

Alexi Keskinen

# SUSTAINABILITY OF TIRE TEXTILE REINFORCEMENTS

Bachelor's Thesis  
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Reviewers:  
University Lecturer, Docent Terttu Hukka  
MSc Tech Joonas Pekkonen  
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# ABSTRACT

Aleksi Keskinen: Sustainability of Tire Textile Reinforcements  
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Tires are an important part of the everyday life of a human being. Without tires, the logistics and transportation industries would look a lot different than what we are used to seeing today. Modern pneumatic tires can be described as complex composite structures that consist of many different parts. One category of these parts are textile reinforcements. Reinforcement materials are used in tires because the rubber used in the outer parts of a tire isn't strong enough on its own to hold the structure together. Textile cords made from textile fibers are the most used textile reinforcements in tires.

Sustainability of different materials is a growing concern worldwide. It is no different for textile materials used in tires. The textile industry is known to consume vast amounts of energy, water, and chemicals every year in the manufacturing and processing of new textile materials. Additionally, many of the processes currently in use are polluting and have high greenhouse gas emissions.

In this thesis, the production and recycling processes of a few selected textile reinforcements are discussed in the form of a literature review. The materials are regenerated cellulosic fibers (rayon, lyocell), poly(ethylene terephthalate), polyamide 6, and polyamide 6,6. The aim is to form an understanding of what kind of different processes and methods are in use and what kind of alternatives are being developed today to be used in the near future.

For each of the materials studied, there were several methods that are being used and researched both in the manufacturing and recycling processes. For most of the materials, the older, more established processes are used especially in the manufacturing processes. Many of the newer, environmentally friendlier, sustainable methods are still limited by the expensiveness and lack of optimization and development. Although not many of these new processes are not in use yet, the trend seems to be that as soon as a suitable, environmentally sustainable, alternative method is found to be efficient enough economically, some manufacturers will try to commercialize it.

Keywords: textiles, sustainability, regenerated cellulosic fibers, poly(ethylene terephthalate), polyamide 6, polyamide 6,6

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# TIIVISTELMÄ

Alexi Keskinen: Renkaiden tekstiilivahvikkeiden ekologinen kestävyys  
Kandidaatintyö  
Tampereen yliopisto  
Teknis-luonnontieteellinen  
Kesäkuu 2022

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Renkaat ovat tärkeä osa ihmisten jokapäiväistä elämää. Ilman renkaita logistiikka- ja kuljetusalat näyttäisivät erilaisemmalta kuin mihin olemme tottuneet nykyisin. Nykyaikaisia ilmalla täytettäviä renkaita voidaan kuvata monimutkaisiksi komposiittirakenteiksi, jotka koostuvat monista eri osista. Tekstiilivahvikkeet ovat yksi näistä monista osista. Renkaissa käytetään vahvikemateriaaleja, koska renkaiden ulko-osissa käytettävä kumimateriaali ei ole itsessään tarpeeksi vahvaa pitämään rakennetta koossa. Eniten käytetyt tekstiilivahvikkeet ovat tekstiilikuiduista valmistettuja tekstiilikoordeja (engl. textile cords).

Eri materiaalien kestävyys (engl. sustainability) on kasvava huolenaihe maailmanlaajuisesti, myös renkaissa käytettävien tekstiilien osalta. Tekstiiliteollisuus kuluttaa vuosittain valtavan määrän energiaa, vettä ja kemikaaleja uusien tekstiilimateriaalien valmistamisessa ja jalostamisessa. Lisäksi monet tällä hetkellä käytössä olevista valmistusprosesseista ovat ympäristölle haitallisia saastuttavia prosesseja, jotka aiheuttavat suuria kasvihuonekaasupäästöjä.

Tässä työssä tarkastellaan muutamien valittujen tekstiilivahvikemateriaalien valmistus- ja kierrätysprosesseja kirjallisuuskatsauksen muodossa. Tarkasteltavat materiaalit ovat regeneroidut selluloosakuidut (rayon ja lyocell), poly(etyleenitereftalaatti), polyamidi 6 sekä polyamidi 6,6. Tavoitteena on muodostaa käsitys siitä, millaisia erilaisia prosesseja ja menetelmiä on käytössä sekä millaisia vaihtoehtoja ollaan kehittämässä käytettäväksi lähitulevaisuudessa.

Jokaista tutkittua materiaalia voidaan valmistaa ja kierrättää useilla erilaisilla menetelmillä. Myös useita uusia, vaihtoehtoisia menetelmiä ollaan kehittämässä näille materiaaleille. Useimpien materiaalien kohdalla käytössä olevat valmistus- ja kierrätysmenetelmät ovat vanhempia ja vakiintuneempia prosesseja. Tämä nähdään erityisesti valmistusmenetelmien kohdalla. Monia uudempia, ympäristöystävällisempiä ja kestävämpiä menetelmiä rajoittavat vielä toistaiseksi niiden kalleus sekä optimoinnin ja kehittämisen puute. Vaikka suurin osa näistä uusista menetelmistä ei vielä ole käytössä, tulevaisuuden trendi vaikuttaa olevan se, että heti kun sopiva, kustannustehokas ja ympäristöystävällinen kestävä menetelmä kehitetään, ainakin osa valmistajista yrittää kaupallistaa sen.

Avainsanat: tekstiilit, kestävyys, regeneroidut selluloosakuidut, poly(etyleenitereftalaatti), polyamidi 6, polyamidi 6,6

Tämän julkaisun alkuperäisyys on tarkastettu Turnitin OriginalityCheck –ohjelmalla.

# PREFACE

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Tampere, 3.6.2022

Aleksi Keskinen

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## LIST OF ABBREVIATIONS

AA	Adipic acid
BHET	Bis(2-hydroxyethyl)terephthalate
CRU	Constitutional repeating unit
DMT	Dimethyl terephthalate
EG	Ethylene glycol
GHG	Greenhouse gas
HMDA	Hexamethylene diamine
MA	Muconic acid
NMMO	<i>N</i> -methyl morpholine- <i>N</i> -oxide
PA 6	Polyamide 6
PA 66	Polyamide 6,6
PEN	Poly(ethylene naphthalate)
PET	Poly(ethylene terephthalate)
rPET	Recycled poly(ethylene terephthalate)
TPA	Terephthalic acid
vPET	Virgin poly(ethylene terephthalate)

# 1. INTRODUCTION

The wheel is considered to be one of the most important inventions in the human history. Wheels today are used in many applications. Tires, the modern wheels, are especially used in the logistics and transportation industries that affect the everyday life of a human being. [1, p. 653]

Textiles are important in the manufacturing of a tire. They can be used to strengthen the tire's structure and without textile reinforcements, the structure will either be too heavy for practical use or too weak to carry the loads they are subjected to. The sustainability of these textiles is a growing concern as the textile industry consumes an enormous amount of energy, water, and chemicals in the manufacturing and processing of new textiles every year [2, p. 2]

In this thesis the sustainability of textile reinforcement materials that are being used in tires are studied in the form of a literature survey. The aim is to form an understanding of what kind of textile materials are used, how they are produced and how they can be recycled.

Chapter 2 will present the basics of modern tires and act as a brief introduction to what textile reinforcements are, what materials are used and how they are made. In chapter 3, a deeper dive is taken into what sustainability means in the textile industry, what are sustainable strategies of the future, and how the raw materials used in textiles are produced. Chapter 3 also discusses new methods of production and how the different materials can be recycled to be used as new materials as well as what the advantages and disadvantages of the different methods and processes currently are.

## 2. TIRES

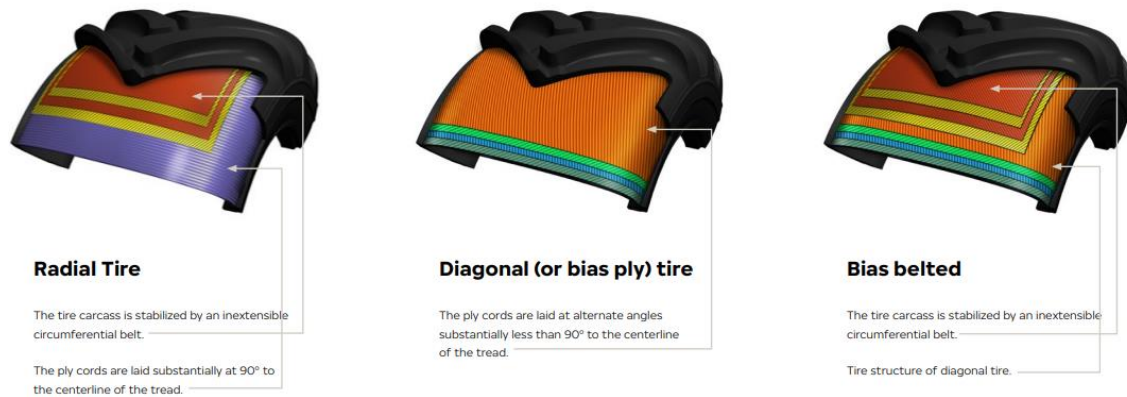
The most familiar function of a wheel is to be able to move objects around with them along with the ease of transportation that they allow [3, p.155] In fact, the only components to transfer forces between the road and the vehicle are tires [4, p. 1]. As such, tires are one of the most important parts of any vehicle. The modern wheels, pneumatic tires, were first developed for use in tricycles in the 1880s. Since then, pneumatic tires have been engineered to fulfill a fundamental set of functions that differ a lot from the first developed tires. [1, p. 653] Ikeda et al. [3, p. 164] mention that there are four basic functions of tires: tires support the vehicle's load, transmit braking and acceleration forces to the road, maintain and change the vehicle direction, and absorb shocks from the road surface. Rodgers and Waddell [1, p. 654] give a more detailed list, in which, in addition to Ikeda et al.'s list, they mention that tires also need to provide cornering force and dimensional stability, resist abrasion, have a low rolling resistance, and be durable within the expected lifespan.

