

# Nonwoven textiles based on polylactide

Rostislav Vilém

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L.S.

doc. Ing. Roman Čermák, Ph.D.  
*děkan*

doc. Ing. Tomáš Sedláček, Ph.D.  
*ředitel ústavu*

Příjmení a jméno: VILÉM ROSTISLAV

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## **ABSTRAKT**

Kyselina polylaktická je polymer se slibnou budoucností. Biodegradabilní polymery jsou aktuální téma ve společnosti, právě proto netkané textilie na bázi kyseliny polylaktické. Cílem této práce je představit syntézu kyseliny mléčné a polylaktické. Dále pak výrobu netkaných textilií a nakonec výrobu netkaných textilií z kyseliny polylaktické.

Praktická část je zaměřena na charakterizaci elongační viskozity kyseliny polylaktické v závislosti na přídavcích plastifikátoru. Na základě znalosti elongační viskozity chceme určit, který materiál je vhodný pro zvlákňování.

Klíčová slova: netkané textilie, kyselina polylaktická, zvlákňování, biodegradabilita

## **ABSTRACT**

Polylactic acid is a promising future polymer. Biodegradable polymers are a topical issue in society, which is why this topic, the nonwoven polylactic textiles, was created. The aim of this work is to present the synthesis of lactic acid and polylactic acid. Furthermore, the production of nonwoven fabrics and finally the production of nonwoven fabrics from polylactic acid. The practical part is focused on characterization of elongation viscosity of polylactic acid in dependence on additions of plasticizer. Based on the knowledge of elongation viscosity, we want to determine which material is suitable for spinning.

Keywords: nonwoven fabrics, polylactic acid, spinning, biodegradability

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I hereby declare that the print version of my Bachelor's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

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## INTRODUCTION

Polylactic acid has been selected for its biodegradability and good mechanical properties. These are very promising features in the future. Meanwhile, the widespread use of polylactic acid prevents its cost. However, the price difference will be erased with the advancement of technology and higher oil prices in the future. Environmental degradable nonwovens can be useful in disposable packaging, disposable tissues, or medicine.

Only the pure polymer was not characterized, but the elongation viscosity was also characterized as a function of the addition of plasticizer. Whether the plasticizer significantly affects spinning or not.

The aim of this thesis was to characterize elongation viscosity of the melted polymer. So, even before the demanding spinning process, know if it will spin well or poorly. It is generally known that higher viscosity materials are better for spinning. Therefore, we wanted to find out which material has the highest elongation viscosity.

## **I. THEORY**

## 1 LACTIC ACID

Lactic acid (2-hydroxy propionic acid) is one of the most widespread carboxylic acid in nature and which specifically belongs to the group of hydroxy acids. Lactic acid can be prepared by the process of chemical synthesis or carbohydrate fermentation. [1]

### 1.1 Properties of lactic acid

We can find lactic acid in the L- and D- isomeric forms presented in Figure 1, it is also known in racemic form. In the product gained by fermentation process, we can find up to 99.5 % L-isomer and the rest is D-isomer. The melting point of both forms D- and L- forms is 18 °C and 53 °C it is for the racemic form. The boiling point is 122 °C at a pressure of 2000 Pa. When we have lactic acid in the form of colourless crystals, -it is hygroscopic. If it is possible, lactic acid easily forms a cyclic dimer. Cyclic dimer is not very hygroscopic and is a fit starting material for production of high purity monomer. [2]

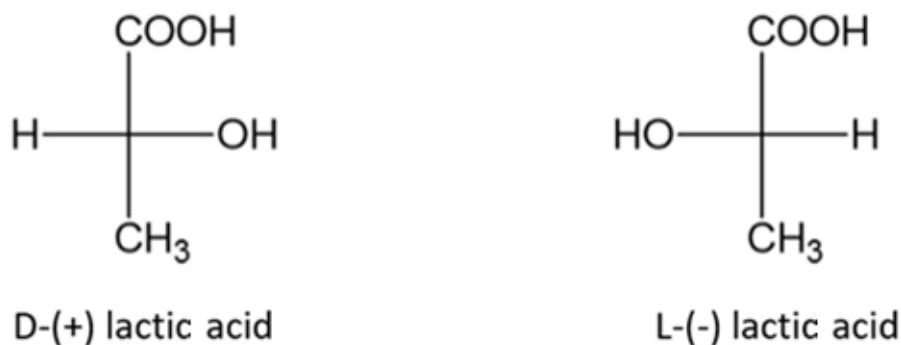


Figure 1: *Structural formula of lactic acid* [1]

### 1.2 Use of lactic acid

For the first time, lactic acid was prepared in 1847 when Mr. Blondeau obtained it by fermentation. However, interest in lactic acid began to grow in the 1940s, when carbon, heterochain polymers and aliphatic polyesters started to use in production of fibres, films and plastics. But in these years, lactic acid has not been studied on a larger scale. We can find lactic acid in various areas of use for example in textile industry and medicine, but especially in the food industry, because it inhibits spreading of many species of microorganisms, which can cause many unwanted side effects. That means it has antiseptic effects. For higher mammals and humans is harmless. In the biosphere decomposes into water and carbon dioxide (CO<sub>2</sub>) so it is also harmless to the environment. [2]

### 1.3 Production of lactic acid

Lactic acid can be prepared by bacterial fermentation or synthetically by hydrolysis of lactonitrile. However, about 90 % of this acid in the world is produced by fermentation. [3]

#### 1.3.1 Chemical synthesis

The most widely used chemical synthesis is based on lactonitrile. The main steps of chemical synthesis are:

- Adding hydrogen cyanide to acetaldehyde to produce lactonitrile, a presence of a base is necessary,
- Reaction occurs in the liquid phase and high atmospheric pressure is required,
- The lactonitrile is then hydrolysed to lactic acid, in a presence of concentrated HCl or H<sub>2</sub>SO<sub>4</sub>, to form a by-product, corresponding ammonium salt,
- Then the esterification of lactic acid with methanol forms methyl lactate,
- Methyl lactate is purified by distillation, hydrolysed by water in presence of acid catalyst,
- Lactic acid and methanol are formed, methanol can be recycled.

