
<td>PEA 7</td>
<td>0.226</td>
<td>0.39</td>
<td>0.30</td>
</tr>
<tr>
<td>PEA 8</td>
<td>0.217</td>
<td>0.31</td>
<td>0.37</td>
</tr>
<tr>
<td>PEA 9</td>
<td>0.217</td>
<td>0.58</td>
<td>0.14</td>
</tr>
<tr>
<td>PEA 10</td>
<td>0.119</td>
<td>0.38</td>
<td>0.46</td>
</tr>
<tr>
<td>PEA 11</td>
<td>0.117</td>
<td>0.43</td>
<td>0.40</td>
</tr>
<tr>
<td>PEA 12</td>
<td>0.121</td>
<td>0.47</td>
<td>0.34</td>
</tr>
<tr>
<td>PEA 13</td>
<td>0.270</td>
<td>0.04</td>
<td>0.69</td>
</tr>
</tbody>
</table>

To determine the mechanical properties, the polymers synthesized on microcompounder were directly transferred in injection moulding machine to make tensile test specimens in accordance with DIN EN ISO 527-2 5A.\textsuperscript{20} In Figure 3.9 is given the schematic representation for the preparation of tensile test specimens. The direct processing of the already molten polymers serves the advantage that the second thermal exposure of the
polymers and thereby, the associated possible degradation was prevented. As no water extraction was done, there were still slight remains of the CLA monomer in the prepared tensile test bars of PEA. This can influence the results of the mechanical tests. This inaccuracy is negligible, however, in view of the fact that the dispersion of the measurement results in sample may be greater due to the small number of tensile test bars (3-5) per sample than in the case of a larger number of tensile test bars per sample. Moreover, this approach allowed a less time-consuming qualitative comparison of the samples themselves.

![Schematic representation for the preparation of tensile testing bars](image)

**Figure 3.9:** Schematic representation for the preparation of tensile testing bars: (left) microcompounder, (middle) injection molding, (right) demolding.

Figures 3.10 to 3.12 give an overview of the achieved average mechanical characteristics including tensile-modulus and tensile strength.

![Bar chart showing tensile modulus](image)

**Figure 3.10:** Tensile modulus of the different PEA compositions and PCL and PA-6.

The tensile-E-modulus (see Figure 3.10) of the synthesized PEA has an average around 200 to 400 N/mm², which is comparable to that of the pure PCLO (PCL in the Figures 3.10-3.14). PCLA (PA-6 in the Figures 3.10-3.14) pointed-towards a significantly higher
tensile-E- modulus values between 1480 and 2170 N/mm². For the CLA to CLO ratio of 1:2 and 1:1 the initiator-activator ratio seems not to have an influence on the tensile-E modules, while the samples with the CLA to CLO ratio of 2:1 show on average higher values. In particular, with the initiator content of 3.0 wt.% a higher tensile-E-modulus is observed.

The tensile strength of the PEA (see Figure 3.11) with the CLA-CLO-ratio of 1:2 and 1:1 has values comparable to that of PCLO (between 10 to 15 N/mm²). The tensile strength of the PEA with the CLA to CLO ratio of 2:1 is generally higher with the value of around 25 N/mm², while the tensile strength of pure PCL A is about 60 N/mm². No clear difference in tensile modulus is observed, however, the tensile strength depends on the initiator-activator ratio for samples with the CLA-CLO ratio of 1:2 and 1:1, significantly higher values are achieved with the CLA to CLO ratio of 2:1.

![Figure 3.11: Tensile strength of different compositions of PEA and PCL and PA-6.](image)

![Figure 3.12: Maximum nominal strain of the different PEA compositions and PCLO (PCL) and PCLA (PA-6).](image)
Figure 3.12 gives a graphical representation of the obtained maximum nominal strains. In contrast to the tensile modulus and tensile strength significantly higher values of about 350% for the maximum average nominal strain was achieved in PCLO, as compared with those of PEA as well as PCLA, where the maximum nominal elongation lies between 100-250%. PEA prepared with the CLA to CLO ratio of 1:2 reach higher maximum nominal expansions in comparison with other synthesized PEA samples.

![Stress-strain diagram](image)

**Figure 3.13:** Stress-strain diagram for PCLO (PCL), PCLA (PA-6) and PEA 12.

In Figure 3.13, the stress-strain behavior of PCLO, PCLA and PEA12 are shown. Figure 3.14 is a section of the diagram selected from Figure 3.13 up to an elongation of 15%. As
indicated by the stress-strain curves PCLA is much harder than PCLO. PEA12 has characteristics intermediate between PCLO and PCLA. Both PCLO and PCLA show necking while stretching, however, this is not observed for PEA.

3.4 Conclusion

In this work a series of P(CLA-co-CLO) copolymers were synthesized with almost qualitative monomer conversion via anionic ring-opening polymerization of CLA in the melt of PCLO in a co-rotating twin-screw microcompounder with conic screws. The influence of the initiator and activator concentration as well as the CLA-to-CLO ratio on the thermal properties, molecular weight and crystalline morphology of the synthesized PEAs were studied and evaluated. By using high-molecular-weight PCLO as the starting material, P(CLA-co-CLO) copolymers of high molecular weight were obtained, which can be further processed by fiber spinning or injection molding. It was also found that the polymerization with a higher concentration of initiator and activator (3 mol%) irrespective of the CLA/CLO ratio gives rise to products with higher molecular weight. At room temperature all copolymers form both PCLA and PCLO crystalline domains, implying their block nature. Interestingly, the crystallinity index of the degradable PCLO fragments in the copolymers is always quite low, and remains rather constant except for the copolymer with a very high fraction of the PCLA block, whereas the amount of the α- and γ-phases of PCLA are varying more noticeably with the copolymer composition and initiator/activator concentration.

3.5 References


Appendix

Tensile tests
All the tensile tests were carried out at room temperature.

Device:
Tensile testing machine: Zwick / Roell Z010
Software: TestXpert II
Load cells: Zwick / Roell XForce P 1 kN
Optical Sensor: Aramis 2M 2D the company Gom in Brunswick.
Mechanical distance measurement: measured at crosshead

Sample form:
DIN 527-II sample type 5A

Scanning:
Prior to start of test preload force: 0.1 N

section I
- Condition: 0% to 1% elongation (optional sensor):
- Purpose: To determine the modulus of elasticity
- Speed: 0.4 mm / min

65
section II
- Condition: 1% elongation at break
- Purpose: To estimate the maximum endured nominal voltage and maximum strain
- Speed up to the end of testing: 30 mm / min

Output and calculation of mechanical parameters:
- Recording interval: every 0.1 s or greater at each change as 1N
- Determination of E-Moduls/Tensile module to DIN 527-1: slope of the secant line in the strain range of \(0.05\% \leq \varepsilon \leq 0.25\%\) on the stress-strain curve \(\sigma (\varepsilon)\)
- Calculation of the max. nominal voltage: maximum measured force \((F_{\text{max}})\) related to nominal cross-section of the sample \((8 \text{ mm}^2)\)
- Calculation of the max. elongation: based on travel clamping length \((50 \text{ mm})\) measured from breakage or over 70% drop in force \(F_{\text{max}}\)
Chapter 4

Continuous Synthesis of
Polyesteramide on a Laboratory Extruder

The part of this work was done in collaboration with the group of Prof. Dr.-Ing. Edmund Haberstroh, Lehr- und Forschungsgebiet Kautschuktechnologie, RWTH Aachen University, Eilfschornsteinstr. 18, 52062 Aachen, Germany.

Abstract

In Chapter 3 we have demonstrated a reactive extrusion process for the synthesis of polyesteramides on a microcompounder based on anionic polymerization of $\varepsilon$-caprolactam in the melt of poly($\varepsilon$-caprolactone). In this chapter we report the upscaling of this process on a lab extruder. The optimization of the screw configuration was assisted by a simulation program MOREX that allows calculating the residence time of the polymer melt over the entire length of the designed extruder screw. The products obtained at different screw configurations were investigated by means of different analytical methods in terms of their chemical composition and thermal, rheological and mechanical properties. The process parameters were then assessed and evaluated in accordance with analytical results. With a proper screw configuration, the monomer conversion reached more than 95 %, yielding polymers with pretty high molecular weight.

4.1 Introduction

Aliphatic polyesteramides (PEAs) that are composed of ester and amide groups together in the main chain of polymer are environmental friendly being biodegradable polymers and at the same time offers a wide range of applications.\textsuperscript{[1-2]} On one hand, the readily crystallizable amide groups provide good mechanical and processing properties while on the other hand the hydrolytically cleavable ester groups impart good biodegradability to the PEAs. Such combination of properties makes PEAs quite interesting material for biomedical applications.\textsuperscript{[3]}
Polylactide, polyglycolide and their copolymers are the most famous representatives of aliphatic polyesters, which are often used for medical applications, such as absorbable sutures and implants for bone fixation or in products with targeted drug delivery applications. However, these aliphatic polyesters degrade via bulk erosion process which causes local acidic microenvironment in body due to accumulation of acidic by-products and thus leads to inflammatory responses. PEAs on contrary, are known to degrade via surface erosion process and the incorporation of amide groups further help to solve this problem.

Most of the polymers including PEAs are generally synthesized by batch process which often involves use of solvents because the viscosity of the reaction mass increases with the progress of reaction. But the use of solvent in a process is a disadvantage considering both environmental and economic perspective. Extrusion technique, therefore, serves as an alternative to discontinuous batch process considering its comparatively low investments costs and a high degree of flexibility and adaptability to different requirements.

Reactive extrusion is one of the processes for the continuous production and modification of polymers that represents the chemical conversion of materials. In this process, the extruder screw reactors are continuously fed with monomers/ starting materials which are processed into the polymer during the residence time in the screw. The primary factor for successful reactive extrusion process is the extruder unique ability to pump and mix highly viscous materials as well as to facilitate the staging of multiple process steps (melting, metering, reacting etc.) in a single machine. The extrusion technique, therefore, not only allows a solvent-free polymer synthesis but at the same time promote good mixing quality and the possibility for reaction of chemicals or high viscosity materials. Along with many extrusion processing parameters like processing temperature, screw speed etc., screw geometry is one of the parameters that play very important role in determining residence time of melt as well as product quality with its various mixing elements and configuration options. Therefore, designing and optimization of screw geometry is an important step to achieve desired results for any process. Basically, fast reaction systems can be processed via reactive extrusion process because the screw shaft has a limited length and so the limited residence time. For instance, the reactions
like anionic ring opening polymerization of ε-caprolactam which is an exothermic reaction and takes place in few minutes leading to significantly high degree of polymerization, are best suited for reactive extrusion and hence is technically one of the standard methods for the production of polyamide-sixth.\[17]\n
Although both single and twin-screw extruders are used in reactive polymerization process, twin-screw extruders are favored because of extended control of residence time, better distribution and mixing, and superior heat and mass transfer capabilities.\[17, 23]\n
In literature, the preparation of block and statistic PEA by continuous polymerization via reactive extrusion on a twin screw extruder using ω-lauryllactam (LA) and other cyclic monomers such as ε-caprolactone or ε-caprolactam has been reported using sodium hydride as initiator and N-acetylcaprolactam as cointiator.\[24-25]\n
In spite of many efforts in the past, the production of PEA has never become an industrial process.

In the present work, the process for the synthesis of PEA by reactive extrusion developed on a batch microcompounder is transferred on a lab extruder for the continuous production. The important chemical relationships and the process are systematically examined and assessed. For the calculation and interpretation of the process, a simulation program MOREX is used, which supports the targeted optimization of the process and screw/machine design, thus allows for a successful scaling-up of the process.

4.2 Experimental section

4.2.1 Materials

ε-Caprolactam (CA) (Aldrich) and polycaprolactone (PCL) (Mₙ 80000, Aldrich) were dried at 45°C in a vacuum oven for 12 hours before use. Sodium caprolactamate (C10 in flakes form) and hexamethylene-1,6-dicarbamoylcaprolactam (C20 P in pellet form) were obtained from Brüggemann Chemical (Germany) and used as anionic initiator and activator, respectively. Both were stored in sealed polyethylene lined aluminum drums under nitrogen atmosphere.
4.2.2 Processing

4.2.2.1 Lab extruder

For the continuous production a co-rotating, closely intermeshing cylindrical twin screw extruder (designated as laboratory extruder) with a screw diameter of 16 mm and an overall length of 400 mm from Thermo Fisher Scientific, Germany was used. The synthesis process of PEA12 (as described in Ch-3) was initially performed on a laboratory extruder with an originally given screw configuration.

![Diagram of lab extruder](image)

**Figure 4.1:** Structure of the laboratory extruder with six electrically heated heating zones (Th1-T6).

The extruder barrel consists of six electrically heating zones equipped with thermocouples (see Figure 4.1, thermocouples are located at Th1 and Th6). The extruder is equipped with a cooled feed zone, through which all chemicals are fed to the extruder. At the end of the extruder there can be two different dies configurations (A and B) to be used, which are shown in Figure 4.2 (A) and (B), respectively.

![Diagram of die configurations](image)

**Figure 4.2:** Schematic illustration of die configuration A (left) and B (right).
4.2.2.2 Processing conditions

The reaction zone was heated to about 180°C. The polymer was processed at a low screw rotating speed to achieve at least ten minutes residence time. For dosing, all the chemicals were first mixed together in a beaker, and both dosing hopper with a volumetric metering unit and a dosage cup were used. In addition, the processing was carried out under a continuous supply of nitrogen stream in order to avoid any side reactions or early termination.

4.2.2.3 Design and optimization of screw configuration

In this work three different screw configurations were simulated. They were designed as follows (Figure 4.3). The feed zone is followed by a mixing zone composed of kneading elements. After the subsequent polymerization zone follows in two of the three configurations, a final mixing zone. The two screw configurations with the second mixing zone differ primarily in the length and position of the zones.

![Schematic representation of different basic screw geometries](image)

Figure 4.3: Schematic representation of the different basic screw geometries.

With the simulation program MOREX the melt dwell time at each screw configuration was calculated. The screw element arrays were described in each case in the conveying direction. Neither temperature nor pressure gradient were considered. For the calculation of the residence time a mass flow rate of 0.15 g / min and a speed of 15 min⁻¹ were used. Further, for all calculations it was assumed that that the kneading elements were full filled with reagents and the conveying elements were partially filled. The input data for the calculations with MOREX are therefore defined as follows:

- Mass flow rate: 0.15 g / min

- Speed: 15 min⁻¹
- Screw diameter: 16 mm
- Screw length: 400 mm
- Pressure and melt temperature were not considered.

### 4.2.3 Characterization

#### 4.2.3.1 Degree of conversion

The degree of conversion (X) was determined as follows: PEA samples were ground into powder, weighed (m_{tot}) and stirred in deionized water 3 times for 2 h at room temperature to remove the residual monomer and initiator. After drying in vacuo the polymer samples were weighed again (m_{pol}). The degree of conversion (%) was calculated according to Equation (1).

\[
X = \frac{m_{pol}}{m_{tot}} \times 100 \%
\]  

#### 4.2.3.2 Elementary analysis

Elementary analysis (EA) of carbon, hydrogen and nitrogen were performed on a Carlo Erba MOD 1106 instrument in order to determine the chemical composition of synthesized PEA.