### 2.1 Different types of tires

There are three types of pneumatic tires being manufactured, as shown in figure 2.1. The first two tire types are mainly used in heavy truck and trailer applications. The first type of tires is called diagonal bias tire. The name diagonal bias comes from body ply cords that are laid at angles less than 90 degrees extending from bead to bead. Diagonal tires are easy to manufacture but tread motion and shearing between the body plies results in undesired characteristics such as heat buildup and poor wear resistance. [5, p. 3]

The second type of pneumatic tires are called belted bias tires. As the name suggests, they are bias tires with added layers of belts on top of the body plies. Compared to plain bias tires, the belted bias tires are much stiffer in the tread area. This improves the wear and handling of the tire. Even though the added belts improve the stiffness, belted bias tires suffer from the same disadvantage as diagonal bias tires do in that body ply shear causes heat generation. Additionally manufacturing and materials costs are higher for belted bias tires compared to diagonal bias tires. [5, p. 3–4]





**Figure 2.1** Three types of modern pneumatic tires in use today: radial, diagonal bias, and bias tires. The pictured tires are heavy tires used, for example, in heavy transportation vehicles and tractors. [6]

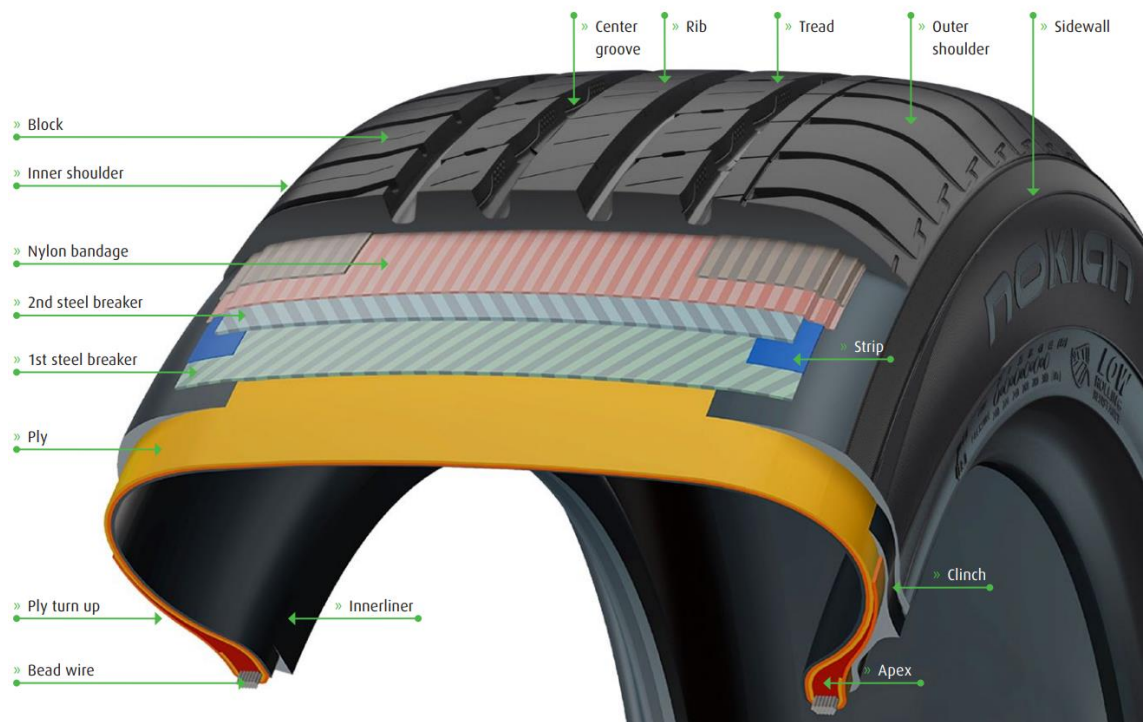
The third and final type of pneumatic tires are called radial tires. The body ply cords of radial tires are laid radially from bead to bead, and they are perpendicular to the beads. Much like belted bias tires, the radial tires also have belts on top of the body plies to help strengthen the structure. Compared to the variants of bias tires, the radial tires generate less heat due to shearing and have a lower rolling resistance. The modern passenger vehicle tires feature variations of radial tires because of their favorable properties compared to the bias tires even though their manufacturing is more complex, and the used materials cost more. [5, p. 4]

## 2.2 The structure

The modern pneumatic tire can be described as a complex composite structure [1, p. 694]. A pneumatic tire is composed of many layers of different materials which include, but are not limited to, natural and synthetic rubber, steel, textiles, adhesives, and other reinforcing materials and chemicals [3, p. 175]. As can be seen in figure 2.2, a tire is a sum of many different parts working together.

The outer layer of tire is called tread. It is the part of tire that contacts the road. Therefore, it needs to provide the necessary traction and wet skid for driving, braking, and cornering. [1, p. 657] The tread's pattern is molded into the tire during the vulcanization or curing process [5, p. 9]. The pattern is designed to be as silent as possible on different surfaces while generating minimal heat buildup [1, p. 657]. The pattern can also help channel water out beneath the tire and provide uniform wear to extend the lifespan of the tire [5, p. 9]. To be able to provide all these features, tread components consist of blends of rubber with various strengthening compounds [1, p. 657].

The outer layer on the sides of a tire is called sidewall. Sidewall compounds consist of rubber blends similar to the tread. [1, p. 656] Sidewall's purpose in tire is to protect the inner carcass layers from external damage such as abrasion, impact, and flex fatigue. To improve handling or stability, lower sidewall reinforcements have been added to some tires. The sidewalls can feature decorative treatments that can be purely visual but can also contain information about the tire itself. [5, p. 8]



**Figure 2.2** Structure and cross-section of a high-performance radial tire. [7]

The belts are layers made of steel or textile. The main function of the belts is to restrict the expansion of the carcass plies, provide impact resistance, and give stiffness to the belt package. This allows for improved handling and wear performance to the tire while also protecting the inner layers of plies from damage and road hazards. [1, p. 658][5, p. 7][8, p. 81]

The carcass plies, also known as body plies, are the main part that supports the tension forces generated by tire air pressure and give a tire its shape. They also provide for sidewall impact resistance. The carcass plies are often made of polyester cords which provide them high strength and dimensional stability. The number of carcass plies varies in different tires and normally there are only one or two in any given tire. [5, p. 7]

The beads are made from single steel wires. A single wire is wrapped around the tire multiple times to form the bead. The wires are coated with bronze or brass to give them a better adhesion with rubber. The main function of beads is to anchor the inflated tire to

the wheel rim. [5, p. 7] Additionally, beads provide load distortion resistance and rim slippage resistance [8, p. 86].

The cap plies are commonly made of polyamides, but aramids are used in some special need tires [8, p. 78–79]. The primary function of a cap ply is to further strengthen the belts and help restrict expansion from centrifugal forces in high speeds [5, p. 10].

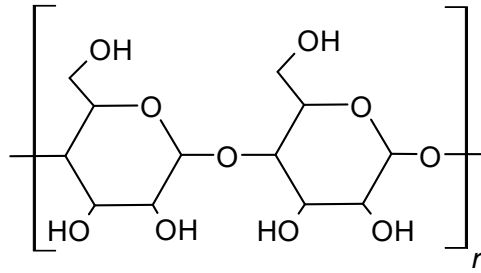
## **2.3 Textile reinforcements**

Reinforcement materials are used in tires because rubber that is used in the outer parts of tires isn't strong enough on its own to support the whole structure. That is why various materials are being used in tire reinforcement. One group of reinforcement materials are textiles. The main textile reinforcements used in tires are textile cords. Their purpose is to provide strength and stability to the tread and sidewalls. Additionally, textile reinforcements help contain air pressure inside the tire. [5, p. 84] Textile cords are used in the carcass, belt, and cap plies. Textile materials usually make up around 3% of a tire's weight [3, p. 175]. The textile cords that are used in tires are all made from organic fibers. While cotton is still used in some tires, it has mostly been replaced by synthetic fibers. The synthetic fibers that are currently used the most are rayon, polyamides, polyester, and aramids. [8, p. 11] The basics of these synthetic fiber materials will be discussed in the following subchapter.

### **2.3.1 Fibers**

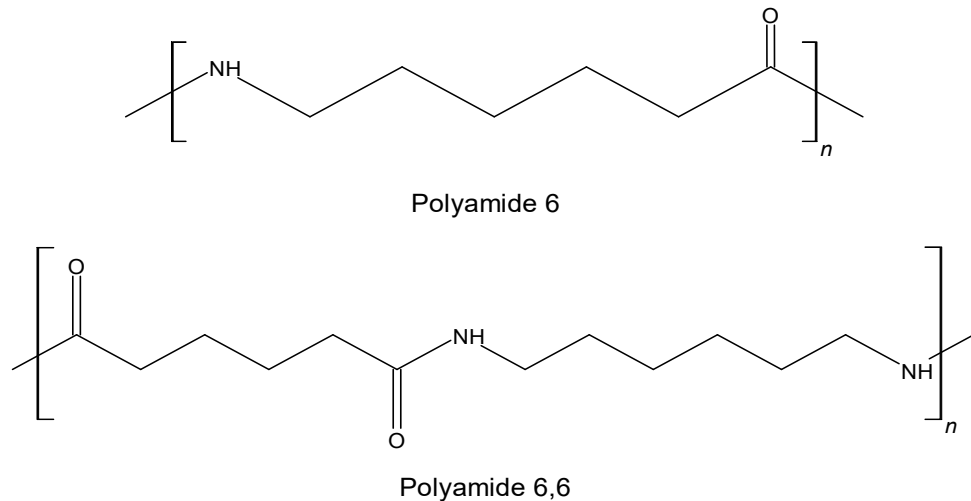
A fiber is defined as a material that's at least 100 times longer than its width and it has high strength in the fiber axis direction [5, p. 83]. Polymer materials are a good example of this kind of material, and it is no surprise that all the textile fibers mentioned above are polymers.

Rayon is the first synthetic fiber material that was used for tires [1, p. 677]. Rayon is produced by treating cellulose. As seen in figure 2.3, rayon is a polymer consisting of regenerated cellulose molecules. Rayon has been a good choice for passenger tires since it has low shrink, high modulus, and good rubber adhesion properties [5, p. 87]. It is also heat resistant up to around 150 °C but it loses strength when exposed to high heat for long periods of time. There are also some special types of rayon that have been developed for use in tires. One example is Lyocell, which is reported to have good physical properties even in high temperatures. [8, p. 14–15]



**Figure 2.3** A single constitutional repeating unit of a cellulose chain.

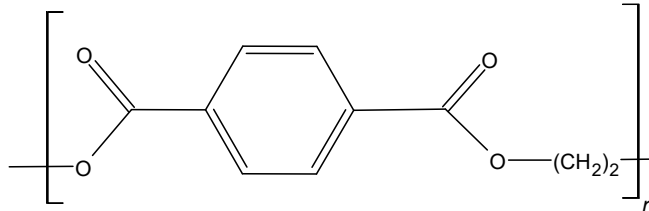
Polyamides, also known as their trade name Nylon, are polymers which feature the amide group (CO-NH) in the main polymer chain [1, p. 677]. The two polyamides that are used as textiles in tires are called polyamide 6 (PA 6) and polyamide 6,6 (PA 66). Their constitutional repeating units (CRU) are presented in figure 2.4. PA 6 and PA 66 both have quite similar properties but producing PA 6 is cheaper. The drawback of PA 6 compared to PA 66 is its higher sensitivity to moisture, which makes it more vulnerable to losing its strength in higher temperatures. [5, p. 87] The linear nature of PA 6 and PA 66's structures make them ideal to be used as fibers for textiles in tires. Polyamides are heat resistant up to 180 °C [8, p. 17].



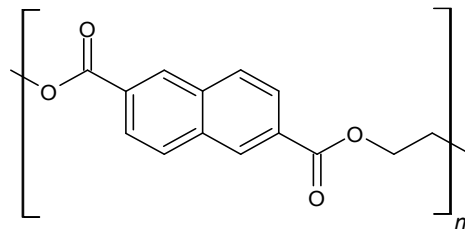
**Figure 2.4** A single constitutional repeating unit of single polyamide 6 and polyamide 6,6 chains.