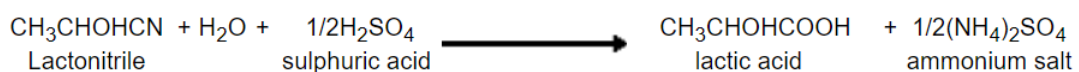
[3]

Here in Figure 2 are the equations describing process of chemical synthesis of lactic acid

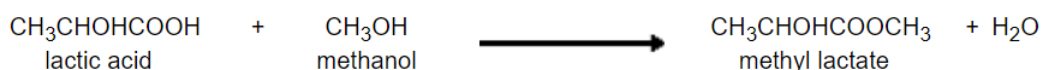
(a) Addition of Hydrogen Cyanide



(b) Hydrolysis by H<sub>2</sub>SO<sub>4</sub>



(c) Esterification



(d) Hydrolysis by H<sub>2</sub>O

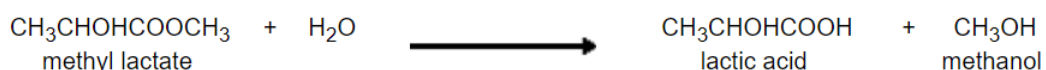


Figure 2: Chemical synthesis of lactic acid [1]

### 1.3.2 Fermentative synthesis

The basis of the fermentative process is starch, which is produced in plants by photosynthesis. The starch is extracted from the plant pulp and converted into a suitable, fermentable sugar, for example glucose, using enzymes. This sugar is then converted to lactic acid by fermentation. Presently, the most used source of sugar is glucose from corn. Many types of bacteria can be used for fermentation and sometimes the different fermentation processes can be distinguished from these bacteria. The lactic acid obtained can be therefore referred to as raw material derived from renewable sources. The whole process is shown in Figure 3. [4]

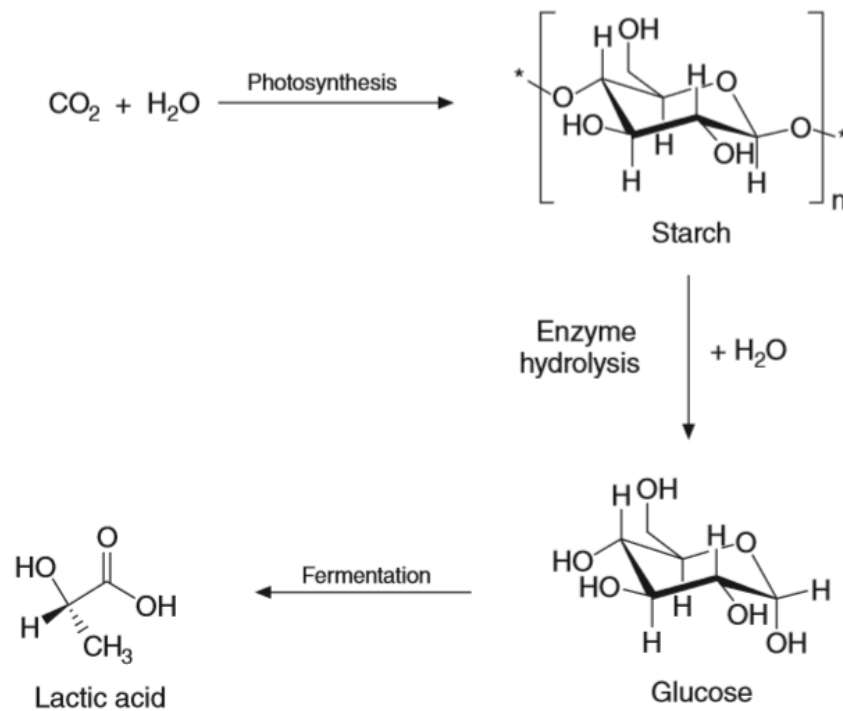


Figure 3: Production of lactic acid from renewable resources [1]

## 2 POLYLACTIC ACID (PLA)

PLA is chemically aliphatic polyester. It is a thermoplastic polymer, which can be both amorphous and semi-crystalline. PLA is also bio-based and compostable product. Interest in PLA has been increasing over the last decade since it has been found, that many features, such as strength, stiffness and gas permeability are comparable to traditional petrochemical-based polymers. However, PLA materials still have their limitations as slow biodegradation, high cost and low toughness.

In general, biodegradable polymers can be divided into two groups: petroleum-derived and microorganism-derived biodegradable polymers. It can be also divided into polymers from renewable and non-renewable sources, see in Figure 4. [5, 6]

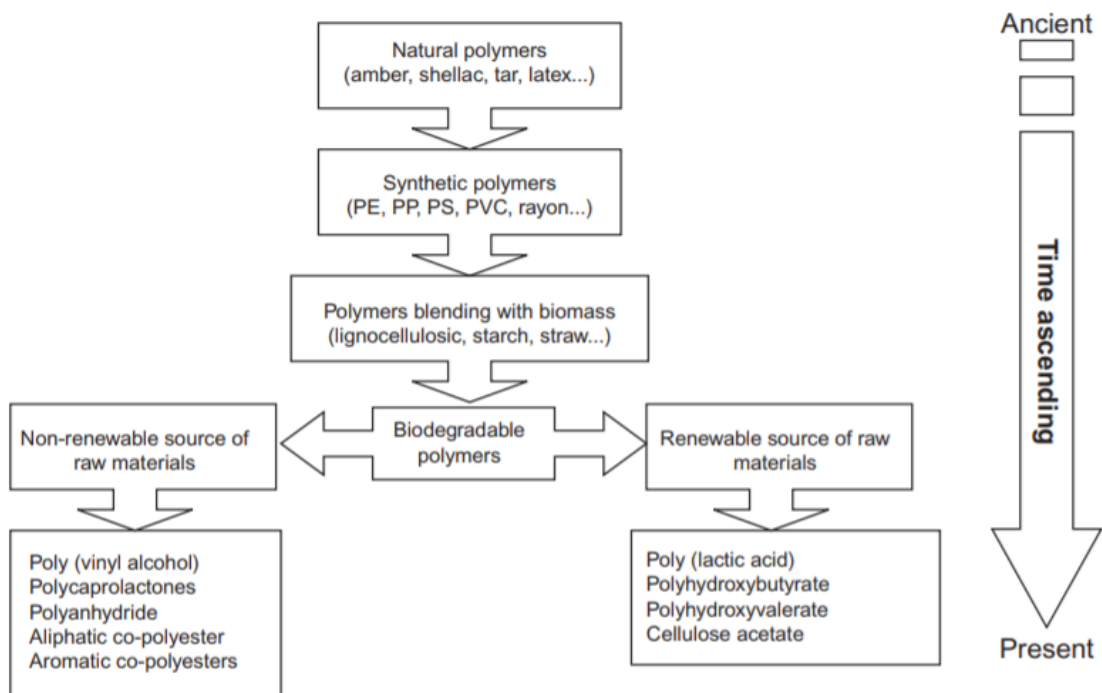


Figure 4: Trends in polymer development [6]

## 2.1 Properties of PLA

PLA (structural formula in Figure 5) has a melting point at 180 °C and glass transition temperature of 60 °C, but these temperatures are correlated with purity level and stereochemistry. PLA have relatively poor strength and lack of shear sensitivity. Tensile strength is 44-59 MPa. The hydrolysis of ester bonds is used to accomplish degradation of PLA. [6, 7]

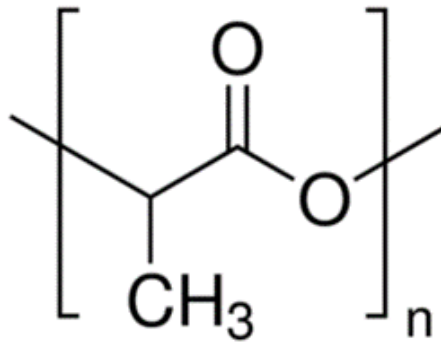


Figure 5: *Structural formula of PLA* [6]

## 2.2 Use of PLA

Because monomers come from non-toxic renewable sources, PLA is a promising polymer for future applications. Good biocompatible and mechanical properties make it ideal for use in medicine for implants, stitches or tissue engineering. [7]

Recent years' discussions about environmental problems and the harmfulness of biodegradable petrochemical based polymers suggest future developments in the use of PLA. The use of PLA has been already growing, for example, in the general consumer market and in biodegradable packaging. It is assumed that the production volume of PLA will gradually increase and the manufacturing process will be improved, thereby eliminating the disadvantage of the high price. [6]



## 2.3 Synthesis of PLA

There are three main ways to synthesize PLA, described in Figure 6.