#### 4.2.3.3 Gel permeation chromatography

Gel permeation chromatography (GPC) measurements were carried out to determine the molecular weight and molecular weight distribution. It was measured on a system equipped with a Waters 1515 Isocratic HPLC pump, a Viscotek 250 model refractive index detector, a Waters 2707 autosampler, a PSS PFG guard column followed by 2 PFG-linear-XL (7 \text{ \mu m}, 8*300 \text{ mm}) columns in series at 40 \text{ °C}. Hexafluoroisopropanol (HFIP, Biosolve) with potassium trifluoro acetate (3 g/L) and toluene (2.5 mL/L) was used as eluent at a flow rate of 0.8 mL/min. The molecular weights were calculated against polymethyl methacrylate standards (Polymer Laboratories, M_p = 580 Da up to M_p = 7.1*10^6 Da).
4.2.3.4 Thermal analysis

A TG-209 thermal gravimetric analysis (TGA) instrument (Netzsch, Germany) was used to study the thermal stability of synthesized polymers. 10-15 mg of the sample were placed in standard Netzsch 85 µL alumina crucibles and were heated in nitrogen flow from 30 °C to 600 °C at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) measurements were carried out on a DSC-204 (Netzsch, Germany) to study the thermal transition behavior of the PEA. 5-8 mg of sample were placed in standard Netzsch alumina crucibles and were heated from 0 °C to 220 °C at a heating rate of 10 °C/min. The flow rate of nitrogen was 10 cm³/min.

4.2.3.5 Mechanical analysis

Samples were first extracted in demineralized water to remove residual monomer. They were then dried in vacuum at 40 °C, followed by melt injection molding to tensile testing bars in a respective form according to DIN EN ISO 527-2 5A. The samples were tested identically to the test specifications described in Chapter 3.

4.2.3.6 Rheological analysis

The rheological behavior of the polymer melt is an important parameter for the calculation in the program MOREX. The steady shear viscosity can be defined by Equation (2).

\[ \eta = \frac{1}{\dot{\gamma}} \]  

where \( \eta \) is viscosity, \( \tau \) is shear stress and \( \dot{\gamma} \) is shear rate.

The viscosity can be measured with a rheometer with stationary shear flow. It is dependent on the temperature \( T \), the shear rate \( \dot{\gamma} \) and the density \( \rho \) of the material.[27]

\[ \eta, \tau = f(T, \dot{\gamma}, \rho) \]  

The rheological characterization of the synthesized PEA was performed by aiXtrusion GmbH, Aachen using a high pressure capillary rheometer Rheograf 2002, with round hole capillary (30/1/180) and pressure sensor (500-6666, nominal 500 mbar).
Unlike for many liquids such as water or oils, which are referred to as Newtonian fluids, the shear stress acting on plastic melt is not proportional to the shear rate. They often show shear thinning or shear thickening behavior.

The basis for the simulative representation and calculation of the extrusion process by means of MOREX is the mathematical description of the viscosity behavior. For the mathematical description, Carreau approach is suitable because it describes well the viscosity behavior of many polymers over a wide range of shear rates.\textsuperscript{[27]}

The viscosity curve can be described by Equation (4).

\[
\eta(\dot{\gamma}) = \frac{A}{(1+B\dot{\gamma})^C} \quad (4)
\]

Here,

A: Zero viscosity

B: reciprocal transition shear rate

C: slope of the viscosity curve in the thinning area

The power approach constitutes another way to describe the viscosity curves. However, it is particularly suitable for the high shear rate ranges and can not explain the Newton area. It is therefore more useful for highly filled melts such as rubbers and is not used in this work.\textsuperscript{[27]}

4.3 Results and discussions

4.3.1 Synthesis of polyesteramide on the laboratory extruder with given screw configuration

Table 4.1: Process parameters for the production of PEA12 on a laboratory extruder with given screw configuration.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA12a</td>
<td>94</td>
<td>103</td>
<td>190</td>
<td>170</td>
<td>190</td>
<td>180</td>
<td>4.3</td>
<td>hopper</td>
</tr>
<tr>
<td>PEA12b</td>
<td>94</td>
<td>103</td>
<td>190</td>
<td>170</td>
<td>190</td>
<td>110</td>
<td>4.3</td>
<td>hopper</td>
</tr>
<tr>
<td>PEA12c</td>
<td>125</td>
<td>200</td>
<td>190</td>
<td>180</td>
<td>190</td>
<td>190</td>
<td>7.3</td>
<td>cup</td>
</tr>
<tr>
<td>PEA12d</td>
<td>125</td>
<td>180</td>
<td>200</td>
<td>190</td>
<td>190</td>
<td>190</td>
<td>7.2</td>
<td>cup</td>
</tr>
</tbody>
</table>
The synthesis process of PEA12 (cf. Chapter 3, CA:CL=2:1, 3wt.-% C10 and 3wt.-% C20) was first transferred to a laboratory extruder with a given screw configuration as shown in Figure 4.4. Table 4.1 shows the different processing conditions used for the processing. High cylinder temperatures were kept in the reaction zone to ensure the initiation of reaction which takes place at about 180°C. Furthermore, as the supplied mass flow was not measurable and hardly controllable, a low screw speed was selected to achieve at least ten minutes residence time.

![Schematic illustration of the given screw configuration](image)

**Figure 4.4:** Schematic illustration of the given screw configuration

Many challenges were faced during the practical implementation of the transfer of the PEA synthesis reaction on the laboratory extruder. As described earlier there is no guarantee of continuous delivery due to the different grain sizes of the chemicals. The mass flow therefore subjects to fluctuations with both dosing methods, i.e. by means of funnels as well as through cups. The process parameter adjustments were made according to the plastogram, i.e. torque vs. time. A high monomer conversion was evidenced by a highly viscous extrudate coming out from the die; meanwhile the liquid-like extrudate implied a low conversion. The product appearance changes frequently despite of the same process parameters. This may possibly be because of the unequal reactant feed and inadequate mixing of the extrudate. For example, for sample PEA12d, both high-viscous (in the following marked as PEA12d) as well as low-viscous (in the following marked as PEA 12 dl) extrudates were obtained during the extrusion process.

### 4.3.1.1 Product analysis

The analytical results of the products obtained on the laboratory extruder with the given screw configuration is discussed below. The influence of the process parameters on the
results particularly on the reaction conversion and molecular weight of the resulting polymers is of the main consideration.

4.3.1.1.1 Monomer conversion

Table 4.2: Monomer conversion on the laboratory extruder with a given screw configuration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monomer Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA12a</td>
<td>88.2</td>
</tr>
<tr>
<td>PEA12b</td>
<td>66</td>
</tr>
<tr>
<td>PEA12c</td>
<td>74.5</td>
</tr>
<tr>
<td>PEA12d</td>
<td>80.3</td>
</tr>
<tr>
<td>PEA12dl</td>
<td>63.3</td>
</tr>
</tbody>
</table>

Table 4.2 provides an overview of the results regarding the monomer conversion. While, in the microcompounder, with the same reaction mixture, a reaction conversion of almost 100% could be achieved, the experiments here clearly showed significantly lower monomer conversion in the case of laboratory extruder in the range of 60 – 90%. In agreement with the extrudate appearance, samples PEA12d and PEA12dl show a large difference in the monomer conversions despite of the same process parameters. While in the viscous material, a conversion of 80% is achieved, in the low viscosity material i.e. PEA12dl, the monomer conversion was only about 60%. This is possibly due to the inhomogeneous dosing of the chemicals resulting in a discontinuous mass flow or due to inadequate mixing by the given screw configuration. Both temperature and screw rotation speed have remarkable influence on the monomer conversion. The temperature at the measuring point before the nozzle i.e. Th6 is of great interest for optimization of the experiments. At a low temperature of 110°C (PEA12b), the reaction conversion was 20% lower than that of the similar process, which was carried out at much higher temperature of 180°C (PEA12a). Comparing the monomer conversion of PEA12a (speed 2 min⁻¹) with PEA12c and PEA 12d (speed 7.3 and 7.2 min⁻¹) suggests that the monomer conversion can be reduced with the increase of the screw rotation speed. This is just due to the reduced residence time with the higher speed. Therefore for the further refinement, it was envisaged to perform experiments at a high reaction temperature and with a long residence time.
4.3.1.1.2 Elemental analysis

Table 4.3: Results of elemental analysis of the PEA samples produced on laboratory extruder with a given screw configuration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical C [%]</th>
<th>H [%]</th>
<th>N [%]</th>
<th>Experimental C [%]</th>
<th>H [%]</th>
<th>N [%]</th>
<th>Theoretical ratio after conversion CA:CL</th>
<th>Experimental ratio CA:CL</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA12a</td>
<td>63.53</td>
<td>9.41</td>
<td>8.24</td>
<td>61.70</td>
<td>9.53</td>
<td>7.50</td>
<td>1.76:1</td>
<td>1.5:1</td>
</tr>
<tr>
<td>PEA12b</td>
<td>63.53</td>
<td>9.41</td>
<td>8.24</td>
<td>61.41</td>
<td>9.16</td>
<td>6.90</td>
<td>1.32:1</td>
<td>1.3:1</td>
</tr>
<tr>
<td>PEA12c</td>
<td>63.53</td>
<td>9.41</td>
<td>8.24</td>
<td>60.70</td>
<td>9.15</td>
<td>7.41</td>
<td>1.49:1</td>
<td>1.6:1</td>
</tr>
<tr>
<td>PEA12d</td>
<td>63.53</td>
<td>9.41</td>
<td>8.24</td>
<td>61.76</td>
<td>9.38</td>
<td>7.23</td>
<td>1.61:1</td>
<td>1.4:1</td>
</tr>
<tr>
<td>PEA12dl</td>
<td>63.53</td>
<td>9.41</td>
<td>8.24</td>
<td>61.37</td>
<td>9.31</td>
<td>7.36</td>
<td>1.27:1</td>
<td>1.5:1</td>
</tr>
</tbody>
</table>

In Table 4.3, are shown the results of elemental analysis. The theoretical CA to CL ratio was 2:1. The experimental results here shown that less CA were incorporated in polymer chain as compared to theoretically calculated values (at 100% conversion). This is supported by the results regarding the monomer conversion. Monomer CA that has not been incorporated can be extracted with water. This means that in the optimization and reconfiguration of the extruder screw, good mixing of the chemicals should be ensured and the polymerization zone must be long enough. Furthermore, supplying a continuous mass flow is a parameter that affects the quality of the polymer, but the available experimental set-up did not allow the implementation of this option.

4.3.1.1.3 Gel permeation chromatography (GPC)

Table 4.4: Molecular weight of PEA synthesized in the laboratory extruder with a given screw configuration measured by GPC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (kDa)</th>
<th>$M_n$ (kDa)</th>
<th>PDI ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA12a</td>
<td>75.7</td>
<td>28.6</td>
<td>2.65</td>
</tr>
<tr>
<td>PEA12b</td>
<td>97.8</td>
<td>53.9</td>
<td>1.81</td>
</tr>
<tr>
<td>PEA12c</td>
<td>113.2</td>
<td>68.9</td>
<td>1.64</td>
</tr>
<tr>
<td>PEA12d</td>
<td>66.8</td>
<td>28.4</td>
<td>2.35</td>
</tr>
<tr>
<td>PEA12dl</td>
<td>113.9</td>
<td>74.9</td>
<td>1.52</td>
</tr>
</tbody>
</table>
Figure 4.5: Molecular weight of the synthesized PEA on the laboratory extruder with given screw configuration.

Table 4.4 and Figure 4.5 summarize the results of GPC measurements. In agreement with the monomer conversion and the appearance of extrudate, the molecular weight of the samples, which were prepared in the laboratory extruder with a given screw configuration, was much lower than that of the PEA 12, which was synthesized in the Microcompounder (Chapter 3). In addition, contrary to what has been listed and discussed in results of this work, the molecular weight increases with decreasing temperature (compared PEA12a with PEA12b). It may be because of thermal degradation at elevated temperatures. In addition, the increase in screw speed probably leads to (comparing PEA12a and PEA12b with PEA 12c and PEA12d) increase in molecular weight. This can be argued as the enhancement in mixing action caused by the screw operating at higher speeds, but the results of the monomer conversion was contrary.

4.3.1.1.4 Differential scanning calorimetry (DSC)

Table 4.5 provides an overview of the thermal properties, determined using DSC. A clear melting point for the ester moiety is detected while the second melting point, which corresponds to the amide moiety is not observed in all samples. Only PEA12a comprises a second melting peak Tm2, after the extraction in demineralised water. The reason is as discussed in the previous chapter, incomplete reaction, the CA monomer hardly reacted to form the amide. This is also supported with the fact that the thermal results are comparable to those of pure polymers PCL (Ch-3).
Table 4.5: DSC measurements of the synthesized PEA on the laboratory extruder with a given screw configuration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating phase</th>
<th>Cooling phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{m1}$  [$^\circ$C]</td>
<td>$\Delta H_{m1}$ [J/g]</td>
</tr>
<tr>
<td>PEA12a</td>
<td>55/57</td>
<td>17/26</td>
</tr>
<tr>
<td>PEA12b</td>
<td>55/55</td>
<td>23/22</td>
</tr>
<tr>
<td>PEA12c</td>
<td>55/55</td>
<td>16/23</td>
</tr>
<tr>
<td>PEA12d</td>
<td>56/57</td>
<td>38/35</td>
</tr>
<tr>
<td>PEA12dl</td>
<td>56/55</td>
<td>29/31</td>
</tr>
<tr>
<td>PEA12 (Microcompounder)</td>
<td>56/57</td>
<td>17/17</td>
</tr>
</tbody>
</table>

4.3.1.1.5 Thermogravimetric analysis (TGA)

Comparable to TGA results discussed in Chapter 3, all the samples here prior to extraction in demineralised water show a 3 step degradation profile with beginning of thermal decomposition (onset point) at around 160°C. However, after the water extraction, only samples PEA12a and PEA12d showed a 2 step degradation profile with an onset degradation temperature of 270°C. For the rest samples the beginning of the thermal degradation after demineralised water extraction is only slightly higher around 165-175 °C, and the degradation profile was still 3-stage. As previously discussed, these results suggest that the reaction was incomplete. Therefore, the TGA results suggested only a small fraction of polymerization and rather the oligomer characteristics. However, there is a point of exclusive consideration by looking at thermal degradation profiles, that a small fraction of reaction took place. Otherwise, one would have the degradation profile comparable to that of PCL (Ch-3).