The polyester poly(ethylene terephthalate) (PET) is the most used textile in passenger and light truck tires' carcass material. The CRU of PET can be seen in figure 2.5. PET is relatively inexpensive to manufacture, and it has good enough properties in terms of cost compared to other options. PET is, however, not used in high demanding applications as it quickly loses its properties in temperatures higher than 120 °C. [5, p. 80, 86–87] A

relatively new fiber, called poly(ethylene naphthalate) (PEN), is also used in some applications that require its specific properties. [8, p. 22] The CRU of PEN is similar to PET, which can be seen in figure 2.6. PEN has a higher glass transition temperature than PET does, and it also has lower shrinkage and higher modulus. PEN is about 2.5 times more expensive to produce than PET which is a disadvantage when considering the use of PEN in the more affordable passenger car tires. [5, p. 88]

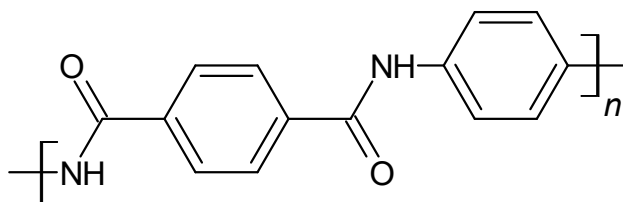


**Figure 2.5** A single constitutional repeating unit of a single poly(ethylene terephthalate) chain.



**Figure 2.6** A single constitutional repeating unit of a single poly(ethylene naphthalate) chain.

Aramids are aromatic polyamides. The most used aramid is called poly(*p*-phenylene terephthalamide) and its CRU is presented in figure 2.7. When comparing aramids to polyamides, the key difference is that aramids aren't very sensitive to moisture.



**Figure 2.7** A single constitutional repeating unit of a single poly(*p*-phenylene terephthalamide) chain, better known as Kevlar® or Twaron®.

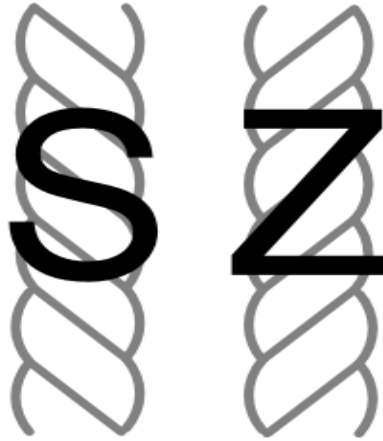
Poly(*p*-phenylene terephthalamide) also has very high heat resistance capability and it can perform well even in temperatures as high as 250 °C. [8, p. 24] Aramids suffer from the same fate as PEN does however, as it is much more expensive to produce them than PET for example. That is why aramids are mainly seen in special needs tires such as tires used in racing cars. [5, p. 87]

### 2.3.2 Yarns and cords

The fibers cannot be used as themselves in tires as they don't have the required length to be used as a reinforcement. That is why the fiber filaments are made into yarns. Yarns are a lightly twisted assembly of filaments. Generally, there are two ways of manufacturing yarns: melt spinning and solution spinning. In melt spinning, the polymer filaments are melted and pumped through an extruder to give it the characteristic yarn shape. After extrusion, the polymer is then cooled into a semi-molten state above the glass transition temperature and stretched, which elongates the filaments to be several times longer than the original length. This increases the filaments' modulus and strength but reduces the breaking elongation at the same time. The filaments are then gathered and lightly twisted to form them into yarns. Melt spinning is used in the manufacturing process of polyesters and polyamides. [5, p. 88–89] [8, p. 15–21]

Solution spinning is used in the manufacturing process of rayon and aramids because their melting temperatures are much higher than the temperatures used in melt spinning. That is why they need to be dissolved into a solution so they can be extruded like polyester and polyamides in melt spinning. After extruding the concentrated solution and either neutralizing the solvent or drying it out, the filaments aren't stretched like in melt spinning since their wanted properties are already on a desired level. Instead, the filaments are given a light twist treatment right after drying them to form them into yarns. [5, p. 89] [8, p. 12-13, 24]

After spinning the filaments into yarns, the yarns can then be twisted into cords. Cords consist of two or more yarns that are twisted together in a helix-like manner. The cords are usually twisted in the opposite direction that the yarns were twisted in. This is called balanced twisting. [1, p. 680] Tire cords are being twisted because it improves the yarns performance as a reinforcement. Twisting gives cords durability and strength while preventing the filaments from breaking as easily as without a twist. Twisting also improves fatigue resistance and makes it easier to weave the cords into fabric. [8, p. 28] As seen in figure 2.8, the twist can be done in two different directions: S and Z. S-twist is when the yarns are twisted counter-clockwise to the left, and Z-twist is when the yarns are twisted clockwise to the right.



**Figure 2.8** Two differently twisted yarns or cords demonstrating the S and Z twists. [9]

When the yarns have been twisted into cords, they can be woven into fabric. Up to 1500 cords are woven together into a sheet of fabric. After this the fabric can be treated in numerous different ways depending on the material of the fabric and the intended usage of it. [5, p. 91]

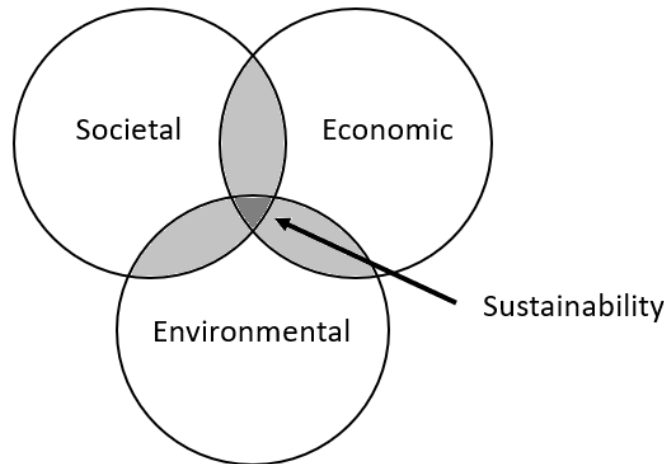
### **3. SUSTAINABILITY OF TEXTILES**

The textile industry is one of the oldest and largest industries worldwide, and as such, it is responsible for a lot of pollution and environmental damage [2, p. 343]. That is why sustainability is a popular topic when it comes to textiles. Sustainability as a whole is a broad topic and as a concept, sustainability is most probably familiar to most. The goal of sustainable production is to preserve the natural resources and diversity of Earth by not using more resources than can be reproduced via renewable resources. Non-renewable resources should only be used to the extent that they are needed. [10, p. 3] In the context of textiles production, these resources not only include the raw materials used in fibers but also water, chemical and energy consumption in the manufacturing processes. The textile materials discussed later in this chapter will be regenerated cellulosic fibers, PET, PA 6, and PA 66.

#### **3.1 Introduction to the sustainability of textiles**

Sustainability can be effectively divided into three fields that define sustainability as a whole: societal, economic, and environmental. Societal sustainability is about the people effecting the manufacturing process of a product. Happy workers with good working conditions, wages and benefits help keep companies' employee turnover rate low and lead to more sustainable production in terms of societal impact. The impact of economic sustainability can be best imagined as the creation of new jobs that leads to more consumer buying power in other fields. Economic sustainability also aims to be more efficient in terms of material and energy consumption that helps lower the cost of the manufactured products. Environmental sustainability is all about the efficient usage of natural resources and how to reduce the emissions of greenhouse gases (GHG) like carbon dioxide in the manufacturing processes. All the fields are related to each other as illustrated in figure 3.1 and each of the fields can have impacts to the other fields in terms of materials, processes, and systems. [11, p. 1–5] While all these fields are important in the bigger picture of sustainability, the focus of this thesis will be in the economic and environmental fields of sustainability. Using renewable materials and recycling non-renewable materials are examples of processes that can be slotted in both categories. Especially recycling of used materials is becoming more and more common every day.





**Figure 3.1** *Three fields of sustainability. Adapted from [11, p. 2].*

A good example of a commonly used recycled material is PET, which is used especially in clothing but also in many other applications like plastic bottles and the carcass plies of tires. Methods of recycling polymer materials can be divided into primary, secondary, tertiary, and quaternary recycling. Primary recycling is about reusing products in their original structure while quaternary recycling has its focus on reusing the energy contained in the materials. Secondary recycling is also known as mechanical recycling. Mechanical recycling means that the materials are reprocessed physically. This can include washing, shredding, and cutting the materials into smaller pieces so that they can be reused as new raw material. However, mechanical recycling can only be used in the recycling process of thermoplastic polymers since they can be melted and reshaped into new products. Tertiary recycling, better known as chemical recycling, is about depolymerizing the waste materials into smaller parts of the polymer chain, potentially all the way to monomers. Chemical recycling is the most advanced of the recycling techniques and there are several different methods of recycling various polymers. The name of chemical recycling comes from the fact that the change in the polymer occurs in its chemical structure. [12, p. 59–60] Recycling methods vary from material to material but most of the methods belong to either mechanical or chemical recycling methods. As such the recycling methods discussed later in the thesis will mostly be about mechanical and chemical recycling.

### **3.2 Future strategies of sustainable textile production**

The future long-term trends of sustainable textile production seem to be divided in four different groups of strategies: replacement, reduction, transformation, and reorganization. Strategies of replacement are all about finding new solutions to the problems of the

existing processes and methods. Understanding of the characteristics of different materials and what is good or bad about them will be vital in the future. To be able to phase out materials of concern and potentially replace them with safe, recycled materials that are designed for disassembly and being recycled again will be valuable considering the sustainability of the future. [13, p. 58]

Reduction strategies focus on the manufacturing processes' GHG emissions and pollution as well as chemical and water consumption without forgetting the problematic high energy consumptions. Lowering the emissions and pollution will be important considering the climate change that we are already experiencing today. Also, being able to consume less energy, water, and chemicals in the recycling and manufacturing processes will be beneficial environmentally as well as economically. [13, p. 58]

The transformation strategies are about the recycling of materials and how to efficiently further use the products obtained from the various methods of recycling. Finding and commercializing appropriate recycling technologies is an important step to further improve the manufacturing of much used materials. [13, p. 58]

The strategies of reorganization overlap the transformation strategies in the context of recycling, namely closed loop recycling, that means recycling a product into other new products or a new version of the old product. Other reorganization strategies include the usage of renewable sources of materials and the responsible way of handling existing resources. [13, p. 58]

While the strategies are important, the biggest responsibility in the future is on the hands of organizations and corporations to implement them. The supply chains and entire production processes need to be traceable and transparent to ensure no needless waste and emissions are produced. Important policies that should be followed include the recycling of waste raw materials and the nonhazardous solid waste as well as the recovery of chemicals used in the processes. Filtration and separation techniques also need to be improved to keep the chemicals from ending up in the environment. [2, p. 14–15]

### **3.3 Regenerated cellulosic fibers**

Cellulose is one of the most abundant polymeric materials available on Earth. Additionally, cellulose is a biodegradable, biocompatible and renewable, natural resource. These factors make cellulosic fibers an attractive material not only in the textiles industry but many other industries as well. [14] The regenerated cellulosic fibers that are used in tires are mainly viscose rayon and lyocell. There are two types of viscose rayon that are being manufactured: textile viscose rayon and high tenacity viscose rayon. Out of these two,

the high tenacity viscose rayon is used in the cords for tires. [15, p. 264] Lyocell is a third generation regenerated cellulosic fiber that has been developed quite recently compared to rayon [16, p. 65]. Some of the good attributes that lyocell has compared to rayon are a low chemical usage in the production process and almost all the water used in it can be recycled [2, p. 179].