- 1) Polycondensation, which provides a brittle polymer with low molecular weight in order to have this polymer practical use, must be extended its chains by the chain extenders.
- 2) Azeotropic dehydrative condensation of the lactic acid, which can provide high molecular weight PLA without the use of special additives.
- 3) Ring-opening polymerization of lactide, which is the main process and provide PLA with high molecular weight. This method has been patented by Cargill (US) in 1992. [8]

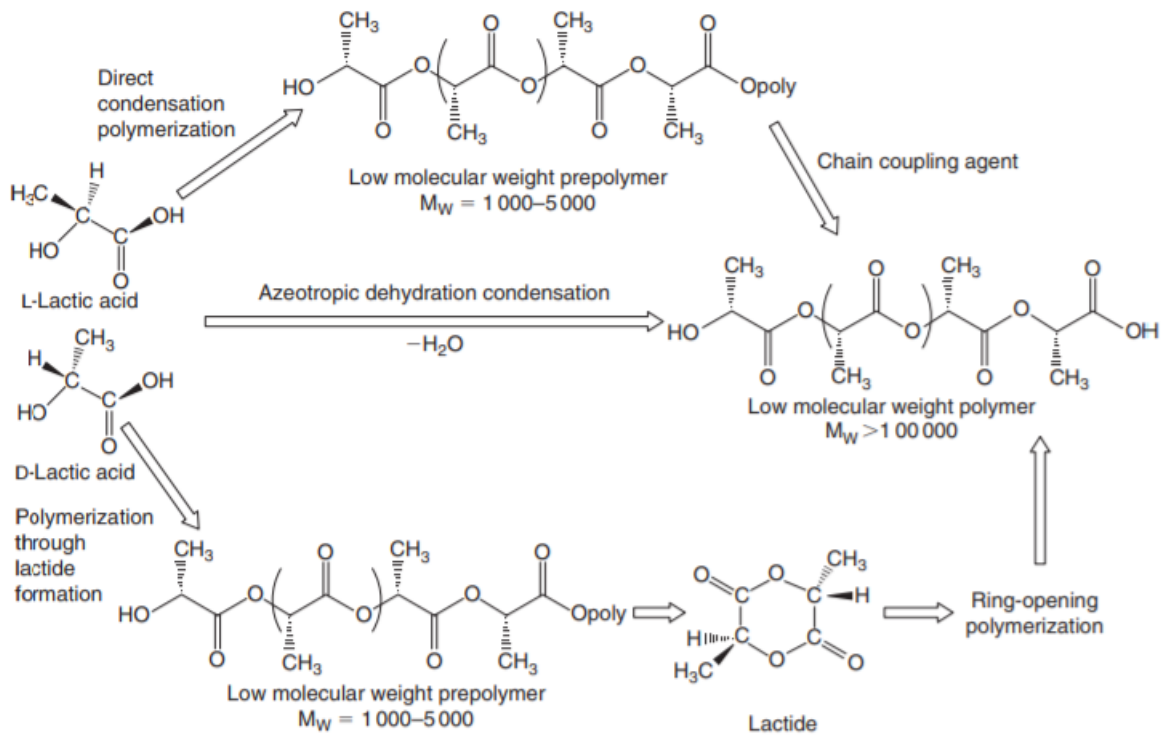


Figure 6: Synthesis methods of PLA [8]

The most of fermentation processes try to use species of Lactobacilli, which produce the high proceeds of lactic acid. Some Lactobacilli such as Lactobacilli amylophilus produce mainly the L isomer, some species, such as Lactobacilli acidophilus produce the D isomer or a mixture of L and D, see in Figure 7. [8]

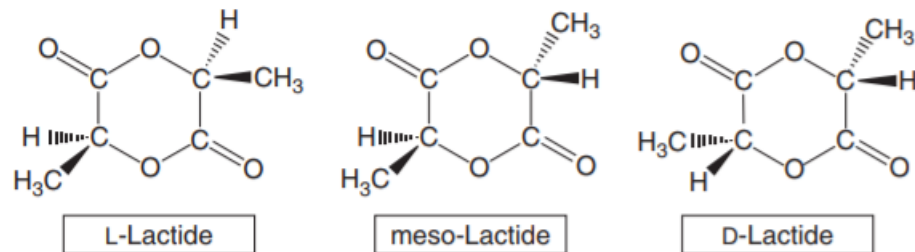


Figure 7: Chemical structures of L-, meso- and D-lactides [8]

### 3 FIBRES

Definition of a fibre according to the Textile Institute (Denton and Daniels, 2002) says that *it is a textile raw material, generally characterised by flexibility, fineness and high ratio of length to thickness.* [9]

In the second half of the 20<sup>th</sup> century, fibre dimensions ranged from 10 to 50  $\mu\text{m}$  in diameter and were greater than 1 cm in length. Useful measure of fibre fineness is linear density. The standard unit is  $\text{tex} = \text{g}\cdot\text{km}^{-1}$ , but  $\text{dtex} = \text{g}\cdot 10 \text{ km}^{-1}$  is also widely used. The previously mentioned dimensions correspond roughly to 1 to 25 dtex.

There are several main groups of fibres: natural and artificial fibres with good strength and breaking extension, high-tenacity fibres and elastomeric fibres, organic and inorganic high-moduli and synthetic polymer fibres with high toughness. There are also inorganic fibres, such as rock wool, but they are of limited use. [9]

For fibre production, we must first prepare the polymer and then convert it into a fibre. If we have fibre based on raw materials from natural sources, we skip the polymer preparation. The main processes converting polymer to fibre are spinning or extrusion and post-spinning operations, which include drawing and heat-setting.