4.3.1.1.6 Rheological properties

Only selected samples were investigated for rheology because of the lack of samples from all polymeric materials synthesized. An example is shown in Figure 4.6, where the viscosity curve for sample PEA12d at different temperatures was demonstrated. It pointed on an untypical course of viscosity, as the viscosity measurement of other PEA blends was reproducible. For comparison, in the Appendix A.1 of this chapter, viscosity curves of PCL and PA-6 are represented.
Unlike typical of pseudoplastic materials, is not the shear rate of independent field (Newton area or Newtonian plateau) in the illustrated viscosity curve of the polyesteramide is seen. The viscosity decreases strongly with shear rate between 10-100 1/sec. After reaching a minimum between 60-120 1/sec (transition range), the viscosity increases significantly again for higher shear rates, even on the zero viscosity level before it again decreases. Therefore, in principle two independent viscosity curves can be determined for lower and higher shear rates. The reason for such untypical viscosity behaviour cannot be explained by the current state of knowledge. As for the synthesis of polyesteramide, a comparatively long residence time of about 10 minutes are required, the extruder screws are operated at low speeds.

![Viscosity profile diagram](image)

**Figure 4.6:** Viscosity profile of PEA samples example of PEA12d.

The simulation employed Carreau parameters are therefore out of the first portion of the viscosity curve, i.e. removed from the region of low shear rates. To determine the parameter of the zero shear viscosity also an auxiliary straight line was set into the diagram. This temporary line drawn or set was based upon the polymers typical viscosity profile in the existing curve, however, it was noted that this has the direct influence on the values referred. As the simulation will be used in support of the experimental work, a zero viscosity value is desirable, but not mandatory. The synthesis also requires temperatures of about 180°C. Therefore, the Carreau-parameters for viscosity measurements at 150°C were chosen for further calculations. This is refered in Annex A.2. The inclusion of a viscosity curve at higher temperatures was not possible, as the polymer became of low viscosity on the one hand and on the other hand showed signs of
degradation. In principle, it lends itself to a power law to describe the relative viscosity carried out. As illustrated in Figure A.3 of the Annex, a correct description of even using Carreau approach is possible. A study conducted by accounting the power-law approach yielded a straight line, which was completely like using the Carreau approach calculated line, such that no cons arises from the method used.

4.3.1.2 Summary of the results of synthesized polyesteramide in laboratory extruder with a given screw configuration

For the continuous synthesis of polyesteramide by reactive extrusion, first a laboratory extruder with an already configured screw was used. Focus of work was to define the process conditions as well as the requirements for the screw, as a direct transfer of the micro-compounder process to an extrusion process is only conditionally possible. The experiments have shown that a continuous synthesis on a laboratory extruder in principle is realizable. The results, however, indicate the deficits in the reaction and process stability, and the reaction remained incomplete. This may be due to the inhomogeneous dosing and the consequences associated are non continuous mass flow and inadequate mixing of the chemicals. Therefore, for an optimization of the screw configuration, followings aspects should be considered:

- Care should be taken to have a constant material supply, to ensure a continuous mass flow.

- Up to the nozzle should be kept high cylinder temperatures, so that the entire screw length is available for the reaction and polymerization

- To introduce little friction in the material and to ensure comparable process conditions as in the micro compounder, in the reaction zone kneading elements should be omitted.

On the basis of the results presented so far, in the next section is the designing of screw reactor using the simulation program MOREX to optimize the continuous synthesis of PEA.
4.3.2 Designing and optimization of screw configuration

In accordance with the work of Bartilla\textsuperscript{[28]} and Rothe\textsuperscript{[29-30]} on reactive extrusion of \(\varepsilon\)-caprolactam, the work of Kim and White\textsuperscript{[24-25]} on reactive extrusion of different lactams and lactones, as well as in this work developed, three different screw configurations were considered suitable for process control. However, the process-based design of screw reactors requires a detailed technical understanding. Moreover, the economic aspects such as machinery material and time costs in a screw design should not be underestimated. Therefore, at early stage of practical experiments, different screw configurations have to be tested for their suitability in this work of PEA synthesis. For this a supportive simulation work was conducted using a simulation program MOREX. Based on the results from section 3.3.1 and 4.3.1 in this section is therefore the interpretation of the screw reactor for an optimized process for the continuous synthesis of PEA on a laboratory extruder.

4.3.2.1 Mechanical and technical limitations in design and optimization process

For the design and optimization of the process the following were the mechanical and technical limitations before:

- Chemicals could be fed only through the feeder of the extruder (see Figure 4.1). A material supply elsewhere was not possible.

- As already discussed before, due to the restrictions regarding the dosage, no certain mass flow can be defined, so that the latter subject to fluctuations.

- The barrel was made up of six electrically heated heating zones with thermocouples (T1-T6) and a cooled feed zone. Due to heat conduction processes in barrel, an actual temperature difference of only about 90°C was achieved between the feed zone and the first heating zone.

- Degassing was not available, so that the possibility of the residual monomer extraction was not given at the end of the process or at the end of the screw.
- The opening and the entire screw extruder course were flooded with nitrogen, to keep out the reaction-inhibiting contaminants. Nevertheless, addition or demolition reactions could not be completely eliminated.

- There were two dies for use: die A and B, whose schematic structure is shown in Figures 4.2 (a) and 4.3(b) respectively. From consideration of the geometrical differences it follows that die B exerts a reinforcing effect on the residence time. The polymer melt lingers much longer in die B than in die A.

4.3.2.2 Functions and practical requirements of reactor

The extruder screw should satisfy various tasks and functions depending on the course of reaction such as inclusion and mixing of the fed chemicals, reaction initiation at defined location, sufficiently long polymerization-zone as well as discharging highly viscous melt.

It is crucial to promote fed chemicals quickly from the feeder area to the barrel zone to avoid material accumulation and the non-uniform conveying of the material. In addition, the temperature of the feed zone should be kept low to prevent the melting of the chemical; otherwise an uncontrollable reaction can result. A continuous intake of chemicals can be ensured by conveying elements.

The mixing of the chemicals plays an essential role to ensure uniform and to guarantee consistent product quality. It is to ensure that besides dispersive also distributive mixing occurs. For this, the use of different widths of kneading elements proved successful. \[28\] For the design, however, the pressure-consuming elements such as kneading elements must be sufficiently far away from the feed zone to avoid material backflow from the conveying elements to the feed zone. Due to the relatively short length of the screw and the long reaction time of about ten minutes, the temperature of the mixing zone following the reaction and polymerization zone should be raised sharply in a short time. The initiation of the reaction is, therefore, already started in the Mixing zone on the basis of heat conduction processes.

The polymerization and reaction zone represents the most important area for this process. All other zones of the screw must be as designed so that the material has a long residence
time to spend in the polymerization zone. This zone is composed solely of conveying elements to reduce shear effects and consequently to avoid reduction of the molecular weight. Furthermore, a rapid and complete sequence of the reaction is ensured only by a minimum temperature of 180°C.

Since in this work the synthesis of PEAs is in the foreground, therefore, in contrast to most extrusion processes, the shape of the extrudate is of least importance.

4.3.2.3 Design of new screw configurations and calculation of melt residence time

On the basis of above requirements, three different screw configurations which were considered suitable for process control are presented as well as their pros and cons are discussed.

For the three basic configurations, the intake and the first mixing zone are established identical. The cylinder bore through which the chemicals are fed is located here at the level of the second and third conveying element. After the fourth conveying element, follows the first mixing zone, which consists of twelve successive kneading discs, corresponding to this principle, the length of three successively lying kneading elements, is constructed. The kneading discs were designed in such a way that there be a neatly flush connection, and thus a homogeneous transfer of the conveying elements, with the first mixing zone and a continuous transition from the mixing zone with which adjoining polymerization zone was realized.

4.3.2.3.1 Screw configuration A

Subsequent to the feeding and first mixing zone follows conveying elements for built-in reaction zone. A further mixing zone, is adjusted consisting of eight kneading disks is the reaction zone. They are arranged identical to the first eight kneading discs of first mixing zone. Through the last four kneading discs, representing a promoter active, neutral kneading element, the local residence time of the melt got extended due to pressure build-up properties in the reaction zone and melt backpressure effect. Such a zone could increase the degree of conversion of the reaction due to the longer residence time. Precluding the fact that through additional kneading element, a higher shear is introduced into the material and through friction the degree of polymerization of the polymer chains
formed can be reduced. In addition, the residence time of melt increased by the use of active supporter kneading elements has an adverse effect on the product homogeneity and uniformity. This means that the molecular weight distribution would be wider. It becomes clear that, especially in the mixing zones an increase of the residence time can be observed.

![Figure 4.7: Simulated residence time over the entire length of the screw A.](image)

### 4.3.2.3.2 Screw configuration B

In comparison with the screw configuration A in this configuration the second mixing zone was entirely omitted. With this a low-shear reaction zone was achieved. A long residence time of the melt in the reaction zone can be achieved in this configuration but only through low mass flows and speeds, which from an economic perspective would be uneconomical for industrial applications. Furthermore, there is probability of incomplete reaction and the polymer melt will not be properly homogenized that may have an adverse effect on product quality. As seen from Figure 4.8, in the absence of a second mixing zone, the calculated residence time is shortened as compared to configuration A.

![Figure 4.8: Comparison of the calculated residence times in different screw configurations over the length of the screw.](image)
4.3.2.3.3 Screw configuration C

Screw configuration C differs in configuration A, that subsequent to the second kneading zone follows one opposite promoting element. Thus, in compared to configuration A, the melt residence time increased. The use of opposite promoting elements for reactive extrusion, however also entails disadvantages: Besides leading to increase in shearing effect, the backflow of the material increases residence time and thus influences the product uniformity.\textsuperscript{[28]} Figure 4.8 shows comparison of residence time calculated by means of computer simulations among the above described screw configurations. The melt residence time in configuration C is slightly higher than configuration A because of the opposite promoting element.

4.3.2.4 Selection of the screw geometry for practical implementation

To summarize the discussion in the previous sections different screw configurations are set up in Table 4.6 with their advantages and disadvantages.

Table 4.6: Advantages and disadvantages of different screw geometries.

<table>
<thead>
<tr>
<th>Screw</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-long time of the melt in the reaction zone, -possibly, increase the conversion efficiency</td>
<td>-use of a second kneading zone -low product homogeneity</td>
</tr>
<tr>
<td>B</td>
<td>-maximum, low-shear reaction zone -possibly, high degree of polymerization</td>
<td>-sufficient residence only at low speeds and mass flows -possibly, lower degree of conversion -low product homogeneity</td>
</tr>
<tr>
<td>C</td>
<td>-long time of the melt in the reaction zone -possibly, high degree of conversion</td>
<td>-Use of a second kneading zone, and one opposite promoting elements -possibly, lower degree of polymerization</td>
</tr>
</tbody>
</table>

After considering all the arguments, screw configuration C was selected for implementation at the laboratory extruder. That was a compromise between a sufficiently long residence time in the polymerization zone and sufficient product homogeneity. Since there is no defined and continuous mass flow possible in practice and hence the residence time of the polymer melt in the screw is influenced significantly, stand the foreground realization of as possible long reaction zone with long residence time. Therefore, the
geometry is selected, which enables a long residence of polymer melt in barrel by means of opposite supporting element. The second mixing zone by facilitating more shearing and friction of the polymer chains may adversely affect the degree of polymerization, but it also allows a balance of the continuous dosage not thereby possible. Figure 4.9 gives an example of the theoretical calculated residence time at different mass flow rates and speeds for screw configuration C. It clearly shows that these two aspects significantly influence the residence time. However, with a too long residence time and the associated high thermal stress the polymer was however already at degradation.

![Figure 4.9: Calculated residence time of the polymer melt for screw geometry C at different mass flow rates and speeds.](image)

4.3.3 Synthesis of polyesteramide in the laboratory extruder with laid out screw configuration

In Table 4.7, the process parameters used for the synthesis of Polyesteramide on the laboratory extruder with the screw configuration C are listed.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA12e</td>
<td>72</td>
<td>195</td>
<td>195</td>
<td>195</td>
<td>195</td>
<td>195</td>
<td>200</td>
<td>10</td>
<td>B</td>
</tr>
<tr>
<td>PEA12f</td>
<td>72</td>
<td>195</td>
<td>195</td>
<td>195</td>
<td>180</td>
<td></td>
<td>200</td>
<td>10</td>
<td>A</td>
</tr>
</tbody>
</table>

87
In spite of designing and optimization of screw, the problem of non continuous and non-homogeneous mass flow due to improper feeding of chemicals was there. The chemicals were weighed and added in small batches in order to prevent segregation of the chemicals. At a screw speed of 10 min⁻¹, the material required 19 minutes (measured with a stopwatch for samples PEA12e) to emerge out of die. A constant color and constant high appearing viscosity of the extrudate was extruded initially without any problems from die B (see Figure 4.10).

![Image of extruder](image.png)

**Figure 4.10:** Continuous extrusion of PEA of high viscosity.

Due to a rapid increase of the driving torque, die pressure and leakage of extrudate between the cylinder modules after about an hour test period, had the first continuously elapsed process is aborted and the laboratory extruder was opened. However, this also opened the possibility to take a look inside the extruder and to see the different stages of the reaction progress in a "frozen" state. In Figure 4.11 a recording of the open laboratory extruder is shown. It was found that the reaction progress as discussed above and corresponded to the states adopted in the theory. The first mixing zone leads to the melting and homogenizing of the chemicals. Only in the middle of the reaction zone, a significant increase in viscosity of the melt could be seen, which was deep yellow. The coloring was there after until the end of the screw. Also an increase in viscosity of the extrudate could be observed from the feed zone to the last screw element. During cleaning of the die it was found that it was no longer freely permeable due to the high viscosity of the extrudate.
Figure 4.11: Opened laboratory extruder after Quitting. Flow direction: from left to right.

In order to avoid a repeated leakage of the polymer melt between the cylinder modules and the setting of the nozzle, die A was used in the subsequent trial for sample PEA12f. Die A due to its geometric interpretation exerts less melt pressure, so that the melt exits more smoothly. In these experiments however, could only be realized a pulsating process flow, which is expressed mainly in the non-uniform viscosity of the extrudate. The extrudate was deducted either as a highly viscous strand (hereinafter referred to as PEA12f) or only liquid (reffered as PEA12fl) could be collected, and exhibited in both cases a yellowish staining. As previously no process changes took place, the different appearance of the extrudate must be the result of a recirculated non-uniform material feed. In die B, due to the larger back pressure, larger backflows occurred, which has a better balancing of the feed stream and thus had constant viscosity of the extrudate as a consequence.

To enable residence time measurement also with die A, following experiments were made during the cleaning of the extruder with a polyethylene (PE), with otherwise constant, process conditions. A polyethylene master batch having a green color was added to the extruder. Here, a green color extrudate came from die after 690 sec. It takes three or four times as long for the extrudate to reach the original colour. Even though the viscosities of PE and the synthetic-based PEA are not identical, this experiment clearly shows that a desired residence time of about 10 minutes is possible, however the product believed to have a broad molecular weight distribution.