### **3.3.1 Cellulose pulping**

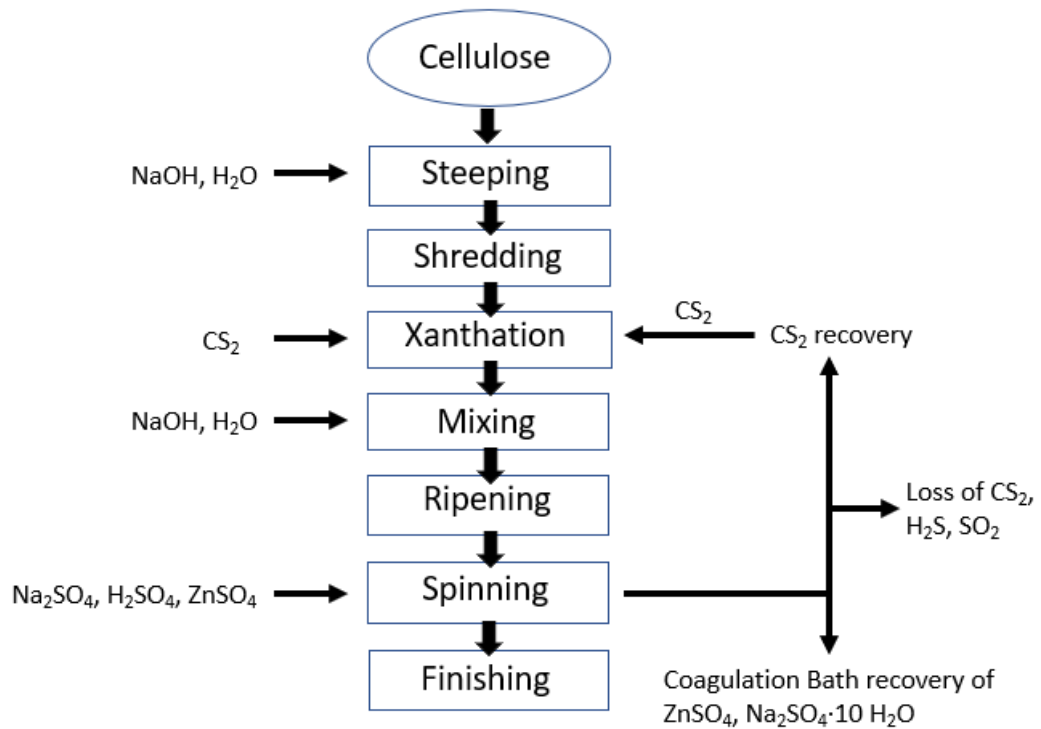
Regenerated cellulosic fibers are solvent spun from cellulose pulp [2, p. 171]. Pulp is processed cellulosic raw material that is mostly made from wood. There are various classifications of pulp but in fiber production the most used pulps originate from hardwood and softwood. This is because cellulose cannot be melted, so to produce fibers from cellulose, it must be able to be dissolved at least in some form before it can be spun. Before the raw wood can be pulped though, it needs to be cut into smaller pieces. [17, p. 33–34]

The two dominant ways of pulping are chemical and mechanical pulping, from which the former is the most common and efficient. That is why mechanical pulping is only used in the paper and board industries these days. In chemical pulping, all the non-cellulose matter is dissolved from the raw wood using many different chemicals. The most used chemical pulping method is called the Kraft process, which uses pre-hydrolysis alongside a sulfate process. Pure sulfate process is the other used chemical pulping method. The problem with chemical pulping processes is the usage of chemicals. Even though the modern processes can recycle most of the chemicals used, some of them still end up in the surrounding environment and are able to pollute the ground and water. The new pulping methods that are being developed are trying to lower the usage of chemicals or replace them. Some concepts propose the usage of enzymes and fungi to replace chemicals. [17, p. 34–36]

### **3.3.2 Viscose rayon manufacture**

Along the years, there have been several different methods of manufacturing viscose rayon. These days, the most common and versatile method for manufacturing rayon is known as the viscose method, which is shown in figure 3.2. [2, p. 175] As can be seen, the process involves lots of different chemicals in the many stages of the process. Especially the chemicals containing sulfur are extremely toxic and can cause many problems if they are not controlled and neutralized before letting them out into the environment [17, p. 42]. If the untreated chemicals were to be released in the surrounding nature, the

whole flora and fauna would perish. Untreated chemical leaks are reported to be the cause of massive fish deaths. [15, p. 270] The toxicity of the used chemicals is mainly seen as a problem in the still developing countries since the concern of environment isn't always put first there instead of economical questions [17, p. 42]. Viscose production process also uses a lot of energy, and it has a high demand of labor [14].



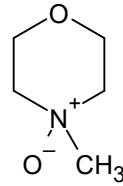
**Figure 3.2** Viscose process which is the most used process to manufacture viscose rayon. Adapted from [2, p. 176] and [17, p. 41].

The wastes of viscose process can be treated to recover about 70% of the used chemicals effectively [17, p. 42]. For example, caustic soda can be recovered from the alkaline wastes and zinc sulfate and sodium sulfate can be recovered from the acidic wastes. These wastes can be treated by equalization and neutralization processes after which they are coagulated. The coagulated effluent can then be clarified. After clarification, there are several different secondary treatment methods that can be used. The most effective treatment method is called the aerated lagoon. [15, p. 270–271]

### 3.3.3 Lyocell process

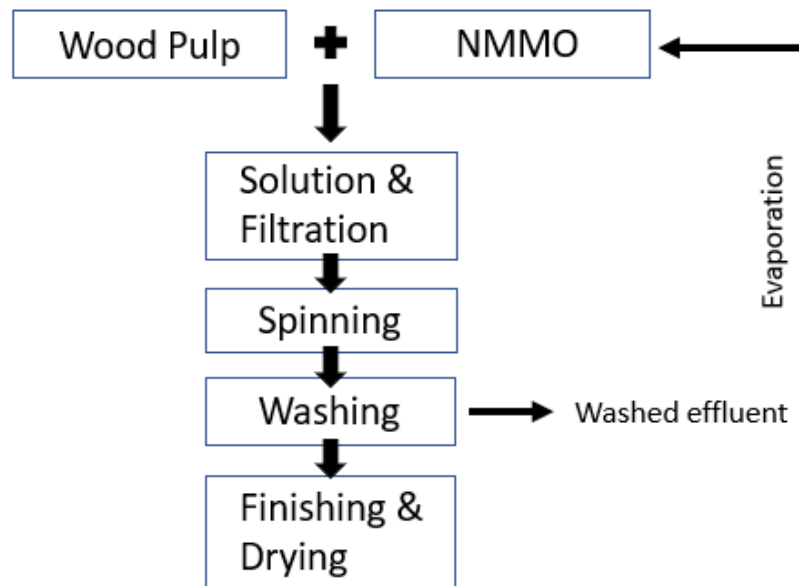
Compared to the viscose process, the lyocell process requires fewer steps and only few chemicals, out of which *N*-methyl morpholine-*N*-oxide (NMMO) is the most important. NMMO, which structure is shown in figure 3.3, is an easily regenerated organic polar solvent that dissolves cellulose with a higher capacity than other known solvents. As a

polar solvent, NMMO forms hydrogen bonds with the hydroxyl groups in cellulose. [17, p. 42] However, certain mechanisms of the dissolution and swelling process are still not well understood due to them being extremely complex [14].



**Figure 3.3** Structure of *N*-methyl morpholine *N*-oxide.

NMMO is used as an aqueous solution in the lyocell process, which is shown in figure 3.4. Lyocell is a comparatively simple process and what makes it a sustainable process is that more than 99% of the used solvents including NMMO can be recycled. Also, possible small NMMO emissions can be taken care of in the wastewater treatment plants so it can be considered a nontoxic solvent as well. [17, p. 43] Some of the drawbacks of NMMO are that it is an oxidant and somewhat unstable as a molecule [18, p. 54]. Also, pretreating high lignin content wood with recycled NMMO was reported to not be as effective after five cycles of use [19, p. 41]. The other chemicals used in the process also do not pose a threat to the environment [2, p. 179–182].

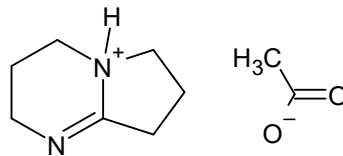


**Figure 3.4** Closed loop manufacturing cycle of lyocell fiber. Adapted from [2, p. 180] and [17, p. 43].

Until this point, the manufacturing of lyocell can be considered a sustainable and eco-friendly process. The problematic parts of lyocell manufacture are turning the fibers into

fabrics and dyeing the fabric, where the use of some toxic and hazardous chemicals is needed. Research to replace or recycle these chemicals is on the way to make this process close to being fully sustainable in the future. [2, p. 181] Another good thing about lyocell process is that there is flexibility in what kind of cellulose can be used. Waste cotton, rayon and paper can be recycled to be used as raw materials in the process. [2, p. 182]

There is also a relatively new lyocell based process being developed. This process utilizes ionic liquids. Ionic liquids can be used to dissolve cellulose like NMMO does but also in the creation of media to functionalize cellulose in other applications. [14] One of the ionic liquid based lyocell fibers is called Ioncell-F. Ioncell-F is produced using 1,5-diaza-bicyclo[4.3.0]non-5-enium acetate which is a superbase-based ionic liquid and its structure is presented in figure 3.5. Ioncell-F is reported to be the first ionic liquid based lyocell fiber that has similar properties to traditional lyocell fibers. The drawback of Ioncell-F production at the moment is that recycling of the solvent used isn't as efficient as recycling NMMO is, so the process isn't as sustainable as the traditional processes are. [18, p. 54]



**Figure 3.5** Chemical structure of 1,5-diaza-bicyclo[4.3.0]non-5-enium acetate.

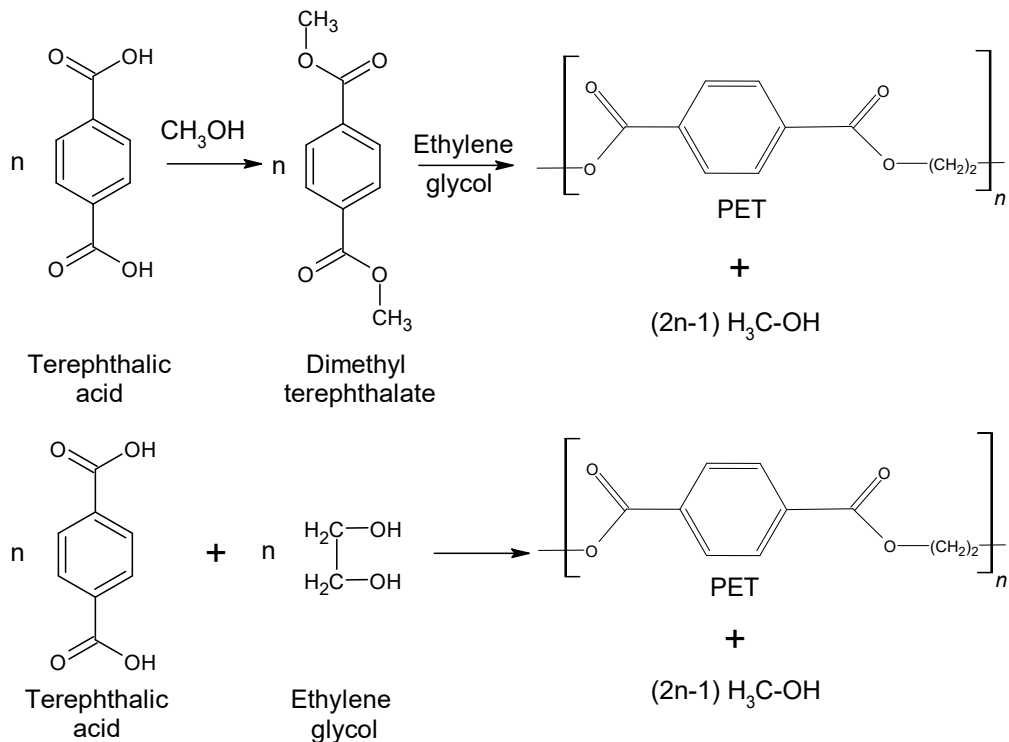
Overall, the lyocell process utilizing NMMO is an environmentally friendlier process than the viscose process. The direct dissolution of cellulose in the lyocell process is a simpler process and it reduces the use of chemicals over ten times compared to the viscose process. Also, NMMO recycling is easier since no byproducts are formed. The disadvantages holding lyocell process back are the high cost of NMMO and high energy usage since the cellulose dissolution is done at high temperatures (120 °C). [20]

### 3.4 Poly(ethylene terephthalate)

PET is a synthetic thermoplastic polyester. It is one of the most used plastic materials in the world. The majority, around 60%–70%, of PET production is fiber production in the textiles industry. PET bottles' share is about 30% of the production. Most of the PET is produced as virgin PET (vPET) from raw oil and unfortunately only a small amount of it is recycled worldwide. [2, p. 228]

### 3.4.1 Poly(ethylene terephthalate) production

When polymerizing PET for textile applications, there are two main methods that are being used. First of them is a transesterification reaction via dimethyl terephthalate (DMT) and the second one is the direct esterification of terephthalic acid (TPA) with ethylene glycol (EG). [8] Due to purification reasons, the transesterification reaction is the preferred process in PET production [21]. The reactions are shown in figure 3.6.