We have two main ways to convert fibre-forming polymers to fibres: melt-spinning and solution-spinning. Melt-spinning includes extruding the melted polymer through small capillary holes to form fibres. The filaments are afterwards cooled the solid state. Solution-spinning includes the extrusion of a solution to form fibres. There are two main ways to remove the solvent from the fluid filament: vaporization with hot gases in dry-spinning or by the coagulation in wet-spinning. The methods are illustrated in Figure 8. [10]

Nanofibers can also be made, most often by electrospinning from solution. Microfiber is often produced by melt-spinning, which has a modified spinning head, or there is a method “islands in the sea”. The most recent form of nanofiber are carbon nanotubes. [9]

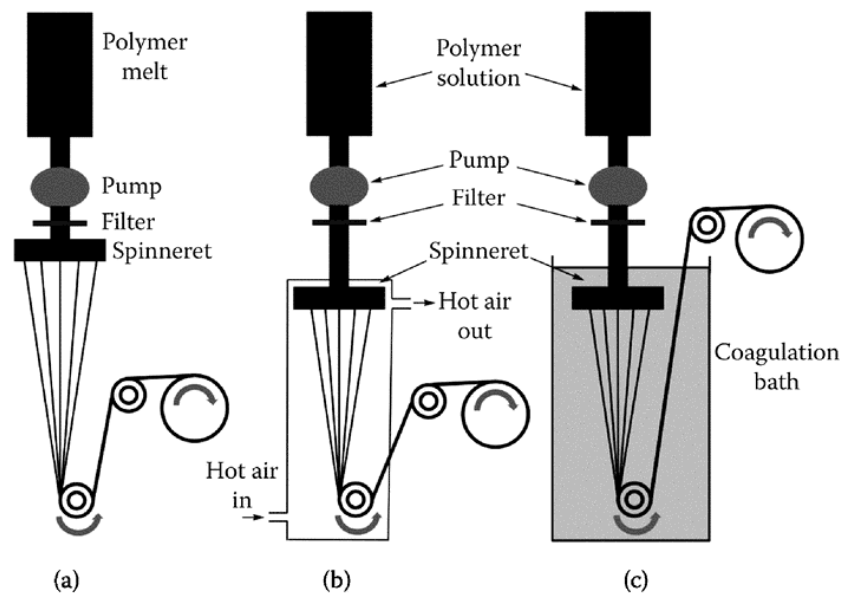


Figure 8: Scheme of three major spinning techniques: (a) melt-spinning, (b) solvent-spinning, (c) wet-spinning [11]

### 3.1 Melt-spinning

Melt-spinning is a simple extrusion process, because addition and removal of solvent are not required. This method is preferred for those polymers that can be melted by thermal treatment, which do not cause thermal degradation and are stable in the temperature range required for the desired viscosity of the polymer in extrusion. If possible, melt spinning is preferred to solution, the reasons will be explained below. Polyamide, polypropylene and polyester fibres are produced by the melt-spinning process.

Figure 9 shows schematically the melt extrusion process. In the first step polymer granules are being fed into a screw extruder, which is heated, because granules of polymer must be melted. Further, the molten granules of polymer is compressed, and the screw action propel is pushing them towards the gear pump. The gear pump ensures a fluent flow of a molten polymer through the spinneret. However, prior to the spinneret, a filtering device must be placed in order to remove unwanted solid impurities that may be present in the polymer granulate. After that the filaments leave the spinneret. The polymer melt is no longer limited by the walls causing- "die-swell" which is an increase in extruded filament volume in the free space. In order for the filaments to solidify, they are drawn through a long cooling chamber towards a take up roller. The cooling of the filaments is achieved by a transverse flow of the air. Of course, the wind velocity and the temperature are the controllable

parameters to achieve the ideal cooling rate. Before the fibres reach the take-up roller, they are gathered into multifilament yarn. The velocity of take-up is roughly in the range of 1000–6000 m.min<sup>-1</sup>. Since this velocity is much higher than the velocity, by which the filaments leave the spinneret, filaments are stretching, causing the ordering of the structure of polymer chains. [12]

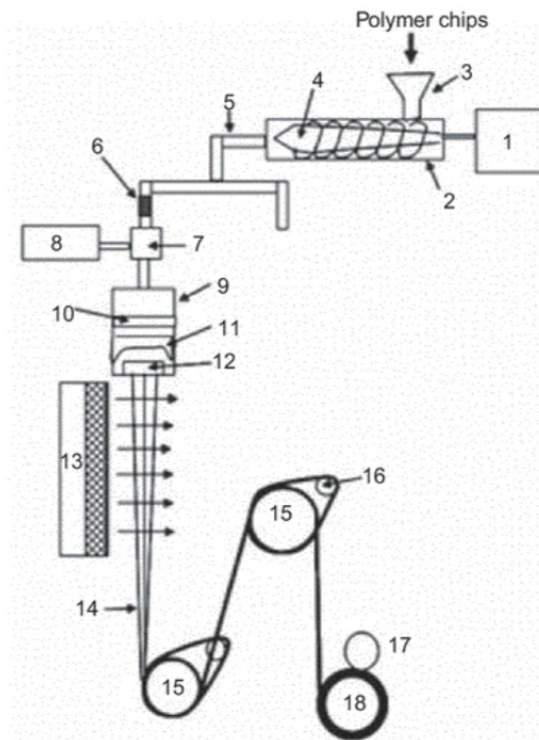


Figure 9: *Schema of melt spinning setup: (1) extruder drive, (2) extruder, (3) hopper, (4) screw, (5) manifold, (6) static mixer, (7) gear pump, (8) gear pump drive, (9) spin pack, (10) mesh filters, (11) distributor, (12) spinneret, (13) quench chamber, (14) freshly spun yarn, (15) godet, (16) idler roller, (17) winder, (18) yarn bobbin* [13]

### 3.2 Solution-spinning

Due to the problems of using solvents and their subsequent removal, this method is only used if the polymer cannot be melted under reasonable conditions. Depending on how the solvent evaporates, we distinguish two solution-spinning processes. The solvent can be removed by heating (dry-spinning) or by coagulation in another fluid which is not solvent for the polymer but is compatible with the spinning solvent (wet-spinning). [10]

### 3.3 Dry-spinning

As the first step in dry-spinning is prepared the spinning solution, which must have good dissolving power. Suitable solvents are also volatility and low cost. In this spinning process, we also need to take into account the risk of solvent ignition, the potential explosion or the toxicity. The dissolution is performed at temperatures of 100 °C or higher in commercially available mixers. The schema of a dry-spinning cell is shown in Figure 8. In this cell the primary function is the removal of the solvent through evaporation. Also in this process filtration of the solution and its deaerating are necessary. Spinning solution is then transported to the metering pump in the spinning head at a certain temperature and generally pressure of 10-20 bars. Furthermore, it is necessary to evaporate the solvent under hot conditions in the spinning tube. The time during which conditions of the evaporation are maintained determines the amount of remaining solvent in the fibres. This remaining solvent depends also on the take off speed, the gas temperature and the length of a spinning tube. In this process, the solidification is achieved by heat evaporating the solvent. However this solidification is slower than the solidification in melt-spinning where filaments are cooled, but still faster than solidification by coagulation. [10]

### 3.4 Wet-spinning

The start of wet-spinning process is similar to methods in dry-spinning such as preparation of the solution and transport of the solution. Mixing and dissolving of the polymer takes place in a vessel with a stirring device. The factors like a solution spinning pressure and a polymer solubility are determining factors of a polymer concentration in the spinning solvents. It is necessary to degas, filter and subsequently homogenize the solution. Thus, treated solution is sent through a metering pump to the spinning machine with a spinneret with many holes, usually about 200-600 holes. Behind the spinneret, there is a coagulation

bath, or a group of coagulation baths where individual filaments are precipitated. This coagulation process is the most critical part of the entire method. It is because during the fibre forming, there are many interactions of numerous factors, which can affect the structure of all filaments. Several of these factors are mentioned below:

- various particular solvents
- polymers
- temperature
- non-solvents used

The velocity of filament in the spin bath is not so high because of the large hydraulic drag. Therefore, the drawing must be determined in the following steps where partially coagulated filaments are washed and dried. [10]

### 3.5 Electro spinning

We use the electro spinning method for the production of nanofibers. This method is schematically shown in Figure 10. High voltage affects the polymer solution through the spinning nozzle. Due to the difference in electric potential between the nozzle, the grounded collector and electrostatic charges in the polymer solution, polymer solution is spun out of the nozzle. This solution jet is then electrostatically stretched into nanofibers. Electrospun nanofibers are mostly collected as a nonwoven web with a randomly oriented structure. [14]

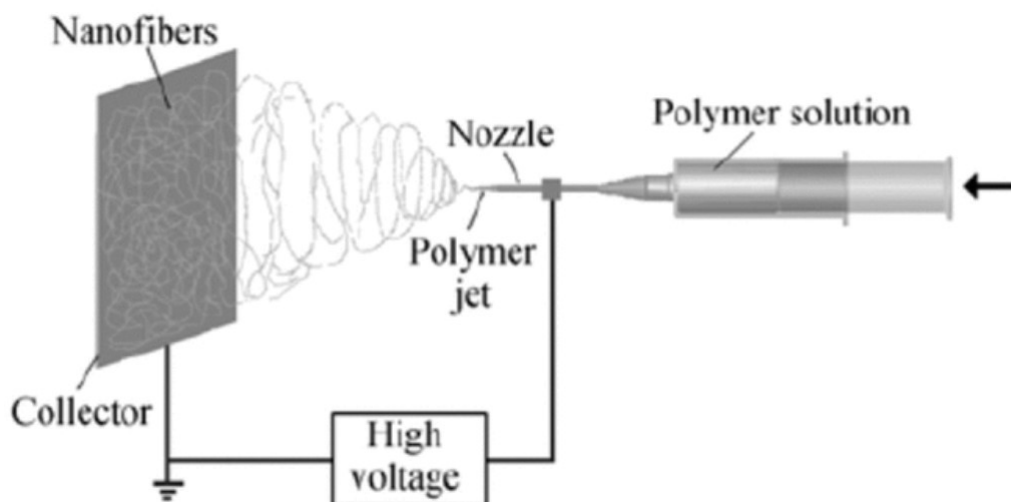


Figure 10: A single nozzle electrospinning setup [14]

## 4 NONWOVEN FABRIC

One of the definitions of nonwoven fabric appears in International Standardization Organization (ISO) 9092 and CEN EN 29092, and updated version was proposed by EDANA and INDA as follows:

*A nonwoven is a sheet of fibres, continuous filaments, or chopped yarns of any nature or origin, that have been formed into a web by any means, and bonded together by any means, with the exception of weaving or knitting. [15]*

Today's market is very diverse and offers a variety of raw materials in various forms, such as wood pulp, polymer chip, staple fibres, adhesives, lubricants and many other major materials or additives. Thus, the nonwoven fabric industry can choose from many varieties of fabrics for fabric manufacturing, which they usually supply in the form of “roll goods”. These rolls are then processed into final products by many means involving processes like cutting, laminating, coating, slitting, folding etc.

The variety of products ranging from wet wipe (20 g.m<sup>-2</sup>) to a geomembrane protector (1000 g.m<sup>-2</sup>), which is highly durable and can resist environmental conditions for many years. Generally, nonwoven fabrics include a wide range of products from disposable products such as wet wipes and tea bags to highly durable products such as synthetic leather and roofing membranes, which last for many years. [15]

One of the other major industries, which is currently gaining an importance, is the incorporation of nonwovens in the area of filtration fabrics. Another significant trend in nonwovens is the shift to polymers gained from renewable sources such as polylactic acid.

In terms of structure and properties, nonwoven fabrics are strongly anisotropic. Their significant properties include porosity and permeability. The orientation of the fibres and fields of their binding points is very random and depends on the setting of the entire production process. By setting of the process parameters, we can control the resulting properties of the fabric, such as the density of the entire web. We can at least partially influence also the fibre orientation in one preferential direction. Nonwovens are anisotropic in terms of structure and properties and are highly porous and permeable. The relative orientation and spatial separation of fibres as well as bond point positions within the fabric are heavily influenced by the combination of processes as well as their settings used during manufacture. The fibre orientation distribution is particularly important because of its



influence on the isotropy of fabric properties. Fibres are usually oriented in many different planar directions in nonwoven fabrics (see in Figure 11), but there is usually at least one preferential direction.

[15, 16]

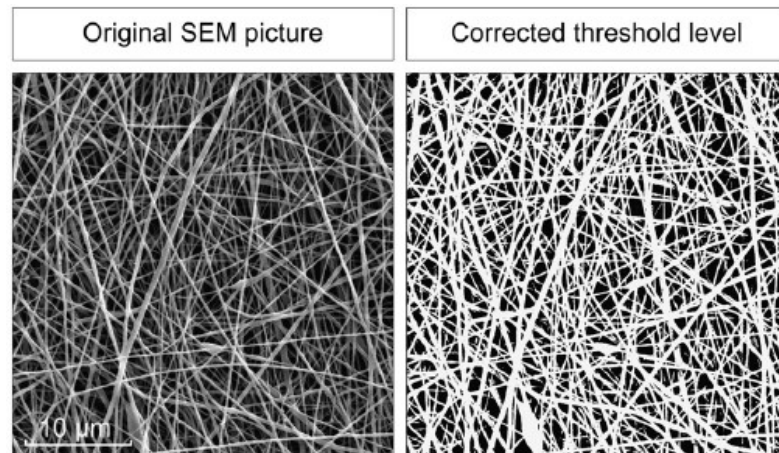


Figure 11: *Nonwoven fabric structure [17]*

Due to the one prevailing preferential direction, individual properties such as the tensile strength may have different values in the machine direction (MD) and the cross-machine direction (CD). The ratio of these two MD/CD has a significant effect on fabric performance during its use. The use of a fabric that has large differences in properties in the individual directions for multi-axis stresses, for example in filter media, could lead to failure. Because such fabric will not withstand this stress. This deficiency can be solved by reinforcing of a fabric to compensate the anisotropic properties. The production of a nonwoven fabric can be simply divided into two stages:

- preparation of a web
- bonding of this web to form a uniform layer of fabric structure

Furthermore, the fabric is then converted into the final product. This final product often consists of a combination of multiple materials. There are many methods of shaping and joining individual strips to create complex properties of the final product. We can choose from these methods for example:

- drylaid (carding and airlaid)
- wetlaid and spunmelt (spun bond and melt blown)
- mechanical processes (stitchbonding, hydroentangling and needlepunching)
- chemical and thermal processes

[15]