4.3.3.1 Product analysis

Physico-chemical, rheological and mechanical properties of PEA synthesized in the laboratory extruder with a laid out screw configuration C, were also examined.
4.3.3.1.1 Monomer conversion

In Table 4.8 the results of the reaction conversion are given. The reaction conversions are much higher compared with the test results which were carried out also on the laboratory extruder but without optimization of the screw. Therefore, by this design and optimization of the screw, an improvement in the process is achieved. However, there is still scope for further optimization as for the micro-compounder prepared PEA, reaction conversions were slightly higher (Ch-3). This might be achieved through improved dosing or feeding process of educts. During the process, however, fluctuations were still present in the values of the reaction conversion. The polymer with significantly lower viscosity, referred as PEA12fl, has a lower reaction conversion than the other two samples.

Table 4.8: Results of the reaction conversion of the PEA samples prepared on laboratory extruder with screw geometry C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA12e</td>
<td>97.5</td>
</tr>
<tr>
<td>PEA12f</td>
<td>98.6</td>
</tr>
<tr>
<td>PEA12fl</td>
<td>95.8</td>
</tr>
</tbody>
</table>

4.3.3.1.2 Elemental analysis

Basis for assessing the ratio of amide to ester units, are shown in Table 4.9 to find the results of the elemental analysis. The theoretical ratio of CA to CL still lies as 2:1.

Table 4.9: Results of the elemental analysis of the PEA samples prepared on laboratory extruder with screw geometry C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical</th>
<th>Experimental</th>
<th>Experimental ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C [%]</td>
<td>H [%]</td>
<td>N [%] C [%]</td>
</tr>
<tr>
<td>PEA12e</td>
<td>63.53</td>
<td>9.41</td>
<td>8.24   63.53</td>
</tr>
<tr>
<td>PEA12f</td>
<td>63.53</td>
<td>9.41</td>
<td>8.24   62.88</td>
</tr>
<tr>
<td>PEA12fl</td>
<td>63.53</td>
<td>9.41</td>
<td>8.24   62.88</td>
</tr>
</tbody>
</table>

The results indicate that for the sample PEA12f and PEA12fl higher incorporation of amide units occurs. As already discussed above, reasons for the discrepancies is the inhomogeneous addition of reactants and possibly present molecules of the initiator-
activator system (Ch-3). PEA12e however, shows less amide units than that of theoretically calculated in the synthesized polymer.

4.3.3.1.3 Gel permeation chromatography (GPC)

Table 4.10: Molecular weight of PEA synthesized in the laboratory extruder with screw configuration C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_a$ (kDa)</th>
<th>$M_n$ (kDa)</th>
<th>PDI ($M_a/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA12e</td>
<td>174.4</td>
<td>87.6</td>
<td>1.99</td>
</tr>
<tr>
<td>PEA12f</td>
<td>227.9</td>
<td>76.6</td>
<td>3.63</td>
</tr>
<tr>
<td>PEA12fl</td>
<td>137.7</td>
<td>58.3</td>
<td>2.36</td>
</tr>
</tbody>
</table>

The results in Table 4.10 and Figure 4.12 clearly show that with the screw geometry C higher molecular weights were achieved than previously with a given configuration of Laboratory screw extruder. The PEA synthesized on laboratory extruder with given screw configuration has the molecular weight of about 100 kDa, whereas, for sample PEA12e and PEA12f which were synthesized with optimized screw geometry, and where, the extrudate was having a high viscosity, the molecular weight was about 200 kDa. As expected, the molecular weight of sample PEA12fl is significantly lower, but still higher than the samples PEA12a to PEA12d, which was prepared with given screw configuration. The results also show that there is still a need for optimization and certainly higher molecular weights can be achieved (see comparison with PEA12 from the Micro Compounder). This could be achieved by providing for a better dosing and mixing of the reactants at the beginning of the screw, as well as possibly by an even longer polymerization.

![Figure 4.12: Molecular weight of synthesized PEA on the laboratory extruder with screw configuration C.](image)
4.3.3.1.4 Differential scanning calorimetry

The following table (Table 4.11) gives an overview of the thermal properties determined by means of DSC measurements. The results show that comparable values as with the Micro Compounder synthesized sample could be achieved. Also, the results between the non-extracted and in demineralized water extracted samples indicated that only small amounts of monomer were included before extraction. This result can be supported by the results of the reaction turnover (see Section 4.3.3.1.1). The melting range of the ester unit is about 56 ºC and for the amide moiety is between 160 and 170 ºC. Although a melting point of the amide moiety was present in sample PEA 12e but no associated second crystallization temperature can be detected. Possibly, the crystalline regions of the amide units is so small that the resolution or the sensitivity of the measurements is not sufficiently high, and this value is therefore, can not be detected.

Table 4.11: DSC measurements of the synthesized PEA on laboratory extruder with screw configuration C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating phase</th>
<th>Cooling phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{m1}$ [$^\circ$C]</td>
<td>$\Delta H_{m1}$ [J/g]</td>
</tr>
<tr>
<td>PEA12e</td>
<td>56/56</td>
<td>26/32</td>
</tr>
<tr>
<td>PEA12f</td>
<td>55/55</td>
<td>18/18</td>
</tr>
<tr>
<td>PEA12fl</td>
<td>55/56</td>
<td>15/20</td>
</tr>
<tr>
<td>PEA12 (Microcompounder)</td>
<td>56/57</td>
<td>17/17</td>
</tr>
</tbody>
</table>

4.3.3.1.5 Thermogravimetric analysis (TGA)

All three samples showed a 2-step degradation profile in thermogravimetric analysis. They also showed high onset temperatures for thermal decomposition both before and after the water extraction. The decomposition of the samples PEA12e and PEA12f began at approximately 260 ºC for both before and after extraction in demineralised water, while the thermal decomposition of the sample with significantly lower viscosity (PEA12fl) was at 250 ºC. This result corresponds to the previously discussed results and shows that from a thermal viewpoint a similar material is synthesized like that prepared in the micro-compounder.
4.3.3.1.6 Mechanical properties

The following figures give an idea of the mechanical properties of PEA synthesized on the Laboratory extruder. To allow a better comparison with the results achieved in the Micro Compounder, in the graphs (Figure 4.13 to 4.15) is also listed the PEA12 samples and the reference materials PCL and PA-6. For sample PEA12 f not enough sample material for the mechanical characterization was available, so that only the samples PEA12e and PEA12fl were examined. As for the tensile-modulus (see Figure 4.13) greater values were achieved than what obtained previously (for PEA12e at almost 550 N/mm² and for PEA12fl at nearly 400 N/mm²), the tensile strength (Figure 4.14) of PEA12e was comparatively high at around 30 N/mm² like the PEA12 from micro-compounder. In the sample PEA12, remaining residual monomer content of \(\varepsilon\)-caprolactam, which was not removed by water extraction is therefore have only a minor influence on the results. PEA12fl has a slightly lower tensile strength, which is at about 20 N/mm² lying between the values of the PEA12 and the PCLs. But still, the values for the tensile modulus and tensile strength are significantly lower than those of PA-6 (see also Ch-3).

![Tensile modulus graph]

*Figure 4.13:* Tensile modulus of the synthesized PEA in the laboratory extruder with a laid out screw geometry.
Figure 4.14: Tensile strength of the synthesized PEA on the laboratory extruder with a laid out screw geometry.

When considering the position shown in Figure 4.15 maximum nominal strains for PEA12e and PEA12fl are detected at lower values than that for PEA12. It shall be determined in future studies where this is justified.

Figure 4.15: Maximum nominal strain of the synthesized PEA on laboratory extruder with a laid out screw geometry.
4.3.3.1.7 Rheological properties

The viscosity curve for sample PEA12f was determined at different temperatures using high-pressure capillary rheometer measurements, (see Figure 4.16). Contrary to that observed in (Figure 4.6) viscosity curve for Sample PEA12d, these measurements show a much more typical behaviour course corresponding to that of pseudoplastic materials, even if the shear rate-independent region is not clearly identified. Neither two viscosity curves for small and large shear rates can be seen, still it has a transition region with a slope of the viscosity (see comparative Figure 4.6). Also, we see that the zero shear viscosity is a power higher than in the previous samples characterized for rheology. So, this different behavior declared, is not clearly visible. Additional samples could not be analyzed because not enough sample material for such measurements was available. Furthermore, it was found that some samples showed markedly lower viscosities, when remelted in a rheometer, as exhibited during the synthesis process. The thermal load of the polymer also conducted in multiple measurements causes degradation which could be seen, and the sample were thus not often be investigated further.

![Viscosity curve](image)

**Figure 4.16:** Viscosity increase in the sample PEA12f.

The figure above shows that the zero shear viscosities values of sample PEA12f at 110 to 130 °C are comparable to those of PCL at 200 to 220 °C (see Figure A.1). At high shear rates the viscosity is between 50 and 100 Pa·sec, so comparable to viscosity characteristic
values of both PCL and PA-6 (see the Appendix of this chapter for Figure A.1 and A.2). Please refer to the Appendix A.2 of this chapter for the Carreau parameter determined at a temperature of 130 °C. Furthermore, refer to Appendix Figure A.3 in that the Carreau approach is very well suited to describe the viscous behavior. For comparison the experimentally determined viscosity curve and the viscosity determined after Carreau are presented.

4.4 Conclusion and outlook

The synthesis for the continuous preparation of PEA could be successfully implemented with a designed screw. This was reflected, for example, in improved reaction conversion, which was 60 to 90% with a given screw geometry and was now more than 95%. Furthermore, a significant increase in the molecular weight was achieved. Considering thermal as well as mechanical properties, comparable results could be achieved with respect to the polymer produced in the micro-compounder. The rheological properties on the other hand must be exploited in further studies to re-examine and to define. It is likely at the time of the first rheological measurements that impurities are present (see Figure 4.6) in the high-pressure capillary rheometer and templates. Therefore, the measurements were distorted to the same extent when reproduced. For the calculation of the residence time over the length of the screw, the Carreau parameters of the first measurements were used. However, it turned out in subsequent calculations with the new parameters, that these do not affect the calculation of the residence.

The experiments also showed that pressure-building tools at the screw end can contribute to longer residence time and for process stability. If the pressure is too high, however, this leads to the leakage of the polymer melt between the cylinder modules, which made an opening of the extruder necessary. However, this had allowed to track the reaction path along the screw in the "frozen state" and to evaluate the influence of different elements on the extrudate. As used herein the designed structure of the screw with configuration C is suitable in principle for the synthesis of PEA. A need for optimization is still present for the dosing of reactants to able to guarantee a homogeneous and constant mass flow rate. Higher molecular weight could be achieved possibly by a longer reaction zone. The use
of a return conveying element could be omitted in order to avoid additional friction of the material.

4.5 References


Appendix

A.1 Rheological properties of reference materials

![Figure A.1: Viscosity curve of PCL at different temperatures.](image_url)
Figure A.2: Viscosity curve of PA-6 at different temperatures.

A.2 Carreau parameters for the simulation and design of the screw reactor

For the simulation using MOREX, the following Carreau parameters were used.

A.2.1 Carreau parameters of PEA12d for 150 °C

A: 250
B: 0.1
C: 2.07

A.2.2 Carreau parameters of PEA12d for 130 °C

A: 3423
B: 0.3778
C: 0.5644

The viscosity profile of PEA12f experimentally and theoretically at 130 °C is shown in Figure A.3
Figure A.3: Viscosity profile of PEA12f at 130 °C and viscosity after Carreau calculations
Chapter 5

Melt Spinning of Polyesteramide Fibers
Synthesized via a Reactive Extrusion Process

Abstract

Polyesteramide (PEA) has generated great interest as one of the promising materials for biomedical applications being thermoplastic and biodegradable. This work reports on the development of novel melt spun PEA fibers with good mechanical properties. The fibers were spun from PEA synthesized via a reactive extrusion process based on the anionic polymerization of ε-caprolactam (CA) in the melt of commercially available polycaprolactone (PCL) on a microcompounder equipped with a melt spinning line. The as spun fibers were then conditioned to improve their mechanical strength. Tensile tests were performed to evaluate the mechanical strength of the as spun and conditioned fibers. Thermal properties were determined by means of DSC and TGA. The correlation between the structure and the properties of the fibers was studied. These PEA fibers can be used for the fabrication of various textile structures for biomedical applications.

5.1 Introduction

Biodegradable polymeric fibers have been widely used in the field of tissue engineering,[1] which is a technology that enables the regeneration of lost tissues and organs[2] for instance with the help of artificial porous structures called scaffolds.[3] The scaffolds provide not only a mechanical support but also a microenvironment for proliferation of cells.[4-6]

These scaffolds are generally made up of biodegradable synthetic polymers, mainly polyesters like (poly-lactic acid) PLA, PCL etc. For instance, the scaffolds fabricated from PCL because of its biocompatibility, biodegradability and mechanical properties has already been used for various tissue regeneration in orthopedics.[7-9] However, the biodegradation of these polyesters occurs via bulk erosion process leading to accumulation of acidic byproducts which cause inflammation.[10-14] Therefore,
polyesteramides which contains both ester and amide groups in the main chain and are known to degrade via surface erosion process\textsuperscript{12} may help to solve this problem of local acidic microenvironment and can be thus a promising candidate for tissue engineering applications.\textsuperscript{16-20}

There are two main types of fiber based scaffolds: nonwoven scaffold and textile scaffold. Nonwoven scaffolds are made by electrospun micro or nanofibers and have very less pore size (few micrometers or less). They thus interrupt the infiltration of mammalian cells which ranges in size from several micrometers to several hundred micrometers.\textsuperscript{21, 22} On other hand, textile scaffolds are created via the weaving, braiding or knitting of fibers with diameter ranging from several ten to several hundred micrometers depending on the application. For instance such textile scaffolds have been used for the regeneration of aortic valves, ligaments, nerves, etc.\textsuperscript{8, 9, 23-26}

Fibers from polymers are generally manufactured by three main fiber spinning techniques: wet spinning, dry spinning and melt spinning.\textsuperscript{1, 27} Dry spinning and wet spinning techniques require use of solvents. In dry spinning, solvents are get rid off by evaporation while in wet spinning, polymer is coagulated in a fluid which is compatible with the spinning solvent but does not serve itself as a solvent for the polymer. Among these three, melt spinning is considered most suitable for the production of fibers for making textile structures. In melt spinning, the polymer melt is first stretched from the spinning die under a constant take-up speed. The stretched polymer melt should get solidified in a small distance and within a short time to result in fibers. As this method requires no solvent, it has an advantage over the dry and wet spinning processes that on one hand it is economic and ecofriendly process and on other hand, it does not affect the cell viability during medical applications.\textsuperscript{28, 29}

In literature, most of the researchers have obtained PEA fibers via an electrospinning process. Only a few articles on melt-spun PEA fibers have been published, and no continuous process was reported. Z. Qian et al first synthesized PEA based on \textepsilon-caprolactam and 11-aminoundecanoic acid via a melt polycondensation process and then prepared fibers from it via melt spinning using a melt flow rate instrument equipped with a single nozzle circular spinning die. In a similar way, C. Liu et al. prepared melt spun
fibers of PEA based on 6-aminocaproic acid, adipic acid and 1,6-hexane diol. They both studied the tensile and degradation properties of the obtained fibers thereafter.\textsuperscript{[30, 31]}

In this work, focus lies on the production of fibers from PEA synthesized via reactive extrusion followed by melt spinning in a continuous process. The challenge is to find proper and stable spinning conditions such as take-up speed, throughput, melting temperature etc. The effect of different compositions of PEA on spinning conditions as well as thermal and mechanical properties of filaments is analyzed.