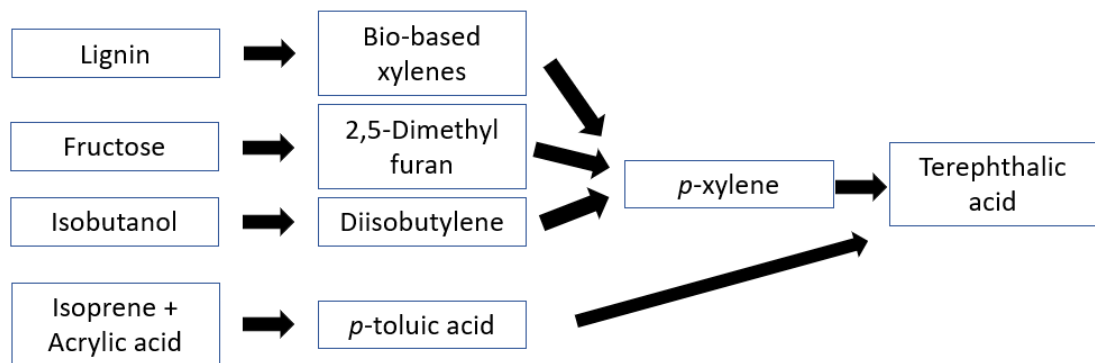
**Figure 3.6** PET polymerization via transesterification (above) and direct esterification (below). Adapted from [8] and [21].

EG is currently produced by the ethylene oxide method, which is done in two steps. The first step can be carried out by two different ways: the direct oxidation process or the chlorine process. In the direct oxidation process ethylene is directly oxidized to ethylene oxide in temperatures around  $250\text{ }^\circ\text{C}$  in the presence of a metal catalyst like silver oxide. In the chlorine process ethylene is transformed into ethylene chlorohydrin by a reaction with hypochlorous acid. Then the ethylene chlorohydrin with calcium hydroxide produces ethylene oxide. Ethylene oxide can then be hydrated into EG by a hydrogenation reaction with water. The reaction temperature is usually in the range of  $60\text{ }^\circ\text{C}$  to  $100\text{ }^\circ\text{C}$  and it is aided with acid catalysts. [22, p. 68–69]

The primary raw materials in the manufacture of TPA are benzene, toluene, and *p*-xylene. There are many methods that are used to convert them into TPA. One example is

the one-step oxidation of *p*-xylene. *p*-xylene is catalytically oxidated into TPA and can then undergo esterification reaction with methanol to produce DMT. [22, p. 69–74]

The EG used in PET production can be produced from plant sources such as sugarcane, corn, or soy by fermentation. Currently, biobased PET can be up to 30% made from natural sources and the remaining 70% from petroleum sources. [11, p. 111] TPA is currently still produced from petrochemicals like *p*-xylene, but there are three methods to produce bio-based *p*-xylene that have been developed. Their routes are shown in figure 3.7.



**Figure 3.7** Routes to produce bio-based terephthalic acid. Adapted from [2, p. 200].

The methods are pyrolysis of biomass, yeast fermentation of sugars into isobutanol, and chemical conversion of carbohydrates. Another method to produce bio-based TPA is by a cyclo-addition reaction between acrylic acid and isoprene. [2, p. 199]

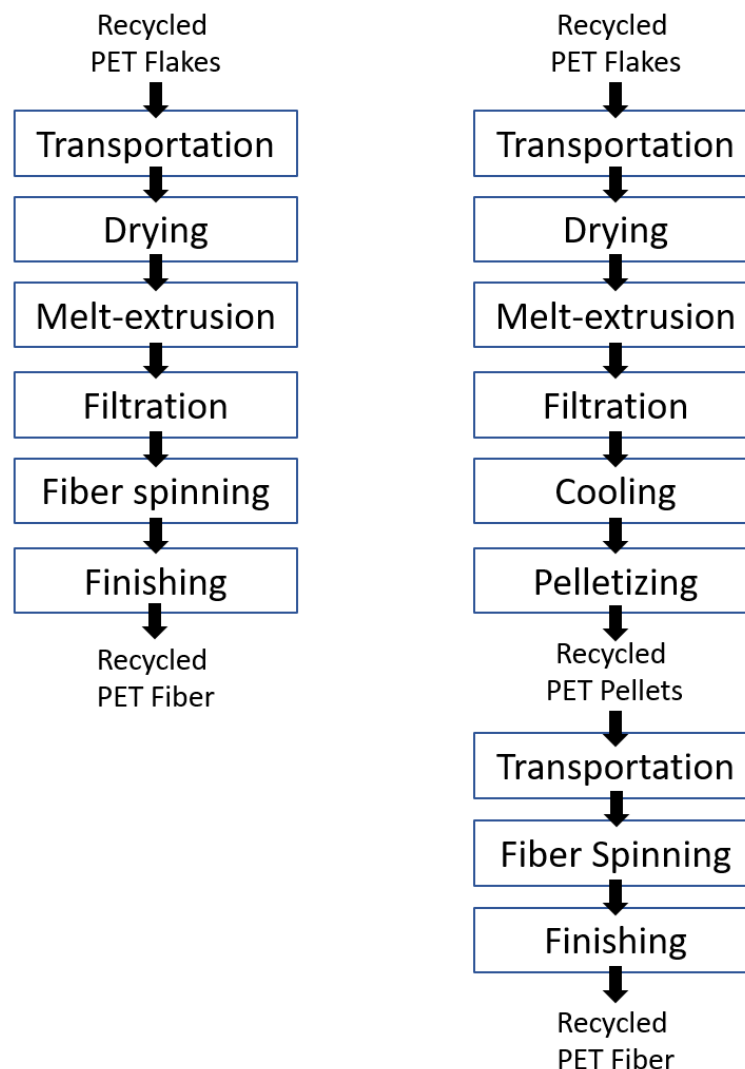
### 3.4.2 Mechanical recycling of poly(ethylene terephthalate)

When talking about the sustainability of PET, it is impossible to not mention recycling. PET is one of the most recycled materials around the world. The most familiar recycled PET product is the plastic bottle. The recycling processes of PET are constantly being developed to be more efficient. There are two reasons why recycled PET (rPET) can be considered sustainable: the energy requirement to produce it is lower than for vPET and it keeps plastic bottles and other PET waste from ending up in landfills [2, p. 228]. Recycled PET fibers are produced mainly by two routes: mechanical and chemical recycling processes.

In mechanical recycling, the materials are reused into new raw materials without changing the chemical structure of the original materials [13, p. 35]. The mechanical recycling of PET process generally follows the same formula that is used for other plastics, and it



is presented in figure 3.8. The process usually starts by cleaning the waste material by washing. [12, p. 132] The efficiency of the cleaning process and the purity of the waste are directly related to the quality of the product [16, p. 12]. The cleansed material is dried and then physically chopped into smaller flakes. The smaller flakes can then be color treated if needed. [12, p. 132] The conversion to fibers can currently be done in two ways in mechanical recycling processes: the flakes can be directly extruded into fibers, or the flakes can be converted into chips or pellets and then extruded into fibers. Out of these, the latter is the more common process, and it is considered a semi-mechanical process because of the pelletizing step. The material efficiency in mechanical recycling processes is usually over 90% and even as high as 99% efficiency can be reached in the directly extruded fibers. [23]



**Figure 3.8** Mechanical recycling of PET by directly extruding recycled flakes into fibers (left) and semi-mechanical recycling of PET by converting recycled flakes into pellets and then melt-extruding the pellets into fibers (right). Adapted from [23].

On paper, mechanical recycling seems to be the perfect way of recycling plastics like PET. In reality, there are some drawbacks to the mechanical recycling processes. Every time PET is extruded, there is irreversible damage done to the polymer chain. This is caused by the fact that PET can undergo esterification, transesterification, and hydrolysis reactions as well as free radical reactions and crosslinking of the chains that all can degrade PET. This directly impacts the recyclability and there have been studies related to how many times PET can be mechanically recycled before it can't be reused anymore. Some solutions to this problem are the use of certain organic phosphates that can prevent the radical attacks and crosslinking of the chains and the use of chain extenders. Chain extenders are oligomers that target reactive chain ends and try to fuse the longer chains back together. Some of the common chain extenders used include isocyanates, epoxides, and carboxylic acids. The unreacted small molecules might leach through materials into the products, so chain-extended PET isn't suitable for food-grade PET production. This doesn't concern textiles, though, so chain-extended PET could be a good choice for textiles. Not all the end-of-life effects of chain-extendors are known or understood well enough yet since the continual reprocessing of chain-extended PET hasn't been researched a lot. Even though these unknown effects can complicate recycling, the popularity of chain-extendors is on the rise. [24, p. 9–11]

### **3.4.3 Chemical recycling of poly(ethylene terephthalate)**

Compared to mechanical recycling, chemical recycling is still only in the early stages of development as an industry and most of the developed technologies and techniques are still in a pilot stage [25]. As such, there are still many different methods being researched to be used. These methods include alcoholysis, aminolysis, ammonolysis, glycolysis, and hydrolysis [21]. With these methods, PET can be depolymerized into monomers and oligomers [25]. Out of these five methods, alcoholysis, glycolysis, and hydrolysis are available to be used commercially in the production of rPET [23]. The products of depolymerizing PET by aminolysis and ammonolysis can be used as feedstock to produce other polymers like polyamides or polyurethanes, but they can't be effectively used to polymerize new PET [25][26].