## 4.1 Carding

Carding is based purely on the mechanical action, by which the fibres are anchored to one surface and the second surface combs them out. The aim is to separate the tangled tufts of fibres and deliver the individual fibres in the form of a web. A carding machine, presented in Figure 12, consists of many cylinders, the main large rotating cylinder covered with needles is in the middle, and metallic teeth or wire. The cylinder is surrounded by many small cylinders. The fibres are fed by feeding rollers and condensed into lap or batting and are fed to the main cylinder. The needles of the main cylinder and small cylinders are inclined in opposite directions and move at different speeds. Usually the velocity of main cylinder is higher than the velocity of small cylinders. This difference between directions and velocities causes the fibre clumps to be teased apart. Moreover there is the stripping roller, which strips the larger tufts and positions them back on the cylinder. The fibres are straightened in the machine direction and form a coherent web on the main cylinder. Finally, doffing comb takes fibres from the doffer. The fibres are then sent further to the manufacturing process. [16]

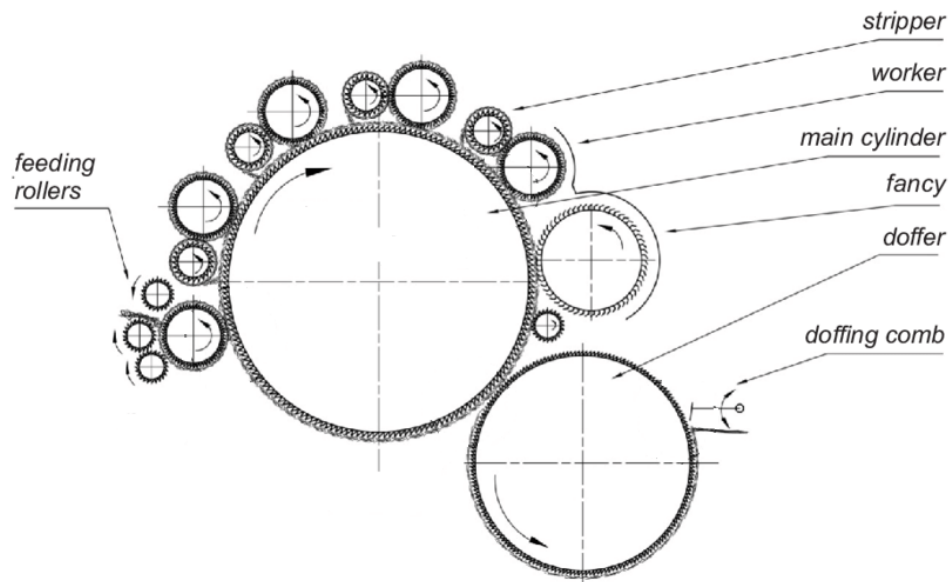


Figure 12: Scheme of carding machine [19]

## 4.2 Air laying

The air laying has one advantage that this process produces the final batt in one stage. There is no needed to make a lighter weight web in the first step. This method is also able to operate at higher production speeds. The diagram in Figure 13 shows the scheme of an air-lay machine, of course, in practice, the production lines could be different from this scheme. Firstly, there is the opening/blending section, which opening fibres. Then fibres are fed into the back of hopper, which delivers the fibres to the feed rollers. Then the opening roller takes the fibres. The opening roller is revolving at high speed. The fibres from the surface of the opening roller pull down a strong airflow and flow them onto the conveyor on which the batt is formed. The stripping rail stops recirculating of fibres on the opening roller. Subsequently, the air flow helps to stabilize the product as shown in D. [20]

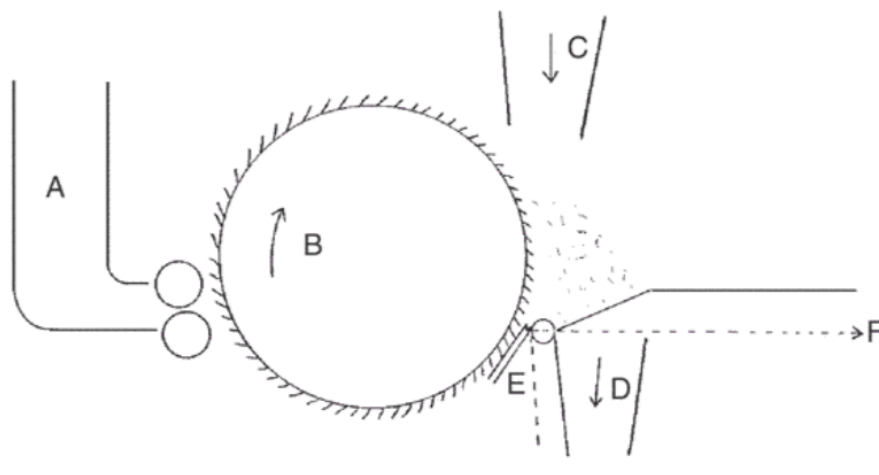


Figure 13: Scheme of air-laid machine: (A) hopper/chute feed, (B) opening roller, (C) air flow from fan, (D) suction to fan, (E) stripping rail, (F) batt conveyor [20]

### 4.3 Wet laying

This process is derived from the paper making process. The diagram in Figure 14 represents an example of the wet laying process. The fibres are cut to a textile standard (6-20 mm). This method is used for materials, which can be dispersed in fluids. These fibres are then dispersed in water. Furthermore, it is necessary to prevent the aggregation of the fibres, which can be ensured by a high dilution rate. For the processing of textile fibres machines known as “inclined-wire machines” are used. In practice, a mixture of textile fibres with wood pulp is often used because it reduces fibre aggregation and also reduces the cost of raw materials. Wet nonwovens do not represent a large share of the world market, only ca. 10 %. Products made using this technology are mainly used as disposable products such as one-use filters, in hospital as drapes and gowns. The method of wet laying is used more frequently in the paper industry. [20, 21]

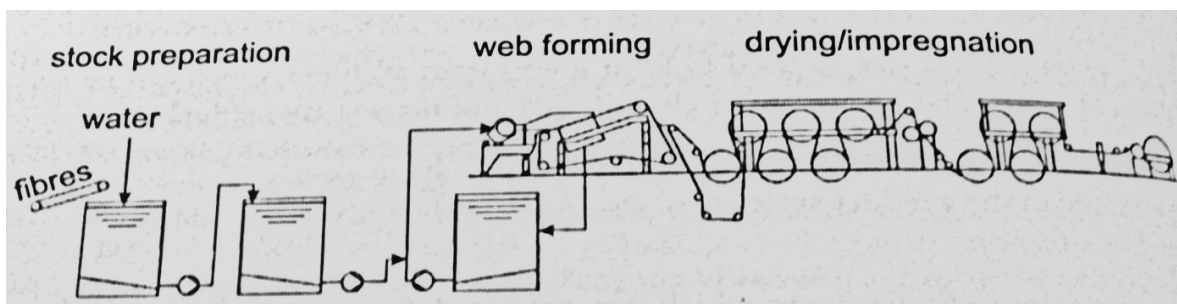


Figure 14: Scheme of wet laying process [21]

#### 4.4 Spun bond

This process is based on the extrusion of continuous filaments, their drawing and their subsequent position in a web. The spun bond process provides the shortest route from polymer chip to a fabric in a single process. The formation of web starts with a melt extrusion. Thermoplastic polymers, mostly polypropylene and polyesters, are commonly used. The important materials are also polyamide, polyethylene, and polylactic acid.