5.2 Experimental section

5.2.1 Melt spinning equipment

In this section the main parts of the melt spinning equipment and their various functions are described. To produce PEA fibers, a DSM Xplore melt spinning machine line was used consisting of 3 major units: (a) An extrusion unit to melt the polymer and to supply definite throughputs; (b) a wind-up unit to supply the take-up speed and (c) a conditioning unit for conditioning/elongating the as spun fibers.

5.2.1.1 Melt spinning line

The specifications for microcompounder is described in Chapter 3 (see section 3.2.2.1). In Figure 5.1 shows the spinning unit, which has a speed-regulated godet roll with a take-up roll coupled to it. The take-up roll ensures that the spun mono-filament can be rolled-up in a neater manner such that later this spool can easily be processed in the DSM Xplore Conditioning Unit. From the touch screen the take-up roll torque, the winding width, pitch and the spin speed of the Godet roll settings can be controlled.

The DSM Xplore Conditioning Unit as shown in Figure 5.2 is equipped with 2 speed-regulated godet rolls that handle the actual conditioning (elongating); the relationship between the two speeds is a measure of the elongation expected in the filament. In addition, the Conditioning Unit has 2 torque-regulated take-up or supply rolls depending on the direction of the filament, which ensure that the filament is returned to the rolls neatly after elongating. In doing so carton bobbin is used for every roll. The Conditioning Unit is equipped with a temperature-controlled “Hot Shoe” (heating oven, heating by
radiation) where conditioning takes place. A system of various ceramic guide rolls ensures that the filament is always fed into the oven in the correct manner. More detailed specifications about the melt spinning equipment can be obtained from fiber spinning manual of DSM Xplore.

**Figure 5.1:** Main components of DSM Xplore micro-compounder along with the winding unit.

**Figure 5.2:** Main components of the DSM Xplore conditioning unit.

### 5.2.2 Material and method

PEA4, PEA6 and PEA8 were selected for spinnability test. They were synthesized in the same way as described in Chapter 3 with the only difference that here we used spin die of 0.1 mm diameter and the polymer after 10 min was stretched from this die under constant take-up speed to obtain corresponding PEA fibers.
5.2.3 Characterization methods

These spun and conditioned fibers were characterized for their thermal and mechanical properties.

5.2.3.1 Diameter measurement

The cross sectional area of the fibers was determined by Mitutoyo Laser Scan Micrometer (LSM-500H) which is fully compatible with Dia-Stron tensile tester and automated sample loading system.

5.2.3.2 Tensile test

The tensile tests for single fibers were carried out on a Dia-Stron, miniature tensile tester (MTT) which comprises of a mechanical unit, control unit, pneumatics unit (PU1100), Windows software (Uv Win) and sample mounting accessories. The single universal control unit (UV1000) along with MTT variants also supports the measurement modules like fiber dimensional analysis system (FDAS76x) and the automated sample loading (ALS1500). The tensile test used a sample fiber length of 30 mm. The tests were performed at a rate of 50 mm/min which is dependent on the elongation of fibers. The tensile device measures and displays the force (F) versus the deformation (δ). The elastic modulus was found in the linear elastic region from general relation E=σ/ε.

5.2.3.3 Differential scanning calorimetry (DSC)

Thermal transition behavior of PEA unconditioned and conditioned fibers was determined by DSC measurement on a DSC-204 (Netzsch, Germany) unit equipped with a accessory unit for cooling via liquid Nitrogen (Netzsch CC200 supply system). 3-5 mg of sample were placed in standard Netzsch alumina crucibles. The DSC measurements were carried out in following steps with heating rate of 10°C/min and a nitrogen flow rate of 10 cm³/min:

For PEA fibers:

1. First heating from 20°C to 220°, 2. Cooling down from 220°C to -50°C, 3. Second heating from -50°C to 220°C
Only the first heating and cooling scans are reported here.

5.3 Results and discussion

Lot of efforts are needed to get continuous production of PEA fibers in a melt spinning process as it is a sensitive process often combined with fiber breakage. Here the PEA melt is stretched under a constant take-up speed from spinning die of 0.1mm diameter. The distance between the extruder and winding unit was about 1m. Therefore, it is important during spinning that PEA melt should get solidified in such a small distance and within a short time. Because of such a process, PEA fibers in fiber formation zone go through high deformation and cooling rate. The as spun fibers so obtained were then conditioned at room temperature or appropriate temperature above their glass transition temperature. In the beginning to optimize the melt spinning process, several parameters were changed to get stable and continuous process for the production of PEA fibers. The properties of the conditioned and unconditioned fibers such as fiber diameter, thermal properties and tensile properties were examined later in order to find the correlation between the composition of PEA and spinning process as well as structure-property relationship of as spun and conditioned fibers.

5.3.1 Selection of composition for spinning experiments

For the spinning experiments, the compositions PEA4, PEA8 and PEA12 were selected because of their better degree of conversion (above 98%) in every particular series of PEA synthesized (see Chapter 3). In addition, the other properties of these above mentioned PEA compositions like molecular weight and tensile properties (see Chapter 3) were most suitable for conducting spinning experiments. Considering such high percentage of degree of conversion in these PEA compositions, the spinning experiments were performed directly after reactive extrusion process without any water extraction step assuming that the effect of residual monomers in synthesized PEA is negligible. Table 5.1 summarizes the composition of PEA used in the spinning experiments.
Table 5.1: Composition of PEA used for spinning experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>amount C10 [mol.-%]</th>
<th>amount C20 P [mol.-%]</th>
<th>ratio CA:CL</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA 4</td>
<td>3.0</td>
<td>3.0</td>
<td>1:2</td>
</tr>
<tr>
<td>PEA 8</td>
<td>3.0</td>
<td>3.0</td>
<td>1:1</td>
</tr>
<tr>
<td>PEA 12</td>
<td>3.0</td>
<td>3.0</td>
<td>2:1</td>
</tr>
</tbody>
</table>

5.3.2 Optimization of spinning parameters

PEAs were synthesized via reactive extrusion under the similar processing conditions as described in detail in Chapter 3. The only difference is that here we used a spinning die with small diameter of about 0.1mm to get fibers later on after the reaction completes in micro-compounder. All the chemicals were fed into the microcompounder at temperature of around 120°C and processing was then carried out at 180°C for 10 minutes at a screw speed of 100 rpm under nitrogen atmosphere. As soon as the polymerization reaction in the microcompounder completed, i.e. after 10 minutes, the screw speed was reduced to 5-10 rpm while the spinning temperature was kept the same i.e. at 180 °C. The resulting opaque polymer melt that was slightly yellowish in color came out of the spinning die in case of both PEA8 and PEA12. The PEA melt was then stretched out from the spinning die under a defined take-up speed or winding speed. Upon spinning, the fibers from PEA8 were still slight yellowish in color where as for PEA12, shiny white fibers were obtained. The take-up speed was optimized in order to prevent problems like instability of spinning line (necking effect), variation in fiber thickness and the breakage of fibers.[32] The take-up speed of winding unit and screw speed of extruder were varied to find stable spinning conditions.

The optimum spinning conditions for PEA8 and PEA12 are listed below.

Spinning temperature: 180 °C

Winding Speed: 10 m/min
Torque: 130 - 150 N/mm

At a winding speed of more than 10 m/min, the fiber breaks; similar is the case when torque was set to value above 150 N/mm. While, at a winding speed less than 10 m/min, fibers with nonuniform diameter were obtained.

The conditioning or hot-drawing of the as spun fibers was done under manual mode settings using following parameters. The conditioned fibers of PEA12 on carbon bobbin is shown in Figure 5.3.

Speed: 300 cm/min
Factor: 2
Torque: 100 N/mm
Hot shoe temperature: 40 °C

![Image](image.jpg)

**Figure 5.3:** PEA12 conditioned fibers on carbon bobbin.

At a speed higher than 300 cm/min or torque more than 100N/m, the fiber breakage occurs during conditioning. Factor 2 here means that the fiber will be elongated or stretched to reduce theoretically 20% of its original fiber diameter or thickness. This is also referred as draw ratio. The draw ratio can be defined as a measure of degree of stretching during the orientation of a fiber or filament, expressed as the ratio of the cross-sectional area of the undrawn fiber to that of the drawn fiber. Drawing causes the orientation of molecular chains along the fiber axis and has a profound effect on the fiber properties, like crystallinity and mechanical strength. The PEA fibers were conditioned at a temperature of 40 °C.
5.3.3 Characterization of fibers

The as spun and conditioned PEA fibers were analyzed for their thickness, thermal as well as mechanical properties. The influence of PEA composition and effect of conditioning on the properties of fibers are of main consideration.

5.3.3.1 Fiber diameter

FDAS 765 high resolution fiber dimensional measurement system was used for determining the cross-sectional area of the resulting fibers. It comprises of the Uv 1000 control unit, dimensional test module including Mitutoyo laser micrometer for measurement of fiber diameter and UvWin applications software for its operation. FDAS765 was incorporated with the MTT675 automated tensile tester as shown in Figure 5.4.

Figure 5.4: FDAS765 incorporated with MTT675 automated tensile tester (Dia-Stron).

At time of measurement, fiber was straightened and rotated in the laser as well as multiple measurements were made by scanning along the length in discrete ‘slices’ to obtain accurate measurements. The fiber diameter of unconditioned and conditioned PEA fibers are given in Table 5.2

Table 5.2: Diameter of unconditioned and conditioned PEA8 and PEA12 fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fiber diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA8</td>
<td>329</td>
</tr>
<tr>
<td>PEA8 (conditioned)</td>
<td>106</td>
</tr>
<tr>
<td>PEA12</td>
<td>169</td>
</tr>
<tr>
<td>PEA12 (conditioned)</td>
<td>126</td>
</tr>
</tbody>
</table>
5.3.3.2 Thermal analysis

Thermal analyses of the as spun and conditioned fibers along with the pristine polymers are depicted in Figure 5.5 and 5.6 and the thermal properties are summarized in Table 5.3. Only the 1st heating and cooling scans were shown which reveals the presence of mainly two endotherms and exotherms. In the first heating cycle of PEA8 and PEA12 pristine polymers as well as corresponding fibers, the melting peak at ~60°C \((T_{m1})\) and ~170°C \((T_{m2})\) can be attributed to the melting of ester and amide crystals respectively.

**Table 5.3:** DSC measurements of pristine PEA8 and PEA12 polymer and corresponding fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling run</th>
<th>First heating run</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T_{c1})</td>
<td>(\Delta H_{c1})</td>
</tr>
<tr>
<td>PEA8</td>
<td>28</td>
<td>-22.5</td>
</tr>
<tr>
<td>PEA8 unstretched</td>
<td>30</td>
<td>-26</td>
</tr>
<tr>
<td>PEA8 stretched</td>
<td>31</td>
<td>-28</td>
</tr>
<tr>
<td>PEA12</td>
<td>16.5</td>
<td>-17</td>
</tr>
<tr>
<td>PEA12 unstretched</td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td>PEA12 stretched</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

* shoulder/small peak in heating or cooling scan; ** cold crystallization; \(^{(a)}\) refers to \(T_{m2low}\); \(^{(b)}\) refers to \(T_{m2high}\)

It was observed from the first heating scan shown in Figure 5.5a that for PEA8 composition the melting enthalpy corresponding to both ester \((\Delta H_{m1})\) and amide \((\Delta H_{m2})\) moieties increases on going from polymer powder to conditioned fibers, indicating the
better crystallinity and apparently also the better orientation in the fibers, which should, therefore, result in improved mechanical properties.

(a)

(b)

Figure 5.5: DSC curves recorded during (a) the first heating scan and (b) cooling scan of PEA8 polymer powder and fibers at a heating and cooling rate of 10Kmin⁻¹.
Figure 5.6: DSC curves recorded during (a) first heating scan and (b) cooling scan of PEA12 polymer powder and fibers at heating and cooling rate of 10Kmin⁻¹.
PEA12 (Figure 5.6a) has a higher amide content than PEA8. It was noticed that in the case of PEA12 both melting point ($T_m$) and associated enthalpy ($AH_m$), which correspond to ester moiety, increases from polymer to conditioned fibers as for PEA8. However, in polymer powder as well as fibers of PEA12, $T_m$ i.e. melting peak for amide moieties splits into two peaks $T_{m2\text{low}}$ at ~140°C and $T_{m2\text{high}}$ at ~170°C attributing to differently sized crystalline domains of the same crystalline phase. In addition in PEA12 composition, a decrease in the melting enthalpy ($AH_m$) for amide moieties was observed from polymer powder to fibers.

As shown in Figure 5.5b, a single crystallization exotherm at ~30°C corresponding to the ester moiety was observed on cooling the melt of the PEA8 samples. Since no crystallization peak was observed for amide groups, it seems that the crystallization of the amide groups is quite slow, and it takes place during the storage at room temperature. The reason may be the shorter length of the amide containing segments in the polymer chain, making it difficult for the amide groups to be organized into a crystalline structure.

On the other hand, as shown in Figure 5.6b, upon cooling the melt of the PEA12 polymer samples, two crystallization exotherms were observed at ~10°C ($T_c1$) and at ~107°C ($T_c2$) corresponding to the ester and amide moieties, respectively. The crystallization temperature was much lower than that of the homopolymers (PCL and PA6). The crystallization is apparently depressed due to the presence of another component.\textsuperscript{[15]}

### 5.3.3.3 Mechanical properties

Mechanical/tensile properties of PEA fibers are mainly determined by two factors, chemical composition and the extent of stretching/conditioning. On conditioning the as-spun fibers, the crystallinity and the chain orientation increases.\textsuperscript{[27]}

Figure 5.7, 5.8 and 5.9 give an overview of the achieved average mechanical characteristics of the tensile-E-modulus, tensile strength and strain at break/breaking strain for the various as spun and conditioned PEA fibers and for the reference material PCL fibers and PA6/66 fibers. The mechanical properties are summarized in Table 5.4
Table 5.4: Mechanical properties of PEA8 and PEA12 fibers along with reference fibers of PCL and PA6/66.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic modulus (GPa)</th>
<th>Breaking stress (MPa)</th>
<th>Breaking strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA8</td>
<td>0.22 ± 0.03</td>
<td>31.28 ± 4.03</td>
<td>431 ± 35.47</td>
</tr>
<tr>
<td>PEA8 (conditioned)</td>
<td>0.29 ± 0.04</td>
<td>101 ± 6.73</td>
<td>181 ± 28.54</td>
</tr>
<tr>
<td>PEA12</td>
<td>1.17 ± 0.27</td>
<td>149 ± 36.29</td>
<td>111 ± 9.92</td>
</tr>
<tr>
<td>PEA12 (conditioned)</td>
<td>1.74 ± 0.81</td>
<td>335 ± 113</td>
<td>69.4 ± 27.18</td>
</tr>
<tr>
<td>*PCL</td>
<td>0.04 ± 0.01</td>
<td>7.7 ± 1.4</td>
<td>847 ± 39.8</td>
</tr>
<tr>
<td>*Polyamide 6 / 66</td>
<td>5.5</td>
<td>645±445</td>
<td>33±18.38</td>
</tr>
</tbody>
</table>

*Source: Literature [33 and 34]

Figure 5.7: Tensile modulus of PEA 8 and PEA 12 fibers along with reference fibers of PCL and PA6/66.
The tensile –E-modulus (see Figure 5.7) of the PEA fibers is around 0.2 to 1.8 GPa in average depending on the composition i.e. CA to CL ratio in the PEA. PCL fibers obtained from gravity spinning[33] have a very low tensile-E-modulus of about 0.04 GPa whereas PA6/66 fibers have tensile-E-modulus ranging from 0.7 to 10 GPa.[34] For PEA8 unconditioned fibers with CA to CL ratio of 1:1, the tensile-E-modulus is about 0.2 GPa. After conditioning, the tensile-E-modulus of PEA8 fibers increases to 0.3GPa. On the other hand, PEA12 fibers with CA to CL ratio of 2:1 exhibit a higher tensile-E-modulus. Tensile–E-modulus value of the conditioned PEA12 fibers is about 1.17 GPa, which is much higher than that of PCL as well as PEA8 fibers, but much lower than that of PA6/66 fibers. With increase of the amide (CA) content in PEA there is an increase of the tensile–E-modulus. In addition, conditioning of the fibers leads to a higher tensile-E-modulus.