The alcoholysis method of recycling PET is basically a reversed transesterification reaction shown in figure 3.6, carried under high pressure and temperature circumstances. In alcoholysis, an alcohol attacks the carbonyl group and breaks the backbone ester linkage, resulting in the formation of EG and alkyl terephthalate as main products. [21][25] There have been reports of alcohols like ethanol and butanol to be used in alcoholysis, but recently methanol has gained the most attention among researchers. The method is

called methanolysis. There are three different approaches to methanolysis: the methanol used can be in liquid, vapor, or supercritical form. Out of these three approaches, supercritical methanolysis has been showing the most promising results. As always, there are advantages and disadvantages of using supercritical methanol. The main advantages are that there is no need to use catalysts in the process and the produced DMT has quality identical to virgin DMT. Also, EG and methanol can be recovered and reused in the production of new PET. Lastly, secondary depolymerization as the side reaction could be lessened when using supercritical methanol, giving a better yield of DMT. The disadvantages of methanolysis are mainly related to the high cost of separation and refining of the reaction products. Additionally, newer PET production processes use TPA as the raw material instead of DMT. Converting DMT to TPA via hydrolysis adds a substantial cost to the methanolysis process. [21]

Glycolysis is one of the oldest and simplest methods to chemically recycle PET [25]. It is also easy to implement industrially, and it is an economically advantageous method [26]. These days the most used degradation agent in glycolysis of PET is EG. The carbonyl group (C=O) of PET reacts with the free electron pairs on the oxygen of glycol. The ester C-O bond breaks while a new C-O bond with glycol forms. PET gradually breaks into smaller oligomers, then into bis(2-hydroxyethyl)terephthalate (BHET) dimers and finally into BHET monomers. [25] Glycolysis is most often carried out in temperatures between 170 °C and 300 °C in atmospheric pressure [26]. A wide range of different catalysts can be used, both homo- and heterogeneous, to speed up the process [25][26]. There have also been studies of utilizing microwaves in the glycolysis process to make the reaction time shorter [21]. An advantage of glycolysis is that the BHET produced can be reasonably easily purified by recrystallization in water and used as a starting material for producing new PET. As a downside, the PET waste used in glycolysis needs to be high enough quality to produce high quality PET without further purification. In the context of textile fibers, this is not a problem, as this mainly concerns the rPET used in the food packaging industry. [25]

Hydrolysis of PET is carried under high pressure and temperature conditions and the medium used can be either neutral, alkaline, or acidic [21][25]. In hydrolysis, a water molecule causes the esteric bond of PET to break by chain scission [21]. The end products of hydrolysis are TPA salt, which can be purified to pure TPA, and EG [25][26]. This makes hydrolysis a good method to produce new PET, since both end products are used in the production of PET. Alkaline hydrolysis is the most commonly used commercial scale hydrolysis method in the production of new PET [23]. Alkaline hydrolysis is usually

done in the aqueous solution of alkalines like NaOH and KOH, with a concentration ranging from 4% to 20% alkaline with no catalysts used. A disadvantage of hydrolysis is that the alkalines and acids used in the process and purification steps can cause corrosion and pollution, therefore potentially causing damage to the environment. [21] Although hydrolysis is a good alternative method of recycling PET chemically, methanolysis and glycolysis are the most used methods worldwide [16, p. 13].

Chemical recycling of PET has a tremendous potential in the production of rPET and even other polymer products. Depending on the method used, the yield of the end products can be in the range of 80% to even 100%. As already discussed, there are advantages and disadvantages to the processes developed. The problems mainly lie in the fact that the processes usually need to be carried out in high temperatures and pressures, even while catalyzed, making the energy consumption high. Also, the purification of the end products can be difficult, depending on the method employed. The main research to make chemical recycling of PET more appealing, is done in the field of catalysts and alternate heating sources like microwaves and ultrasound. There is also research being done to optimize the reaction variables like time, temperature, PET/catalyst ratio, and PET/reagent ratio that have influence on the depolymerization performance of these chemical recycling methods. [21]

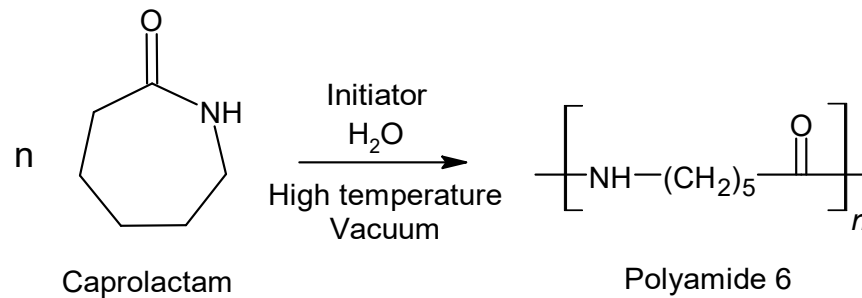
### **3.5 Polyamide 6 and polyamide 6,6**

Like PET, PA 6 and PA 66 are synthetic thermoplastic polymers produced mainly from petrochemicals. Even though PA 6 and PA 66 aren't produced as much as PET, they are the most produced polyamides worldwide. Polyamides are versatile materials, that can be used, for example, as fibers in various applications like clothing, carpets, parachutes, and car parts. [2, p. 213]

#### **3.5.1 Polyamide 6 production**

PA 6 is produced by the hydrolytic or catalytic ring opening polymerization of caprolactam, shown in figure 3.9 [27]. Small amount of caprolactam is first converted into  $\epsilon$ -aminocaproic via acid a catalyst to help the polymerization process. The catalyst can be water, which controls the reaction better than acid or base catalysts that can be used too. Especially base catalyst systems have high production rates, and the obtained polymers have high molar mass. The downside to base catalysts is that the reaction can't be controlled as well as with water as the catalyst. Water is the commercially used cata-

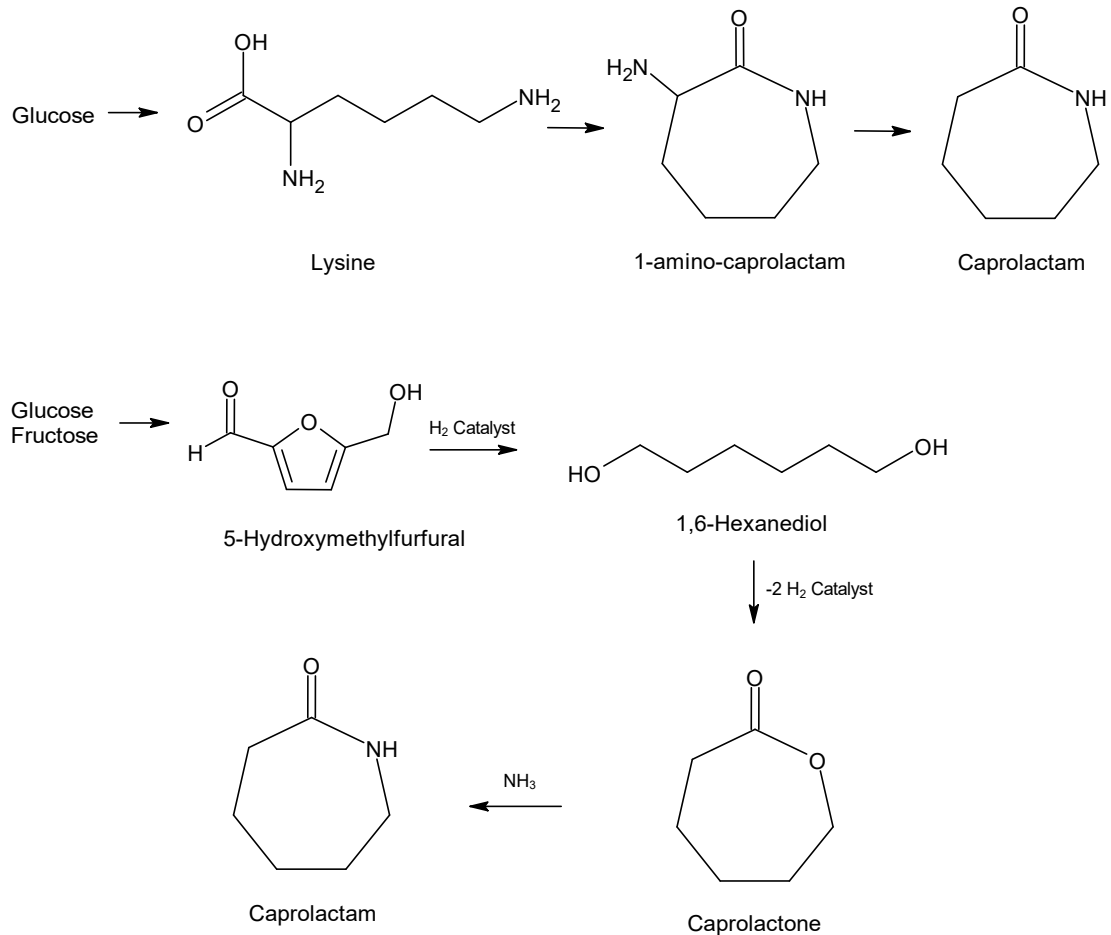
lyst, but base catalyst systems have shown promise to be used in the future.  $\epsilon$ -aminocaproic acid then readily converses into PA 6 in high temperatures and a vacuum. [22, p. 44]



**Figure 3.9** Synthesis of polyamide 6 by the ring opening polymerization of caprolactam. Adapted from [27].

Caprolactam is synthesized commercially mainly by three processes that use petrochemicals as the feedstock. The first process, catalytic hydrogenation of phenol and subsequent dehydrogenation of the resulting cyclohexanol, is still used, but not as much as the other two processes. The two most significant processes are one step catalytic hydrogenation of phenol using a palladium or carbon catalyst and catalytic oxidation of cyclohexane to a cyclohexanol/cyclohexanone mixture. [22, p. 45–46]

Due to its high amount of GHG emissions, the process of producing PA 6 is considered an environmentally polluting operation [2, p. 219]. Therefore, the research of PA 6, and polyamides in general, has been focused on alternative ways of production in a sustainable way. One example of this is bio-based feedstock. Two ways of synthesizing bio-based caprolactam from sugars are presented in figure 3.10.



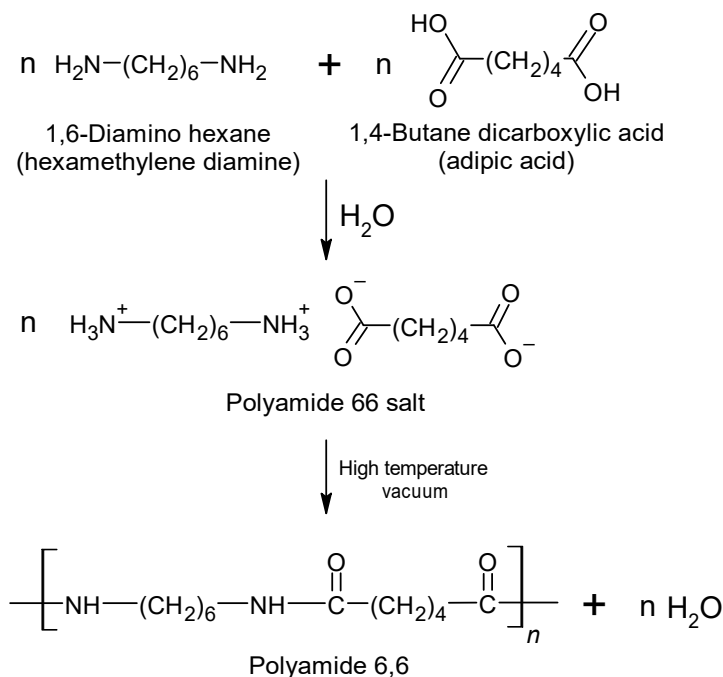
**Figure 3.10** Synthesis of caprolactam via lysine (above) and 5-hydroxymethylfurfural (below). Adapted from [28].