As shown in the Figure 15, the polymer is supplied from a polymer hopper to screw extruder where it is melted and then through metering pump conveyed to the spinneret plate. The spinneret plate has many holes in it and the polymer is extruded through them. The fibres begin to solidify in the air. Airflow drawing is used to achieve the correct fibre structure and mechanical properties, such as a modulus. The drawn fibres must be conveyed to the storage belt equally. The bonding of fibres to the agglomerations must be avoided because these agglomerations could produce visible strings in the resulting structure. One possible solution to this problem is the passage of the fibres through the Venturi system (high-velocity and low-pressure zone) which is encouraged by fanning. Our goal is the most uniform web as possible in mass per unit area and the desired distribution of filament orientation. [15]

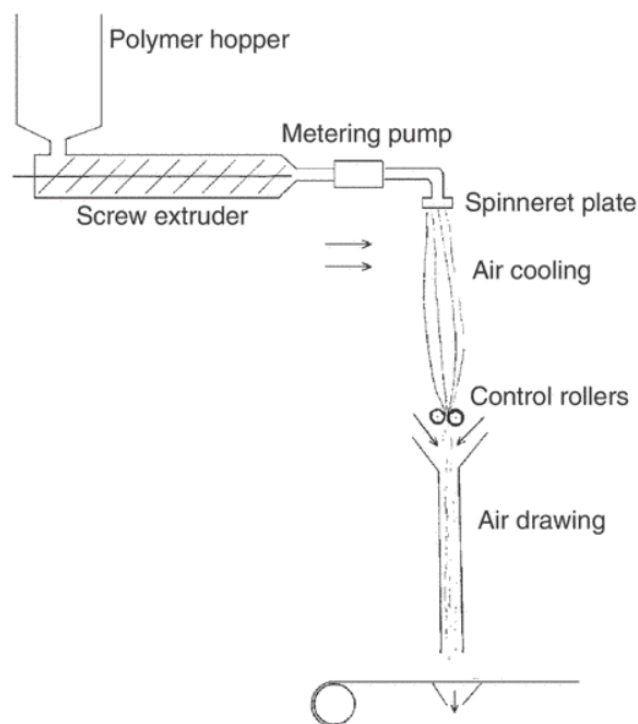


Figure 15: *Scheme of a spun-laid process [20]*

## 4.5 Melt blown

The melt blown process enables the extrusion of the extremely fine fibres, that are collected in a matrix to form a fabric. The process for producing melt blown fibres is shown schematically in Figure 16. The polymer is first collected in a hopper and then melted in an extruder. The extruder has a substantially similar structure to that used in extrusion of films and tapes. The air supply nozzle is directly part of spinning die. Temperatures in this process are usually higher than those of the melt spinning. The fine fibres are carried by the air flow onto the collecting belt where they form a web. [10]

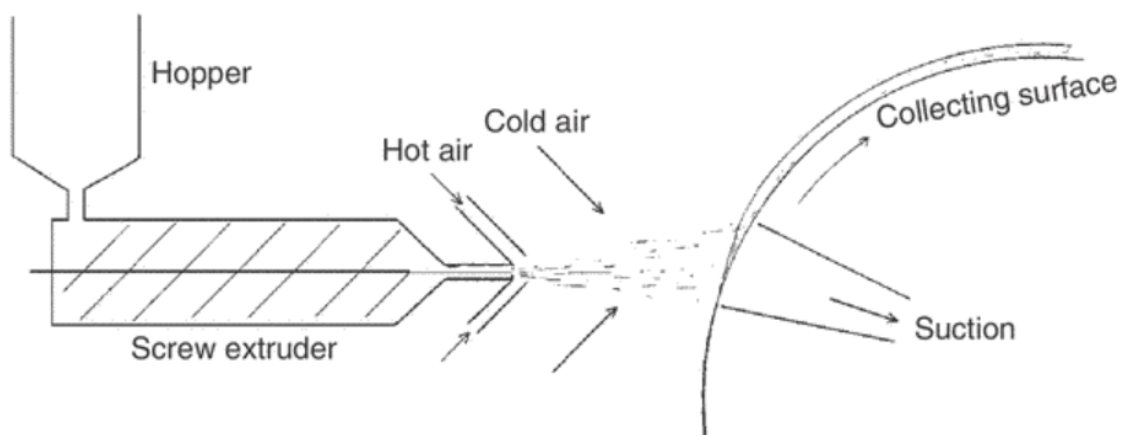


Figure 16: *Scheme of melt blown equipment [20]*

#### 4.6 Spun bond + Melt blown

Compared to traditional fabrics, nonwoven fabrics have some advantages such as reduced cost and especially random overlapping of fibres. This randomness produces the filtering properties of the nonwoven fabric. The size of the pores can range from 1-100  $\mu\text{m}$ . The smaller the pores, the more effective barrier properties are. Surface weight of nonwoven fabrics can be as low as  $5 \text{ g.m}^{-2}$ , which is lesser than for lightweight woven fabrics ( $90 \text{ g.m}^{-2}$  to  $160 \text{ g.m}^{-2}$ ). All this mentioned properties make nonwoven fabrics ideal for the use in medical garments, drapes and in filtering devices. However, the nonwoven fabrics are found in many other applications. The spun bond fabrics are used on mattresses' covers and cloth-feel baby diapers. The fibres produced by the spun bond are thicker and therefore stronger. On the other hand, the melt blown fibres are finer and have better filtration properties. Therefore, these two technologies are often combined. The melt blown fabrics create the highly impermeable layer and the spun bond ones provide the strength layer. [22]

There are many types of structural combinations, the most commonly used are the spun bond-melt blown-spun bond (SMS) or the spun bond-melt blown-melt blown-spun bond (SMMS). In the SMS constructions, the spun bond fibres are on the outer layer to provide strength and support for the overall layer system and surface abrasion resistance. The melt blown fibres reduce the liquid penetration and remains vapour permeable. [15, 23]

## 4.7 Use of nonwovens

Table 1 lists some of the possible uses of nonwovens.

Table 1: *Examples of using nonwovens*

Hygiene	baby diapers, ladies' hygiene products, dry and wet pads, incontinence products...
Healthcare	operation drapes, gowns and packs, face masks, swabs...
Automotive	boot liners, shelf trim, oil and cabin air filters, airbags, tapes...
Construction	roofing and tile underlays, thermal and noise insulation...
Filtration	air and gas, Hevac, Hepa, Ulpa filters...
Home	wipes and dusters, tea and coffee bags, fabric softeners, food wraps...
Geotextiles	asphalt overlay, soil stabilization, drainage...