Figure 5.8: Tensile strength of PEA 8 and PEA 12 fibers along with reference fibers of PCL and PA6/66.

The tensile strength of the PEA fibers (see Figure 5.8) with a CA to CL ratio of 1:1 and 2:1 has values much higher than that of PCL (7.7MPa). For conditioned PEA8 fibers, the value of the tensile strength is about 101 MPa that is lower as compared to the
conditioned PEA12 fibers with value of around 335 MPa. The PEA12 fibers have a
tensile strength significantly higher than PCL but lower than PA6/66. Therefore, similar
to tensile-E-modulus, significantly higher values of tensile strength were obtained for
PEA fibers with CA to CL ratio of 2:1. This shows that the incorporation of amide unit in
the molecular chain makes sufficient contribution to the improvement of the mechanical
strength.

![Graph showing strain comparison](image)

**Figure 5.9:** Breaking strain of the PEA 8 and PEA 12 fibers along with reference fibers
of PCL and PA6/66.

Figure 5.9 depicts a graphical representation of the obtained breaking strain for PEA
fibers and reference materials. In contrast to the tensile modulus and tensile strength,
significantly higher values of about 850% was obtained for PCL fibers (as mentioned in
the literature) compared with those of PEA fibers as well as PA6/66 where the breaking
strain was in range of about 20 to 430%. PEA8 fibers with a CA to CL ratio of 1:1 has a
higher breaking strain of around 430% in unconditioned fibers which reduced to 180% in
the case of the conditioned fibers. PEA12 fibers with CA to CL ratio of 2:1, which have
higher tensile modulus and tensile strength, however, suffer from a lower breaking strain
as compared to PCL and PEA8 but its breaking strain is higher than that of PA6/66.

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Summarizing, the conditioning of the fibers results in the significant increase of tensile modulus as well as tensile strength but decrease in breaking strain. Similar effect was also observed for tensile properties with the increase of amide segments compared to ester segments (CA:CL ratio) in PEA backbone.

5.4 Conclusion

In this chapter we have shown that fibers can be successfully obtained through melt spinning of PEA synthesized via a reactive extrusion process. Optimized spinning conditions were determined for stable and continuous production of PEA fibers of different compositions. These melt spun fibers were then conditioned, resulting in significant enhancement of the crystallinity as well as the chain orientation in the fibers. The conditioned fibers exhibit improved mechanical properties as compared to the unconditioned ones of similar composition. The influence of the copolymer composition on thermal and mechanical properties of PEA fibers was also studied. The higher the amide content in the polymer backbone, the better the mechanical properties of the fibers.

5.5 References


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Chapter 6

Synthesis and Characterization of Poly(esteramideamide)s of Different Alkylene Chain Lengths

Abstract

In this work, a series of aliphatic segmented poly(esteramideamide) (PEAA) copolymers were synthesized by melt polycondensation of a tailor-made amide-containing monomer based on 1,4-diaminobutane and ε-caprolactone and different dicarboxylic acid methyl esters with a varied number of methylene groups. The chemical structure of the synthesized PEAA was characterized by $^1$H-NMR spectroscopy, FTIR-spectroscopy and gel permeation chromatography. The thermal behavior of these new polymers was studied by thermal gravimetric analysis and differential scanning calorimetry. All polymers exhibit a melting point at around 150°C and a decomposition temperature above 350 °C.

6.1 Introduction

Aliphatic polyesters derived from lactide and glycolide are biodegradable but offers only limited applications due to lack of sufficient mechanical and processing properties. On the other hand, aliphatic polyamides exhibit generally sufficient mechanical and thermal properties but are not biodegradable. An approach to combine the characteristics of both polymer groups is to synthesize polyesteramides (PEAs) with either randomly distributed amide groups$^{[1-12]}$ or well-defined amide blocks/segments$^{[13-19]}$ in the polymer chain.

PEAs of different microstructures i.e. random, alternating and segmented (blocky) co-polymers can be prepared depending upon the monomers used and synthetic route followed.

Segmented PEAs have a microphase separated structure due to presence of a rigid amide phase and a flexible ester phase and thus are a class of thermoplastic elastomers.$^{[20-22]}$ Such polymers form a homogeneous melt on heating above the melting temperature of the hard segments and thus can be easily processed while cooling results in the
segregation of the rigid amide and soft ester domains leading to microphase separated structure at room temperature. The amide rich rigid phase constitutes the crystalline lamellae serving as a thermoreversible physical crosslinker for the often amorphous ester phase that is responsible for providing flexibility and extensibility to the polymer. Therefore, the properties of PEA can be tuned simply by varying the amide and ester contents.\textsuperscript{[20, 21, 23]}

Several research groups have synthesized aliphatic segmented PEAs having uniform amide blocks. Preformed bisamide-diols, oligoesters, bisamide-esters were reacted with diols and dimethyl adipates to get high molecular weight segmented PEAs.\textsuperscript{[16-19, 24]} The effect of the ratio of hard to soft segments on the physico-chemical properties of synthesized PEAs were studied in detail. Lips et al.\textsuperscript{[20]} synthesized segmented PEAs via melt polycondensation by reacting a preformed bisamide-diol with 1,4-butanediol and dimethyl adipate. The bisamide-diol was based on 1,4-diaminobutane and ε-caprolactone. A series of high molecular weight PEAs with varied hard and soft segment ratio were prepared. With the increase of the hard segment content from 10 to 85 mol.-\%, the modulus increased from 70 to 524 MPa and stress at break increased from 8 to 28 MPa. A single glass transition temperature was observed for all the polymers, and it increased with the increase of the hard segment content. Two melt transitions at low and high temperatures corresponding to the melting of crystals comprising of single ester amide (EA) sequences and two or more EA sequences, respectively, were observed. The low transition temperature was independent of the polymer composition, meanwhile the high transition temperature increased with the increase of the hard segment content.

Similarly, Garg et al.\textsuperscript{[21]} have synthesized segmented PEAs via melt polycondensation with defined amide blocks consisting of isolated amide groups, two adjacent amide groups or three adjacent amide groups, which were then randomly incorporated into the polybutylene adipate backbone. Different preformed monomers used were α,ω-diols, α,ω-amino alcohols and α,ω-diamines with a built-in amide group. Varying the amount of these preformed monomers in the reaction mixture leads to different content of the amide groups in the PEAs and thus resulting in the different physico-chemical properties of the synthesized PEAs. It was demonstrated that the amount as well as the length of the hard amide segments significantly affect the properties of the segmented PEAs.
In this work a series of polyesteramideamides (PEAA) were synthesized by melt polycondensation of a tailor-made amide-containing monomer and dicarboxylic acid methyl esters of varying alkylene chain length. The influence of alkylene chain length on the physico-chemical properties of synthesized PEAA was then studied.

6.2 Experimental section

6.2.1 Materials

\(\varepsilon\)-Caprolactone (97%), 1,4-diaminobutane (99%), and dimethyl adipate (98%) were purchased from Aldrich. Dimethyl suberate (99%), and dimethyl sebacate (97%) were obtained from Alfa Aesar. Titanium IV isopropanoxide was obtained from ALCHEM. 2-propanol (absolute) was purchased from Fluka. 2,2,2-trifluoroethanol was purchased from Sigma Aldrich. The solvents like tetrahydrofuran, and methanol were purchased from VWR. All the chemicals were used without further purification.

6.2.2 Synthesis

6.2.2.1 Synthesis of monomer

Tailor-made monomer \(\alpha,\omega\)-amino alcohol (OH-(CH\(_2\))\(_5\)-CO-NH-(CH\(_2\))\(_4\)-NH\(_2\); monomer AA) was prepared according to the procedure described in literature.\(^{[25]}\)

A solution of \(\varepsilon\)-caprolactone (100.0 g, 0.88 mol) in THF (80 mL) was prepared and added dropwise to a solution of 1,4-diaminobutane (271.04 g, 3.08 mol) in THF (260 mL). Here we used, less amount of 1,4-diaminobutane (3.5 times instead of 4 times) then what is described in literature to save the cost of production. This reaction mixture was stirred continuously for 20 h at room temperature. Afterwards, the excess of 1,4-diaminobutane as well as solvent (THF) were removed in high vacuum (up to \(10^{-2}\) mbar) by slowly raising the temperature up to 60°C. The crude product so obtained was then dissolved in methanol and clear solution so obtained was then precipitated in cold diethyl ether. The white coloured product was filtered and dried in high vacuum to give a pure product in 80% yield (mp 75°C).
6.2.2.2 Synthesis of polyesteramideamides

The PEAA was synthesized via 2-step melt polycondensation method according to scheme 6.1. Equal moles of tailor made monomer AA and dicarboxylic esters of different alkylene chain length (dimethyl adipate, dimethyl suberate and dimethyl sebacate) were added in a reactor which is equipped with a mechanical stirrer. Titanium(IV) isopropoxide (5 mg/g of dicarboxylic acid ester) in isopropanol (1% w/w) was then added in the reactor under the inert atmosphere. The reaction mixture was then slowly heated at 170°C under 100mbar vacuum for 5 hours. The precondensate was cooled and left overnight in vacuum. Further reaction was then next day performed by heating the reaction mixture slowly at 180°C, and decreasing the pressure to 1mbar. After attaining this temperature, reaction was carried out for 4 hours under 10⁻² mbar high vacuum. At the end, the resultant melt was taken out of reactor, dissolved in 2,2,2-trifluoroethanol and precipitated in diethyleneether. The polymer so obtained was filtered and dried at 50 °C in a vacuum oven for overnight.

6.2.3 Characterization techniques

6.2.3.1 Nuclear magnetic resonance spectroscopy

1H-NMR spectra were carried out on a Bruker DPX 300 at 300 MHz. Deuterated-trifluoroacetic acid was used as solvent with TMS as internal standard.

6.2.3.2 Elemental analysis

To determine the chemical composition of synthesized PEAA, elementary analysis (EA) of carbon, hydrogen and nitrogen was performed on Carlo Erba MOD 1106 instrument.

6.2.3.3 Fourier transform infrared spectroscopy

FT-IR spectra were collected using Thermo Nicolet Model Nexus 470 spectrophotometer equipped with a DTGS detector using 100 signal-averaged scans at a resolution of 8 cm⁻¹. Each sample was in a form of thin film of polymer (25mm×10mm) placed on KBr disc. Data were collected in the spectral range of 500-4000 cm⁻¹.

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6.2.3.4 Gel permeation chromatography

GPC measurements were carried out to determine the molecular weight and molecular weight distribution. It was measured on a system equipped with a Waters 1515 Isocratic HPLC pump, a Viscotek 250 model refractive index detector, a Waters 2707 autosampler, a PSS PFG guard column followed by 2 PFG-linear-XL (7 μm, 8*300 mm) columns in series at 40 °C. Hexafluoroisopropanol (HFIP, Biosolve) with potassium trifluoro acetate (3 g/L) and toluene (2.5 mL/L) was used as eluent at a flow rate of 0.8 mL/min. The molecular weights were calculated against polymethyl methacrylate standards (Polymer Laboratories, Mp = 580 Da up toMp = 7.1*106 Da).

6.2.3.5 Thermogravimetric analysis

A TG-209 (Netzsch) thermo-gravimetric analysis (TGA) instrument was used to study the thermal stability behaviour of synthesized polymers. 2-4 mg of the sample were placed in standard Netzsch alumina 85 μL crucibles and were heated in nitrogen from 30°C to 700°C at a heating rate of 10°C/min.

6.2.3.6 Differential scanning calorimetry

DSC measurements were carried out on a DSC-204 (Netzsch, Germany) to study the thermal transition behavior of the PEAA. 5-8 mg of sample were placed in standard Netzsch alumina crucibles and were heated from 0°C to 220°C at a heating rate of 10°C/min. The flow rate of nitrogen was 10 cm³/min.

6.3 Results and discussions

Segmented PEAA are made up of hard and soft domains formed via self organization of the polymer chain segments. The hard domains consist of amide segments which contribute to good thermal and mechanical properties as they can easily crystallize due to the formation of hydrogen-bonding between each other. The soft domains consist of the ester groups, which contribute to the degradable character of polymer.
Scheme 6.1: Synthesis of PEAAx via melt polycondensation of a tailor-made \( \alpha,\omega \)-amino alcohol and dicarboxylic acid methyl esters with different alkylene chain length.

In this work, an \( \alpha,\omega \)-amino alcohol AA with a built-in amide bond (\( \text{OH}-(\text{CH}_2)_3\text{-CO-NH-(CH}_2)_4\text{-NH}_2 \)) is condensed with dicarboxylic acid methyl esters of different alkylene chain length to yield PEAAx (where \( x \) is the number of methylene groups in the alkylene chain) with a hard segment content of around 66.7\% and a soft segment content of 33.3\% according to the stoichiometry. The synthesized polymers are referred as PEAA4, PEAA6 and PEAA8, depending on the number of methylene groups in the dicarboxylic acid methyl ester used for their synthesis.

The PEAAs were synthesized via a 2-step melt polycondensation reaction. The first step, the transesterification leads to the formation of oligomers with the release of methanol. In the second step, post-polycondensation took place and after 4 h reaction time the polymer was obtained.

6.3.1 \( ^1\text{H-NMR} \) spectroscopy

Figure 6.1: \( ^1\text{H} \) NMR spectrum for PEAA8 in d-TFA.
\(^1\)H-NMR was used to characterize PEAA4, PEAA6 and PEAA8. A representative \(^1\)H NMR spectrum for PEAA8 is shown in Figure 6.1. The microstructure of PEAAs were determined from the \(^1\)H-NMR spectrum according to Equation (1) and (2).