In the first method, lysine, that is obtained from glucose, is cyclized and aminated to produce caprolactam. The second method is to convert 5-hydroxymethylfurfural, obtained from glucose or fructose, into  $\epsilon$ -caprolactone in two steps. Afterwards, the  $\epsilon$ -caprolactone is transformed into caprolactam using ammonia. These bio-based processes have yet to be established in the commercial production of PA 6. [28] Another bio-based production method of caprolactam is by converting waste wood into levulinic acid that is similar to the caprolactam molecule. The researchers claim that this process creates no waste. [2, p. 221]

### 3.5.2 Polyamide 6,6 production

PA 66 is produced by the condensation reaction of hexamethylenediamine (HMDA) and adipic acid (AA), shown in figure 3.11. HMDA and AA are first reacted in methanol at an elevated temperature to create a PA 66 salt intermediate that is then purified and polymerized at high temperatures in a vacuum to obtain PA 66. The process these days

has been developed to be a continuous process instead of a batch process, that was the earlier favored way of producing PA 66. [22, p. 42]



**Figure 3.11** Synthesis of polyamide 6,6 from hexamethylene diamine and adipic acid. Adapted from [27].

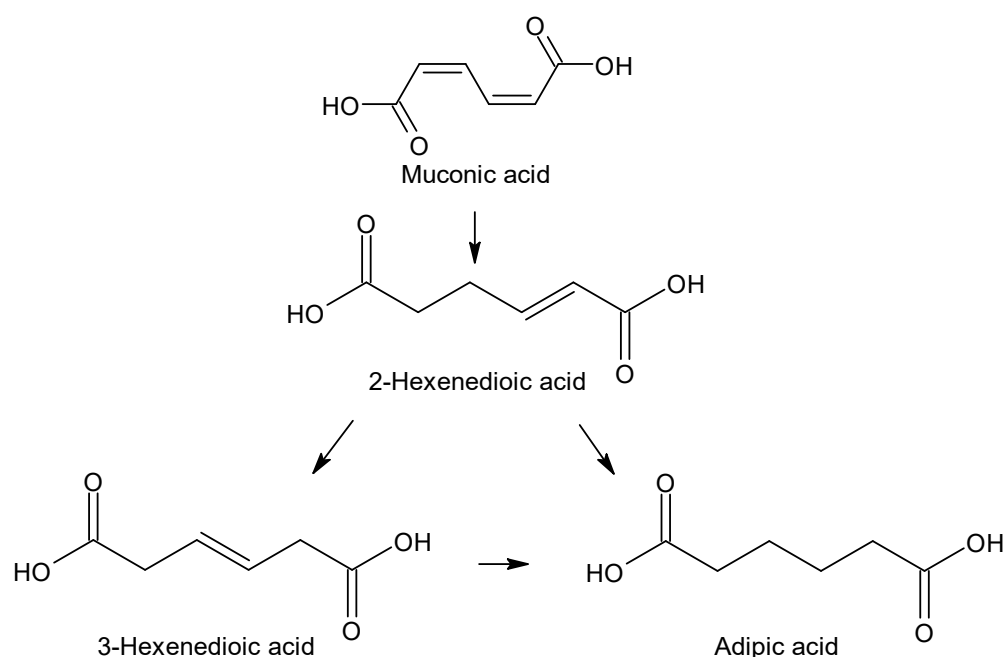
The commercial production of the first monomer of PA 66, AA, is usually based on a two-step oxidation of cyclohexane. First, cyclohexane is oxidated by air into a mixture of cyclohexanone and cyclohexanol. This mixture is then oxidized with nitric acid to produce AA. The reactions are catalyzed by a soluble cobalt oxidation catalyst and carried under pressures around 1 MPa and temperature of about 150 °C. [22, p. 43]

Another, although less popular, production method of AA is a two-step carbonylation of butadiene. The first step involves a reaction where butadiene is reacted with carbon monoxide and methanol in the presence of dicobalt octacarbonyl and a heterocyclic structure containing a tertiary nitrogen mixture of pyridines, picolines, quinolines and isoquinolines. This step is carried out in a pressure of 60 MPa and a temperature of 120 °C. Before the second step, unreacted butadiene is removed. The second step of carbonylation is done the same way as the first step, but instead at a pressure of 3 MPa and a temperature of 185 °C. The product of the second step is dimethyl adipate, which is then isolated by distillation and converted into AA by hydrolysis. [22, p. 43]

Like in the case of PA 6, PA 66 is mainly produced from petrochemical sources, and therefore, there has been research to produce AA and HMDA from more sustainable processes and bio-based sources. Especially sustainable AA is under a lot of research as it is one of the most important chemicals in the chemical manufacturing industry. One

problem in the manufacturing process of AA is the emission of nitric oxide and nitrous oxide. [2, p. 214–215] Particularly nitric oxide is a problematic GHG that depletes the ozone layer, causes acidic rain, and has 300-times more global warming potential than carbon dioxide [29]. It has been reported that nitrous oxide-free processes utilizing hydrogen peroxide or molecular oxygen are in the development that are similar to the two-step oxidation of cyclohexane method [2, p. 215][29]. However, the traditional processes are still being preferred to these new nitrous oxide-free processes if benzene prices stay low. Also, some analyzes have shown that the current nitrous oxide-free processes in development could have an even greater negative environmental impact in terms of unwanted side reactions, energy usage, and pollution. [29]

One example of a bio-based AA is AA produced from *cis,cis*-muconic acid (MA). It is a polyunsaturated dicarboxylic acid that can be produced renewably via the biological conversion of sugars and lignin. In the research of Vardon et al. [30], MA was produced by biologically converting benzoate. The final purity of recovered MA was reported to be as high as 99.8%, which is pure enough to be used in the commercial scale polymerization methods. MA was then hydrogenated into AA via the intermediate hexenedioic acid, as shown in the figure 3.12. [30]



**Figure 3.12** Hydrogenation of muconic acid via the intermediate hexenedioic acid to produce adipic acid. Adapted from [30].



The second monomer of PA 66, HMDA, is commercially produced by hydrogenating adiponitrile via a 6-aminocapronitrile intermediate [22, p. 43][31]. The process is a continuous liquid phase process usually catalyzed by a chromium containing Raney nickel catalyst and aqueous sodium hydroxide. The reaction is carried out under 3 MPa pressure and a temperature of 75 °C. [22, p. 43]

HMDA has also been researched to be produced from renewable sources. The review of Lee et al. [31] mentions a couple ways of converting bio-based substances into HMDA. Adiponitrile used in the hydrogenation process can be produced from biomass feedstocks via heterogeneous catalysis. Feedstock for adiponitrile can be ethanol, for example. Furfural and 1,4-anhydroerythritol can also be used as feedstock for HMDA production. Converting 5-hydroxymethylfurfural to HMDA is another way to produce HMDA from renewable sources. 5-hydroxymethylfurfural can be synthesized from glucose via isomerization-dehydration processes. A disadvantage for these processes is that for now, it is cheaper to produce HMDA from petroleum sources. Although these biomass-based synthesis routes also act as a carbon sink, which is an advantage compared to the petroleum-based processes, it has been shown that they can also have a higher environmental impact on eutrophication. [31]

Rennlon® is a PA 66 polymer produced by Rennevia. It is claimed to be 100% bio-based. The bio-based AA and HMDA monomers are produced from glucose and high-fructose corn feedstock. The company claims that the production costs for AA and HMDA will be even 25% lower than the petroleum-based AA and HMDA. The estimated GHG emissions of AA are claimed to be even 85% lower than that of the petroleum-based counterparts. For HMDA, 50% reductions are to be expected. [2, p. 221]

### 3.5.3 Recycling methods of polyamide 6 and polyamide 6,6

Mechanical recycling is the easiest way to recycle polyamides. Melt extrusion is the method that has the most potential applications. However, the cost of waste separation and cleaning is high, which lowers the interest in this approach. Additionally, it is difficult to separate PA 6 and PA 66 waste from each other mechanically. Lastly, the mechanical recycling of polyamides faces the same difficulties as the mechanical recycling of PET does: the recycled material degrades over time and the mechanical properties aren't sufficient after a certain number of cycles. [32]

Therefore, polyamides are generally recycled in two ways: chemical recycling and thermal recycling, namely pyrolysis. Pyrolysis is a thermal recycling process where heat is used in the absence of sufficient oxygen to break down the chemical structure of a polymer without combustion. The most common recycling method of PA 6 is hydrolysis, but

there are also alternative methods that are under research and development. Recycling methods of PA 66 mainly consist of chemical recycling methods. The most used methods are hydrolysis and ammonolysis. Like PA 6, many alternative methods have been developed to better recycle PA 66. The largest supply of waste for recycling polyamides comes from used carpets. [12, p. 102–103]

In the hydrolysis process of PA 6, the recycled material is first dissolved in high-pressure steam in an elevated temperature. The dissolved material is then continuously hydrolyzed with superheated steam in temperatures around 350 °C to form  $\epsilon$ -caprolactam. The recovery rate for the obtained caprolactam can be up to 98% with high purity. Afterwards, the obtained virgin-quality caprolactam can be repolymerized into new PA 6 fibers. This process is also known as the two-stage selective pyrolysis method. The hydrolysis process can also be done in acidic conditions with acids like nitric, formic, benzoic, or hydrochloric acid. In the presence of superheated steam, the acid hydrolysis of PA 6 wastes produces aminocaproic acid, which is then converted into  $\epsilon$ -caprolactam under the acidic conditions. Catalysts used in this process include orthophosphoric, boric and phosphoric acid. [12, p. 102] The problems of these methods are that high energy input and extensive separation is required [33].

An alternative method that has been researched in the recycling of PA 6 includes the ring closing depolymerization with the help of hydrophilic ionic liquids. The depolymerization process is carried in solventless conditions under microwave irradiation and it is practically a reversed process of the reaction shown in figure 3.9. A combination of acetic anhydride and an organocatalyst called 4-dimethylaminopyridine were used to convert PA 6 into *N*-acetylcaprolactam. The reaction happens in optimal conditions in a relatively short time, about 15 minutes, and yields of over 50% can be obtained. *N*-acetylcaprolactam can then be converted into  $\epsilon$ -caprolactam using 2-aminoethanol to transfer the acetyl functionality. The obtained  $\epsilon$ -caprolactam can then be used to produce new PA 6. There are a few advantages of using this method compared to the hydrolysis method. Lower temperatures than in the hydrolysis method, around 280 °C, can be used, resulting in less energy consumption. Also, the ionic liquids and catalysts used can be efficiently recovered with yields of over 80%. [33][34]

Another alternative sustainable method of depolymerizing PA 6 has been described by Kumar et al. [35]. The method is a hydrogenation reaction in the presence of a ruthenium pincer catalyst with dimethyl sulfoxide as a catalyst at 150 °C and H<sub>2</sub> pressurized to 70 bar. The researchers were able to produce the monomers not only from PA 6 but PA 66

and other polyamides as well. Up to 99% of the hydrogenated material was depolymerized with high monomer conversion rates. The process isn't at a practical level yet, but it has a promising direction. [35]

The depolymerization of PA 66 via hydrolysis can be done in acid- or base-catalyzed processes since the amide linkages of PA 66 are vulnerable to them. One process used is hydrolyzing PA 66 in with aqueous NaOH in isopropanol. The reaction is carried under a pressure of 2.2 MPa and a temperature of 180 °C. HMDA is separated from the residue by distillation and AA is then obtained by acidifying the aqueous phase with yields of over 90%. The monomers obtained can then be repolymerized to produce new PA 66. [36, p. 705–706] Studies of microwave-assisted hydrolysis of PA 66 have also been done with promising results [37].

Ammonolysis is the current preferred way of recycling PA 66. PA 66 and PA 6 mixtures can be depolymerized at a temperature of 330 °C and pressure of about 7 MPa. The reaction is catalyzed by ammonium phosphate. The monomer products obtained from PA 66 are HMDA, adiponitrile and 5-cyanovaleramide.  $\epsilon$ -caprolactam, 6-aminocapronitrile and 6-aminocaproamide are obtained from PA 6. The obtained aminocapronitrile and adiponitrile can be transformed into extremely pure HMDA by hydrogenation to produce new PA 66. [36, p. 707–708]

Glycolysis and amino-glycolysis processes have also been researched to be used in the recycling of PA 66. In the research of Datta et al. [32], glycolysis was carried out using excess of EG as a decomposing agent in the presence of a diammonium hydrogen phosphate catalyst. In the amino-glycolysis process, a mixture of EG and triethylenetetramine was used as another decomposing agent. One of the proposed products of the depolymerizations is HMDA, which means these processes could be used partly in the production of new PA 66. An advantage of these processes compared to some of the others is that they do not require the use of an elevated pressure. [32]

## 4. DISCUSSION

In the previous subchapters, the focus was on the existing production and recycling methods and processes that are being used and researched today. Based on the information gathered, the trend seems to be that most of the research has been focused on limiting energy consumption and reducing waste material as well as chemical usage and wastewater in the processes.

For regenerated cellulosic fibers, two different manufacturing processes were discussed: traditional viscose rayon process and newer lyocell process. Advantages and disadvantages of these processes are laid out in table 4.1.

**Table 4.1** Advantages (+) and disadvantages (-) of viscose rayon and lyocell processes.

	Viscose rayon	Lyocell
<b>Advantages</b>	<ul style="list-style-type: none"> <li>+ A cheaper process overall</li> <li>+ Dissolving cellulose does not require high temperatures</li> </ul>	<ul style="list-style-type: none"> <li>+ Environmentally friendlier process</li> <li>+ Does not require the use of many chemicals</li> <li>+ Chemicals used can be recycled almost entirely</li> <li>+ NMMO can be considered a non-toxic solvent</li> <li>+ The manufacturing process requires fewer steps</li> </ul>
<b>Disadvantages</b>	<ul style="list-style-type: none"> <li>- Requires the use of many toxic chemicals</li> <li>- Especially the chemicals containing sulfur are extremely toxic</li> <li>- Not all used chemicals can be recycled</li> <li>- Untreated chemical leaks have been reported to be environmentally damaging</li> <li>- Used especially in still developing countries where the legislation is more forgiving</li> </ul>	<ul style="list-style-type: none"> <li>- NMMO is expensive</li> <li>- NMMO can lose its effectiveness in certain cases</li> <li>- Requires high temperatures in the dissolving process</li> <li>- Turning fibers into fabrics requires the usage of toxic and hazardous chemicals</li> </ul>

In the case of PET, a heavier focus on the recycling processes was taken, as it is one of the most recycled materials in the world. The main advantages and disadvantages of

vPET and rPET produced via mechanical and chemical recycling routes are listed in table 4.2.

**Table 4.2** Advantages (+) and disadvantages (-) of virgin PET, mechanically recycled PET, and chemically recycled PET. There can be both advantages and disadvantages to some of the main points (+/-).

	Virgin PET	Mechanically recycled PET	Chemically recycled PET
<b>Advantages</b>	<ul style="list-style-type: none"> <li>+ Production methods are well established</li> <li>+ Many ways of producing bio-based feedstock for synthesis have been developed</li> <li>+ Water consumption in production is lower than for natural fibers [13]</li> </ul>	<ul style="list-style-type: none"> <li>+ Mechanically recycled rPET has properties almost similar to vPET</li> <li>+ Prevents plastics from polluting environment</li> <li>+ Reduces GHG emissions when used instead of vPET or blended in with vPET</li> </ul>	<ul style="list-style-type: none"> <li>+ Chemically recycled rPET has superior quality, equal to vPET, when compared to mechanically recycled PET</li> <li>+ The products received from depolymerization can also be used to produce other products than PET, if needed</li> <li>+ There are many different depolymerization methods in development</li> </ul>
<b>Disadvantages</b>	<ul style="list-style-type: none"> <li>- Most of PET is still produced from non-renewable petroleum-based feedstock</li> <li>- PET is mostly manufactured in developing countries with sloppy legislation leading to environmental pollution and GHG emissions [13]</li> <li>- Energy consumption during the manufacturing processes is high [13]</li> </ul>	<ul style="list-style-type: none"> <li>- There is a limited number of times PET can be mechanically recycled due to irreversible damage done to the polymer chains</li> <li>+/- Chain extenders have been used to prevent the problem above, but not all end-of-life effects are well known yet.</li> <li>- Chain extenders can further complicate recycling</li> </ul>	<ul style="list-style-type: none"> <li>- More expensive than mechanical recycling due to the depolymerization reactions requiring high temperatures and pressures leading to high energy consumption</li> <li>- Purification of the end products of depolymerization can be difficult leading to more costs</li> <li>- Acids and alkalis used in some methods can be sources of pollution and corrosion</li> </ul>

Lastly, for PA 6 and PA 66, both production and recycling methods were discussed. As mechanical recycling of polyamides isn't very popular, a focus on production methods

from renewable sources and chemical recycling was taken. The main advantages and disadvantages of these processes are collected to table 4.3.

**Table 4.3** Advantages (+) and disadvantages (-) of virgin polyamides 6 and 6,6. There can be both advantages and disadvantages to some of the main points (+/-).

	PA 6 and PA 66 production	Chemical recycling of PA 6 and PA 66
<b>Advantages</b>	<ul style="list-style-type: none"> <li>+ The feedstock for polymer synthesis can be produced from renewable bio-based sources</li> <li>+ A fully bio-based PA 66 polymer can be produced</li> <li>+/- Many different processes utilizing feedstock from renewable sources are in development, although the processes using petrochemical sources are being preferred because they are cheaper for now</li> </ul>	<ul style="list-style-type: none"> <li>+ Virgin quality polyamides can be produced from the depolymerized products</li> <li>+ The depolymerization products can also be used as feedstock to produce other polymers</li> <li>+ There are many different methods of recycling being researched</li> <li>+/- Many of the processes are not at a practical level yet but they show promising potential</li> </ul>
<b>Disadvantages</b>	<ul style="list-style-type: none"> <li>- Polyamides are mainly produced from nonrenewable petrochemicals</li> <li>- The manufacturing processes require high temperatures and pressures, which make them energy intensive processes</li> <li>- Production methods in use today have high GHG emissions and are generally considered to be highly polluting</li> <li>- Nitric oxide and nitrous oxide emissions in the manufacturing processes are particularly problematic as they deplete ozone, cause acidic rains, and have a high global warming potential</li> </ul>	<ul style="list-style-type: none"> <li>- Most of the methods need a high temperature and pressure for the depolymerization reactions, meaning the energy consumption and costs are high</li> <li>- Some of the processes require extensive separation of materials</li> <li>- Some of the processes are catalyzed by acids or bases, which can cause corrosion and pollution</li> </ul>

Overall, there are many good things about every material studied in this thesis. Every material and method have their advantages and disadvantages, but when considering the near future developments, PET seems to be that one material that could reach a higher potential than the others in a short amount of time. There are already large-scale

PET recycling programs established in developed countries that helps reduce the PET that ends up in landfills. This is a huge advantage compared to the other materials. Also, bio-based production for PET has been developed longer than for the other materials so it is closer to being commercialized in a large scale. It remains to be seen, though, how the problems of the renewable bio-based feedstock supply are managed if the production is ramped up to a larger scale.

For the other materials, PA 66 and lyocell seem to be the most promising ones behind PET. PA 66 can already be produced from bio-based feedstock but the production methods can be really polluting and environmentally unfriendly. Lyocell is almost an environmentally friendly sustainable material, but the high energy consumption of dissolving cellulose and chemicals used in the post-processing can make it unappealing for some consumers. It will be interesting to see if the problems of these materials can be solved as they do show potential to be fully sustainable in the future.

## 5. CONCLUSIONS

The goal of this thesis was to study the sustainability of textile reinforcements used in tires. The textiles studied were rayon, lyocell, PET, PA 6, and PA 66. The environmental and economical sustainability of these materials was studied with a focus on the manufacturing and recycling processes used and researched today.

For the regenerated cellulosic fibers, rayon and lyocell, mainly manufacturing processes were discussed. Cellulosic fibers as textile reinforcements are a good choice since cellulose is a renewable natural material that is also biodegradable. Considering the sustainability of the production processes, some disadvantages were found for both the viscose rayon and lyocell processes. The pulping and viscose processes use a lot of chemicals to treat cellulose. Especially the chemicals containing sulfur are extremely toxic and can cause serious environmental damage if leaks happen. This is mainly seen as a problem in the developing countries. The lyocell process was found out to be the more sustainable manufacturing process out of the two. NMMO and other solvents used can be almost fully recycled between production cycles creating a lot less chemical waste than the viscose rayon process. The lyocell process is much pricier though, as the energy consumption is high and NMMO is an expensive chemical.

The manufacturing and recycling processes were discussed for PET, PA 6, and PA 66. The PET synthesis still mostly utilizes petrochemicals in the production of its monomers EG and TPA, but bio-based sources have been developed and are being implemented in the near future. Recycling methods of PET are being explored too. While the mechanical recycling of PET is the mainstream methods as of right now, the problems with degradation have raised the interest of chemical recycling methods such as glycolysis, hydrolysis and methanolysis. Chemical recycling as an industry is still in the early stages of development compared to mechanical recycling so most of the processes are still being developed to be as optimized as possible for sustainable recycling. The chemical recycling processes also usually require high temperature and pressure to be used even if they are catalyzed. Alongside difficulties in purification, this can easily raise the cost of these processes.

As for the polyamides, petrochemicals are used in the production of the monomers used in the synthesis processes, much like in the case of PET. For both PA 6 and PA 66, bio-based solutions have been developed, but they haven't been commercialized yet for the most part. For example, fully bio-based PA 66 polymer can be produced. The current



production processes for both PA 6 and PA 66 emit lots of GHGs and that's why the alternative methods are important to be further developed. Particularly nitric oxide is a problematic GHG that has a lot of negative environmental impact. Currently, petrochemicals are still preferred to be used as long as the feedstock prices stay low. The recycling methods for both polyamides were found out to be focused on chemical recycling since there can be problems with separation in the mechanical recycling processes. Methods like hydrolysis, ammonolysis, and other alternatives are being used and developed to produce new virgin material from used polyamide products. Similarly to the chemical recycling of PET, the current processes are still being developed and optimized further. Also, the depolymerization reactions require high temperatures and pressures to work, which creates high energy consumption.

Overall, the potential of PET was found out to be the highest for the near future usage of the materials studied in this thesis. While lyocell and PA 66 have the potential to be fully sustainable materials, their processes need to be developed more to reach the same potential as PET.

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