Xamide = Ia/ (Ia + Ie) \hfill (1)

Xester = 1 – Xamide \hfill (2)

Where Ia and Ie were integral intensities of the signal at \(\delta = 3.4\) and \(\delta = 4.1\). All synthesized PEAAs showed a slight deviation from the expected composition. The theoretical and experimentally obtained ratio of amide to ester units in the PEAAs are summarized in Table 6.1. The good agreement between the theoretical and experimental values indicates a qualitative conversion of the monomers.

**Table 6.1:** Composition of synthesised PEAAs.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer (^{(a)}), g</th>
<th>Monomer (^{(b)}), g</th>
<th>((m/n)_{th}) (^{(f)}) (mol %)</th>
<th>((m/n)_{exp}) (^{(g)}) (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nPEAA4 ((x=4))</td>
<td>AA 10</td>
<td>DMA (^{(e)}) 8.71</td>
<td>66.7/33.3</td>
<td>64.7/35.2</td>
</tr>
<tr>
<td>nPEAA6 ((x=6))</td>
<td>AA 10</td>
<td>DMSUB (^{(e)}) 10.11</td>
<td>66.7/33.3</td>
<td>65.3/34.7</td>
</tr>
<tr>
<td>nPEAA8 ((x=8))</td>
<td>AA 10</td>
<td>DMSEB (^{(e)}) 11.52</td>
<td>66.7/33.3</td>
<td>64.7/35.2</td>
</tr>
</tbody>
</table>

6.3.2 Elemental analysis

Table 6.2 summarizes the results of elemental analysis. The theoretical values and experimental results for the amount of C, H and N elements present in the synthesized polymers show a good agreement, indicating a high purity of the obtained products.

**Table 6.2:** Results of the elemental analysis of the PEAAs samples.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Theoretical</th>
<th></th>
<th></th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C [%]</td>
<td>H [%]</td>
<td>N [%]</td>
<td>C [%]</td>
</tr>
<tr>
<td>PEAA4</td>
<td>61.54</td>
<td>8.97</td>
<td>8.97</td>
<td>61.03</td>
</tr>
<tr>
<td>PEAA6</td>
<td>63.53</td>
<td>9.41</td>
<td>8.23</td>
<td>62.82</td>
</tr>
<tr>
<td>PEAA8</td>
<td>65.22</td>
<td>9.78</td>
<td>7.61</td>
<td>64.52</td>
</tr>
</tbody>
</table>
6.3.3 FTIR-spectroscopy

The FTIR spectra of the synthesized PEAAs recorded at room temperature are presented for the wavenumber regions 3600-2700 and 1800-650 cm\(^{-1}\) in Figure 6.2. Characteristic bands were used for the elucidation about the morphology and crystalline structure of the synthesized PEAAs.

![FTIR spectra](image)

**Figure 6.2**: FT-IR spectra for the PEA series for the wave number region (above) 3600-1800 cm\(^{-1}\) and (below) 1800-600 cm\(^{-1}\) measured at room temperature.
All PEAAs show characteristic bands at ~1732 (ν CO ester), ~1635 cm⁻¹ (amide I, (ν CO) and ~1541 cm⁻¹ (amide II ν CN + CO–NH bend), which signifies the presence of both ester and amide bonds in the polymer backbone. IR spectra of these PEAAs also indicate the presence of a strong H-bonding having absorbance bands at ~3300 cm⁻¹ (ν NH H-bonded) with a shoulder at ~3400 cm⁻¹ (ν OH H-bonded).

Several weaker bands at 1474 cm⁻¹ (NH vicinal CH₂ bend), ~1420 cm⁻¹ (CO vicinal CH₂ bend), ~1260 cm⁻¹ (amide III), ~693 cm⁻¹ (amide V) and ~585 cm⁻¹ (amide VI) reveals important structural information about the synthesized PEAAs i.e. these PEAAs crystallize preferentially in the α - form found in nylon 6. [26] The most common crystalline structures of nylon 6 are α and γ phases. The main peaks of the synthesized PEAAs and the characteristic peaks of nylon 6 in α and γ phases are listed in Table 6.3

<table>
<thead>
<tr>
<th>Assignmenta</th>
<th>Nylon6 (α)</th>
<th>Nylon 6 (γ)</th>
<th>nPEAA4</th>
<th>nPEAA6</th>
<th>nPEAA8</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν NH H-bonded</td>
<td>3301</td>
<td>3302</td>
<td>3303</td>
<td></td>
<td></td>
</tr>
<tr>
<td>νa</td>
<td>2941</td>
<td>2938</td>
<td>2935</td>
<td></td>
<td></td>
</tr>
<tr>
<td>νs</td>
<td>2866</td>
<td>2863</td>
<td>2857</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amide I</td>
<td>1638</td>
<td>1635</td>
<td>1635</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amide II</td>
<td>~1540</td>
<td>~1560</td>
<td>1544 (α)</td>
<td>1542(α)</td>
<td>1542(α)</td>
</tr>
<tr>
<td>NH vic. CH₂ bend</td>
<td>~1475</td>
<td></td>
<td>1474(α)</td>
<td>1475(α)</td>
<td></td>
</tr>
<tr>
<td>CH₂ bend</td>
<td>1464</td>
<td>1463</td>
<td>1462 (γ)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO vic. CH₂ bend</td>
<td>1417</td>
<td></td>
<td>1420(α)</td>
<td>1420(α)</td>
<td>1420(α)</td>
</tr>
<tr>
<td>Amide III</td>
<td>1265</td>
<td>1269</td>
<td>1275 (γ)</td>
<td>1261(α)</td>
<td>1259(α)</td>
</tr>
<tr>
<td>ν C–CO</td>
<td>959</td>
<td>977</td>
<td>956(α)</td>
<td>951(α)</td>
<td>949(α)</td>
</tr>
<tr>
<td>Amide V</td>
<td>691</td>
<td>712</td>
<td>693(α)</td>
<td>693(α)</td>
<td>691(α)</td>
</tr>
<tr>
<td>Amide VI</td>
<td>579</td>
<td>623</td>
<td>586(α)</td>
<td>586(α)</td>
<td>582(α)</td>
</tr>
</tbody>
</table>

a ν: stretching mode
A close look at the IR bands reveals the presence of a mixture of $\alpha$ and $\gamma$ crystalline structures for PEAA4 whereas the $\alpha$ crystalline phase predominates in PEAA6 and PEAA8. Wide-angle X-ray diffraction will be performed to determine the crystalline morphology of these polymers.

6.3.4 Gel permeation chromatography (GPC)

The molecular weight and polydispersity index (PDI) of synthesized PEAAs measured by GPC are summarized in Table 6.4. The GPC data show that most of the synthesized PEAAs have a weight-averaged molecular weight in the range of 35000 – 56000 and PDI around 2.

Table 6.4: Molecular weight and polydispersity index of polyesteramideamides synthesized in this work.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mn (Kda)</th>
<th>Mw (Kda)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>nPEAA4 (x=4)</td>
<td>15.7</td>
<td>35.5</td>
<td>2.26</td>
</tr>
<tr>
<td>nPEAA6 (x=6)</td>
<td>34.9</td>
<td>50.7</td>
<td>1.45</td>
</tr>
<tr>
<td>nPEAA8 (x=8)</td>
<td>20.5</td>
<td>55.5</td>
<td>2.7</td>
</tr>
</tbody>
</table>

6.3.5 Thermal gravimetric analysis (TGA)

![Figure 6.3: TGA thermograms of PEAA4, PEAA6 and PEAA8 recorded in nitrogen atmosphere.](image)
The thermal stability of the PEAAs was determined by TGA under nitrogen atmosphere. As listed in Table 6.5 the onset degradation temperature is taken as temperature of decomposition. All the PEEAs synthesized are stable above 350°C. The traces of TGA for these PEEA reflect a complex degradation process involving two steps as shown in Figure 6.3. Since, for all the synthesized polymers, the decomposition temperature is higher, therefore, these polymers can be further processed.

6.3.6 Differential scanning calorimetry (DSC)

DSC was used to elucidate the phase behavior including melting and crystallization temperature and the corresponding transition enthalpy of the synthesized PEAAs. The thermal history of the polymer samples were erased in the first heating run. The DSC curves recorded during the cooling and second heating run are shown in Figure 6.4, and the thermal properties are summarized in Table 6.5.

The crystallization as well as melting temperature of the PEAAs is not strongly dependent of the alkylene chain length of dicarboxylic esters used for synthesis of PEEA. The PEEA6 exhibits the highest melting as well as crystallization temperature in this series. For all PEAAs the crystallization peak is pretty narrow, meanwhile the melting peak is relatively broad. The transition enthalpy, i.e. the polymer crystallinity, increases significantly with the increase of the alkylene chain length. It is most probably due to the increase of the chain flexibility that facilitates the chain folding, which takes place during the polymer crystallization.

Table 6.5: Thermal properties of PEAAs synthesized in this work.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_d$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nPEAA4</td>
<td>385</td>
<td>5.0</td>
<td>152.3</td>
<td>27.2</td>
<td>132.7</td>
<td>24</td>
</tr>
<tr>
<td>(x=4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nPEAA6</td>
<td>412</td>
<td>-</td>
<td>157.6</td>
<td>38.2</td>
<td>137</td>
<td>34</td>
</tr>
<tr>
<td>(x=6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nPEAA8</td>
<td>405</td>
<td>-</td>
<td>149.2</td>
<td>42.7</td>
<td>127.3</td>
<td>36</td>
</tr>
<tr>
<td>(x=8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a): onset of decomposition as measured by TGA; (b): measured by DSC
Figure 6.4: DSC curves of PEAA4, PEAA6 and PEAA8: (above) cooling scan and (below) second heating scan (performed at a heating and cooling rate of 10 K/min).
6.4 Conclusion

Poly(esteramideamides) (PEAAs) of high molecular weight have been successfully synthesized via a two-step melt polycondensation procedure using a preformed \( \alpha,\omega \)-amino alcohol and dicarboxylic methyl esters of varying alkylene chain lengths. All the polymers showed melt transition at around 150°C and thermal degradation above 350°C. However, as demonstrated from DSC data, their ability towards crystallization increases with the increase of the alkylene chain length of the dicarboxylic acid methyl ester used in polycondensation.

Both DSC and TGA data demonstrated that the synthesized PEAAs can be further melt processed without degradation as the decomposition temperature of these PEAAs were significantly higher than their melting temperatures. Therefore, the fabrication of different textile structures using these PEAAs is possible, and this will be discussed in the following chapter.

6.5 References

Chapter 7

Melt Spinning of Polyesteramideamide
Synthesized via a Melt Polycondensation Process

Abstract

Novel polyesteramideamide (PEAA) fibers were prepared via a melt spinning process on a DSM Xplore melt spinning line. The PEAAAs used in spinning was synthesized via melt polycondensation of a tailor-made amide-containing monomer and dicarboxylic acid methyl esters with different length of alkylene group. As a reference material, poly(L-lactide) fibers were also melt spun and characterized. All obtained fibers were conditioned under appropriate conditions. The mechanical and thermal properties of as spun and conditioned fibers were then evaluated and interpreted regarding the structure property relationship.

7.1 Introduction

Excellent processability, variable mechanical properties, and the ability to modify or combine different properties make polymers useful for serving as biomaterials.[1-3] For polymers to be used as biomaterials, along with chemical stability it is also important that when used as implants, it should not lead to inflammatory responses when degrade. Poly(lactic acid) (PLA) and poly(glycolic acid) being FDA approved are the most widely used synthetic polymers in the field of tissue engineering and many other biomedical applications.[4] However, their lower performance regarding thermal, mechanical and processing abilities as well as bulk degradation mechanism leading to acidic microenvironment in cells strictly restricts their practical use as biomaterials.[5-8]

Polyesteramides (PEAs), a class of synthetic biodegradable polymers, emerged as a solution with better mechanical, thermal and processing properties and also on degradation leads to less pH drop due to surface erosion mechanism during degradation. Thus, PEAs reveal a great potential for being used in several medical applications like
sutures, implants, scaffolds etc. However, the efforts to make PEAs available for use as biomaterial commercially is still an ongoing topic of research.\textsuperscript{[9-11]}

Several research groups have put lot of efforts to synthesize bioabsorbable co-PEAs with adjustable profiles in terms of thermal and mechanical properties by tuning the ester and amide contents in the PEAs.\textsuperscript{[12-13]} In Chapter 6 the synthesis of a new series of poly(esteramideamide)s (PEAAs) via melt polycondensation was described. In this Chapter efforts have been devoted (i) to process the synthesized PEAA into fibers (ii) to find stable spinning conditions for these PEAAs and (iii) to investigate the thermal and mechanical properties of spun fibers.

7.2 Experimental section

7.2.1 Materials

PEAA4, PEAA6 and PEAA8 synthesized via melt polycondensation (Chapter 6) were used for melt spinning. As a reference material, PLA obtained from Natureworks were used to produce PLA fibers.

7.2.2 Extrusion and melt spinning line

DSM Xplore melt spinning machine line equipped with an extrusion unit, a wind up unit and a conditioning unit (see description in section 5.2.1), was used for melt spinning of PLA and PEAA fibers.

7.2.3 Melt Spinning

Both the PLA, and the PEAA synthesized via melt polycondensation were dried overnight in vacuum oven at 45°C. Melt spinning of these dried polymers were then conducted on DSM Xplore spinning line using a single filament die of 0.1 mm diameter under nitrogen supply. The processing and spinning conditions are discussed in detail in section 7.3.2 and 7.3.3.
7.2.4 Characterization methods

The spun and conditioned fibers were characterized.

7.2.4.1 Diameter measurement

The cross sectional area of the PEAA fibers was determined by Mitutoyo Laser Scan Micrometer (LSM-500H) which is fully compatible with Dia-Stron tensile tester and automated sample loading system.

7.2.4.2 Tensile test

The tensile tests for single fibers were carried out on a Dia-Stron, miniature tensile tester (MTT) which comprises of a mechanical unit, control unit, pneumatics unit (PU1100), Window software (Uv Win) and sample mounting accessories. The single universal control unit (UV1000) along with MTT variants also supports the measurement modules like fiber dimensional analysis system (FDAS76x) and the automated sample loading (ALS1500). The tensile test used a sample fiber length of 30 mm. The tests were performed at a rate of 50 mm/min which is dependent on the elongation of fibers. The tensile device measures and displays the force (F) versus the deformation (δ). The elastic modulus was found in the linear elastic region from general relation E=σ/ε.

7.2.4.3 Differential Scanning Calorimetry (DSC)

Thermal transition behavior of PEAA unconditioned and conditioned fibers was determined by DSC measurement on a DSC-204 (Netzsch, Germany) unit equipped with a accessory unit for cooling via liquid Nitrogen (Netzsch CC200 supply system). 3-5 mg of sample were placed in standard Netzsch alumina crucibles. The DSC measurements were carried out in following steps with heating rate of 10°C/min and a nitrogen flow rate of 10 cm³/min:

For PEAA fibers:

1. First heating from 20°C to 220°C, 2. Cooling down from 220°C to -50°C, 3. Second heating from -50°C to 220°C. Only the first heating and cooling scans are reported here.
7.3 Results and discussion

7.3.1 Challenges in spinning

Instability in the spinning line is one of the biggest problems to overcome in the spinning process. Takasaki\textsuperscript{[14]} discussed two main failure mechanisms during spinning of PLA fibers—one due to the increase of the surface tension and the other due to the increase of air-friction force. Rauschenberger\textsuperscript{[15]} also studied and developed criteria for stable melt spinning of polymers. Three different mechanisms\textsuperscript{[16]} resulting in the instability of spinning line are discussed below.

i. Brittle failure: In this type of fiber breakage, there occurs no significant plastic deformation. When internal stress in a fiber becomes equivalent to critical tensile stress, the brittle failure occurs.

ii. Ductile failure: In this type of fiber breakage, a significant plastic deformation or strain is observed and the fiber is stretched at one or more points resulting in subsequent increase of stress. When no constant value of the increasing strain is reached along the spinning line, fiber breakage occurs due to the ductile failure.

Both ductile and brittle failures are possible in the melt or after the solidification.

iii. Necking: Necking is a process which causes the instability of melt spinning line and thus leads to the brittle or ductile failure. It itself is not a type of fiber failure. Necking is a process, in which the fiber diameter decreases very sharply at a point along the spinning line and the thus caused instability leads to fiber breakage.

7.3.2 Spinning of PEAA and reference material (PLA)

PEAAs synthesized via melt polycondensation as discussed in Chapter 6 were used for the fiber spinning experiments. The process involved the following steps. The PEAA polymer powder was dried overnight in vacuum. It was fed then into the microcompounder at 180°C and the polymer was molten at this temperature at a screw speed of 100 rpm under nitrogen atmosphere. Afterwards, the screw speed was reduced to 5-10 rpm to spin fibers from a spinning die of 0.1mm in diameter. A shiny yellowish melt came out of the spinning die in case of both PEAA6 and PEAA8; it was then stretched under a defined winding or take-up speed to get fibers. In the case of PLA, the only
difference in the processing conditions was that the processing and spinning temperature was set to 220°C. Shiny white fibers were obtained for PLA.

7.3.3 Optimization of spinning parameters

For stable spinning, the take-up / winding speed of winding unit and screw speed of extruders were changed till almost uniform and continuous fiber spinning was achieved i.e. optimization of take-up speed was done. The optimum spinning conditions for PLA, PEAA6 and PEAA8 are listed below.

i. For PLA
   Spinning temperature: 220°C
   Winding speed: 5 m/min
   Torque: 150 Nmm

ii. For PEAA6 and PEAA8
    Spinning temperature: 180°C
    Winding speed: 5 m/min
    Torque: 110 Nmm

Instability i.e. fiber breakage or non-uniformity in fiber was observed when torque or winding speed was above or below the values given above.

7.3.4 Characterization results

The as spun and conditioned PEAA and PLA fibers were analyzed for their thickness, thermal as well as mechanical properties. The influence of PEAA composition and effect of conditioning on the properties of fibers are of main consideration.

7.3.4.1 Fiber diameter

The cross-sectional area of fibers was determined with FDAS 765 high resolution fiber dimensional measurement system (see section 5.3.3.1). The fiber diameter of unconditioned and conditioned PLA and PEAA fibers are given in Table 7.1.
Table 7.1: Diameter of unconditioned and conditioned PEAA6, PEAA8 and PLA fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fiber diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEAA6</td>
<td>123</td>
</tr>
<tr>
<td>PEAA6 (conditioned)</td>
<td>108</td>
</tr>
<tr>
<td>PEAA8</td>
<td>98</td>
</tr>
<tr>
<td>PEAA8 (conditioned)</td>
<td>79</td>
</tr>
<tr>
<td>PLA</td>
<td>85</td>
</tr>
<tr>
<td>PLA (conditioned)</td>
<td>73</td>
</tr>
</tbody>
</table>

7.3.4.2 Thermal analysis

The DSC curves recorded for the as spun and conditioned fibers along with the polymer powder are depicted in Figure 7.1 and 7.2 and the phase transition properties are summarized in Table 7.2. Only the first heating and cooling scans are shown. They reveal the presence of mainly one endotherm or exotherm peak. In the first heating cycle of PEAA6 and PEAA8 polymer powders as well as the corresponding fibers, the melting peak at ~155°C and ~150°C ($T_{m1}$) were observed for both PEAA6 and PEAA8.

Table 7.2: DSC data of PEAA6 and PEAA8 polymer powder and fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling run</th>
<th>First heating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{c1}$ [°C]</td>
<td>$\Delta H_{c1}$ [J/g]</td>
</tr>
<tr>
<td>PEAA6</td>
<td>89.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>PEAA6 stretched</td>
<td>90</td>
<td>-3</td>
</tr>
<tr>
<td>PEAA6 unstretched</td>
<td>89</td>
<td>-5</td>
</tr>
<tr>
<td>PEAA8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PEAA8 unstretched</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PEAA8 stretched</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
cold crystallization

It was observed from the first heating scan of PEAA6 shown in Figure 7.1a for PEAA6 that the melting enthalpy increases after conditioning, and the unconditioned fibers have the similar melting enthalpy as the powder sample.

However, in the case of PEAA8 (Figure 7.2a) having more methylene groups in the polymer backbone than PEAA6, cold crystallization was observed in all samples and associated enthalpy increases from the polymer powder to conditioned fibers. It was also noticed that melting point ($T_{mi}$) remains almost same but associated enthalpy ($\Delta H_{mi}$) decreases from the polymer powder to conditioned fibers.

(a)

(b)

**Figure 7.1:** DSC curves recorded (a) during the first heating scan and (b) during the cooling scan of PEAA6 powder and fibers at a heating and cooling rate of 10Kmin$^{-1}$.
Figure 7.2: DSC curves recorded (a) during the first heating scan and (b) during the cooling scan of PEAA8 powder and fibers at a heating and cooling rate of 10Kmin⁻¹.

As shown in Figure 7.1b and 7.2b a sharp exotherm peak was observed on the DSC curves recorded upon cooling all PEAA6 and PEAA8 samples. The crystallization temperature and enthalpy of the powder as well as the fiber samples are almost the same, indicating almost no polymer degradation during the melt spinning process.

7.3.4.3 Mechanical properties

As mentioned before, on conditioning the mechanical properties are enhanced and the extent of improvement depends on the conditions and extent of stretching/conditioning. Stretching results in molecular orientation in fibers and thus leads to better mechanical properties.
### Table 7.3: Mechanical properties overview of the PEAA6 and PEAA8 fibers along with reference fibers of PLA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic modulus (GPa)</th>
<th>Breaking stress (MPa)</th>
<th>Breaking strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEAA6</td>
<td>1.49 ± 0.22</td>
<td>237</td>
<td>815 ± 64.63</td>
</tr>
<tr>
<td>PEAA6 (conditioned)</td>
<td>1.44 ± 0.36</td>
<td>262</td>
<td>807 ± 125.4</td>
</tr>
<tr>
<td>PEAA8</td>
<td>0.81 ± 0.25</td>
<td>269</td>
<td>439 ± 17.83</td>
</tr>
<tr>
<td>PEAA8 (conditioned)</td>
<td>0.94 ± 0.52</td>
<td>251</td>
<td>89.7 ± 15.39</td>
</tr>
<tr>
<td>PLA</td>
<td>6.57 ± 3.48</td>
<td>215</td>
<td>5.24 ± 2.12</td>
</tr>
<tr>
<td>PLA (conditioned)</td>
<td>6.70 ± 1.38</td>
<td>458</td>
<td>61.5 ± 7.04</td>
</tr>
</tbody>
</table>

An overview of the mechanical properties of as spun and conditioned PEAA fibers as well as the reference PLA fibers are summarized in Table 7.3 and are illustrated in Figure 7.3, 7.4 and 7.5.

As illustrated in Figure 7.3, PEAA fibers show tensile-E-modulus in the range of 0.8 to 1.5 GPa depending on the chemical composition of PEAA. PLA fibers have comparatively higher tensile modulus of about 6.70 GPa. For PEAA8 unconditioned and conditioned fibers which have more (8) methylene groups compared to PEAA6, the tensile –E-modulus was lower, the reason may be the lower crystallinity as indicated by the DSC data. In the case of PEAA8 fibers, after conditioning the tensile-E-modulus increases slightly from 0.8 to 0.9 GPa. However in case of PEAA6, almost no change was observed on conditioning the fibers and reason may be the not appropriate conditions (room temperature) chosen for the conditioning.
Figure 7.3: Tensile modulus of PEAA6 and PEAA8 fibers along with reference fibers of PLA.

Figure 7.4: Tensile strength of PEAA6 and PEAA8 fibers along with reference fibers of PLA.

Figure 7.4 shows the graphical representation of the obtained breaking stress of PEAA fibers and reference materials. It was observed that the tensile strength of the PEAA6 and PEAA8 conditioned and unconditioned fibers were comparable and higher than the PLA unconditioned fibers. However, on conditioning the PLA fibers, the tensile strength manifolds approx. twice of that of PLA unconditioned fibers. PEAA8 unconditioned fibers showed higher tensile strength than PEAA6 unconditioned fibers. However, after
conditioning, the PEAA6 fibers showed slightly higher tensile strength than PEAA 8 fibers.

As illustrated from Figure 7.5, in contrast to tensile modulus and tensile strength, PEAA fibers showed significantly higher breaking strain compared to PLA fibers. It was also observed that PEAA6 unconditioned fibers showed breaking strain in range of around 800% compared to PEAA8 unconditioned fibers with breaking strain of about 440%. After conditioning, the breaking strain decreases significantly in PEAA8 fibers to around 90%, however, it remains almost the same after conditioning in case of PEAA6 fibers which further points in a direction to opt for better conditioning conditions for PEAA6 fibers. Pondering on the results, it could be suggested that for PEAA6 fibers conditioning should be done above room temperature in order to achieve better orientation of polymer chains leading to further improvement in its tensile properties. Interestingly, for PLA fibers, an increase in breaking strain was observed after the conditioning of the fibers.

![Figure 7.5: Breaking strain of PEAA6 and PEAA8 fibers along with reference fibers of PLA.](image)

In general, the influence of conditioning for these polymers remains a question. More experiments should be carried out to optimize the fiber properties for these new PEAA polymers.

### 7.4 Conclusion
In this chapter we have demonstrated that fibers can be successfully obtained through melt spinning of PEAA synthesized via melt polycondensation process. Spinning conditions were determined and optimized for stable and continuous production of PEAA fibers of different compositions. These melt spun fibers were then conditioned to achieve better molecular orientation in fibers leading to the enhancement of mechanical properties in conditioned fibers compared to unconditioned fibers.

7.5 References


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Chapter 8

Conclusion

Biodegradable polymers have been of great interest not only because they are environmental friendly but also due to their broad range of applications varying from packaging to biomedical field. A biodegradable polymer "aliphatic polyesteramide (PEA)" has the properties of aliphatic polyesters as well as polyamide, therefore carries good biodegradability of aliphatic polyesters and also good mechanical and processing properties of aliphatic polyamides.

In this thesis, aliphatic PEAs of different microstructures were prepared by a batch process via melt polycondensation and by reactive extrusion for the continuous synthesis on twin screw extruder. First, we synthesized a series of polyesteramides, specifically poly(ε-caprolactone-co-ε-caprolactam) copolymers, using a reactive extrusion process and the copolymers were produced by anionic ring opening polymerization of ε-caprolactam in the poly(ε-caprolactone) melt. The process was carried out in a twin-screw microcompounder. By means of gel-permeation chromatography, thermal analysis and wide-angle X-ray diffraction, the extruded products were proven to be polyesteramide copolymers with short polyamide fragments integrated into the polyester backbones. The relationship between the chemical structure, thermal properties and spinnability of these polymers was established.

After having achieved the successful synthesis of PEA in a small scale, the up-scaling was further established on the mini-extruder on a lab extruder. Calculations to determine the residence time of the polymer using a simulation program MOREX were performed in order to avoid time-consuming experiments with a „trial-and-error“ principle. It was shown that at a constant screw rotating rate, the screw configuration with a longer residence time resulted in an improved conversion and molecular weight of the products. We were successful in achieving the monomer conversion more than 95 % using a proper screw configuration. After optimization and configuration of the screw it was possible to transfer the synthesis of the mixture synthesized in the microcompounder to a laboratory extruder process, resulting in comparable analytical results.
Once the PEA was synthesized via reactive extrusion process, the challenge was to find proper and stable spinning conditions such as take-up speed, throughput, draw-down ratio, melting temperature and take-up point. This was important to study as these fibers could then be used for the fabrication of various textile structures for biomedical applications. The fibers were spun from PEA, synthesized via a reactive extrusion process based on the anionic polymerization of ε-caprolactam (CA) in the melt of commercially available polycaprolactone (PCL) on a microcompounder equipped with a melt spinning line. The effect of chemical composition of PEAs on spinning conditions as well as thermal and mechanical properties of the resulting filaments was analyzed.

In the next part of the thesis we synthesized high molecular weight poly(esteramideamides) (PEAAs) by melt polycondensation using tailor-made α,ω-amino alcohol and dicarboxylic acid methyl esters of different alkylene chain lengths under the catalysis of an organo-titanium catalyst. α,ω-Amino alcohol was prepared by ring opening of ε-caprolactam with tetramethylene diamine. A number of PEA copolymers were prepared. The chemical structure of the synthesized PEA was characterized by 1H-NMR spectroscopy, FTIR-spectroscopy and gel permeation chromatography. The thermal behavior of these new polymers was studied by thermal gravimetric analysis and differential scanning calorimetry. All polymers exhibited a melting point at around 150 °C and a decomposition temperature above 350 °C. The spinnability of the synthesized PEAAAs was also tested. Novel PEAA fibers were prepared a melt spinning process on a DSM Xplore melt spinning line. As a reference material, poly(L-lactide) fibers were also melt spun and characterized. All obtained fibers were conditioned under appropriate conditions. We then evaluated the mechanical and thermal properties of the spun and conditioned fibers to interpret the structure property relationship.

In summary, we were succesful in preparing a new class of degradable polymers the polyesteramides by the incorporation of ester and amide groups in a polymer backbone. Continuous synthesis of polyesteramides by reactive extrusion and synthesis of polyesteramideamides by melt polycondensation method were developed. PEAs and PEAA with controlled chemical structure were synthesized with better properties and high molecular weight and spun into fibers.
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**PUBLICATIONS**


**POSTERS AND TALKS**

- **Manisha Gupta**, Carmen I. Filipoi, Rostislav A. Vinokur, Veena Choudhary, Xiaomin Zhu, Martin Möller. COST MP0701, Naples, Italy. (Poster, 02/2011)
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- **Manisha Gupta**, Xiaomin Zhu, Martin Fijten, Helmut Keul, Martin Möller. 17th JCF-Frühjahrssymposium, Münster, Germany. (Oral Talk, 03/2015)