[21]

Main market segments in terms of volume of nonwovens roll goods in 2016 were:

- hygiene (30.9 %)
- wipes for personal care (12.4 %)
- construction (9.5 %)
- civil engineering (6.3 %)
- automotive (5.9 %)
- upholstery/household (3.7 %)
- filtration (3.6 %)

[24]



## 4.8 Materials for nonwovens

Virtually any fibre can be used to produce nonwoven fabrics. The choice depends on the application as well as the cost. The most used are chemical fibres (cellulosic and synthetic), natural fibres and inorganic fibres as shown in Figure 17. [21]

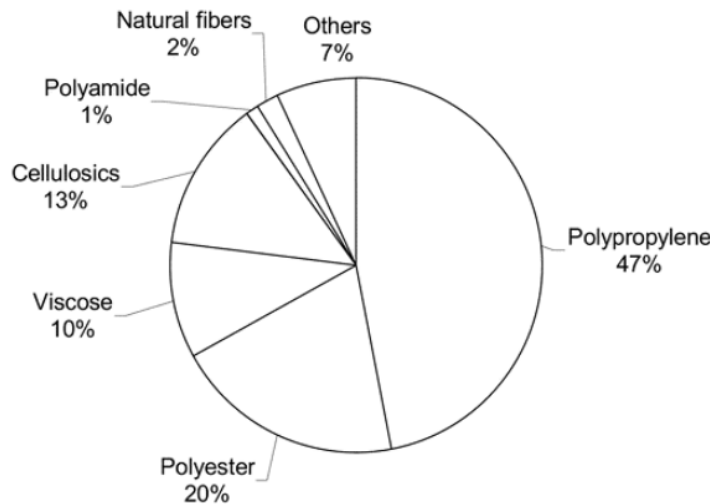


Figure 17: Fibre materials for nonwovens [25]

Nonwovens made by the spun bond process are preferably made from the thermoplastic polymers such as polypropylene (PP) and polyester. Polymers such as polyethylene of high density (HDPE), linear polyethylene of low density (LLDPE) and polyamides (PA) are used less. The great advantages of PP are low price, chemical resistance, hydrophobicity and strength.

Polyethylene terephthalate (PET) is the second most important polymer for the nonwoven extrusion after PP. PET is suitable for applications where high heat resistance and low shrinkage are required, for example bituminated roof covering. The spun bond and melt blown nonwovens for applications, which require a higher intrinsic viscosity, are often made out of PET. In comparison with PP and PET, the polyamides are of minor importance. We find PA to a greater extent only in packaging applications. In the melt blown process, there is a very little orientation after extrusion against the spun bond process. That is reason why a wide range of polymers can be processed besides PP and PET for example HDPE, LDPE, LLDPE, PA, polystyrene (PS) and more. [21]

#### 4.9 PLA in nonwovens

PLA has a great future in nonwovens, thanks to its biodegradability. This could be a great advantage for conventional products such as geotextiles, wipes, packaging materials, filters. Under certain defined conditions, PLA fabrics are completely compostable. PLA is consumed by microbes after hydrolysis at 98% humidity and 60 °C or higher. In the composting process, only carbon dioxide and water are released. However, under the normal conditions, the fabrics are sufficiently durable.

The disadvantage of PLA is so far its high price. However, the price difference between PLA and traditional chemical polymers is being reduced due to the new technologies and rising oil prices. Thus, PLA combines environmental benefits with very good technical performance in the textile industry, as a high mechanical strength. The properties of PLA fibres are between the properties of PA 6 and PET. Generally, the properties of PLA are compared to PET. This comparison is shown in Table 2. [26, 27]

Table 2: *Fibre properties of PLA and PET*

Fibre properties	PLA	PET
Specific gravity	1.25	1.39
Melting point [°C]	130-175	254-260
Tenacity [g.d <sup>-1</sup> ]	6	6
Elastic recovery [5% strain]	93	65
Moisture regain [%]	0.4-0.6	0.2-0.4
Flammability	Continues to burn for 2 minutes after flame removed	Continues to burn for 6 minutes after flame removed
Smoke generation [m <sup>2</sup> .kg <sup>-1</sup> ]	63	394
Limiting oxygen index [%]	26	20-22
Refractive index	1.35-1.45	1.54
Breaking strength [cN.dtex <sup>-1</sup> ]	2.5-5	3.4-6.5
Breaking elongation [%]	35	15-40
Youngs modulus [GPa]	6-7	10-13

[27]

#### 4.10 PLA in spun bond process

Here is a specific procedure for processing the PLA with the spun bond process:

PLA chips – drying – screw extruder – filter – measured – spinning – air cooled – air draft – web formation – needle-punched – points cut and coiling

Process conditions:

- Drying temperature 80-90 °C at least for 4 hours
- Pressure at screw extruder 8-12 Mbar
- Filtered net above 300 µm
- Spinneret diameter 0.25-0.35 mm
- Value of draft speed 5000 m.min<sup>-1</sup>

[28]

#### 4.11 PLA in melt blown process

Here is a specific procedure for processing the PLA with the melt blown process:

PLA chips – drying – melt-extrusion – fibres formed – fibres cooling – web formation – web bonding – edge cutting and winding – finishing treatments

Process conditions:

- Drying temperature 80-90 °C at least for 4 hours
- Spinning temperature 220 °C (too high temperature reduces the molecular weight and ability of turning into fibre)

[28]

For polymeric materials, it is possible to modify them, thus adjusting the mechanical properties of the final product. For example, in a PLA plasticizer affects polymer spinning. If the spinability has been improved or worsened, can be verified before spinning using rheological methods. More in the practical part.

## **II. ANALYSIS**

## 5 THE AIM OF THE WORK

The aim of this work was to relate the elongation properties of PLA melts with their spun bond ability. Pure PLA and PLA with plasticizer addition in concentration 1 %, 3 % and 6 wt.% were characterised using various rheometry experiments:

- Rotational rheometer Advanced Rheometric Expansion System (ARES 2000) equipped with Sentmanat Extension Rheometer (SER)
- Capillary rheometer Göttfert RG25-50 equipped with the Rheotens system
- Cogswell principal with the help of Göttfert RG25-50 Capillary rheometer

Further thermal characterisation of PLA was carried out using Differential Scanning Calorimetry (DSC):

- Mettler Toledo DSC 1/700

At the end the defined rheological properties were discussed in the relation to the spun bond manufacturing process of non-woven webs textiles.

## 6 EXPERIMENTAL CHARACTERISATION

In this chapter are listed the devices and methods used in the experimental part of this work.

### 6.1 Rheology analysis

The extensional deformation behaviour of substances, especially the deformation and stress dependence, were described using selected rheological experiments. The utilised characteristics of deformation behaviour are listed below.

#### 6.1.1 Rotational rheometry with SER geometry

It is used to characterize the flow and viscoelastic properties of polymer melts at low and medium strain rates. A sample in the form of a thin film of thickness approximately 0.5 mm measured for the elongation viscosity is inserted between the rotating cylinders of the measuring geometry (see Figure 18) and its resistance to the elongation flow is recorded by the torque sensor. Measurements by the help of ARES 2000 are based on the rotation of lower geometry and sensing of the torque to and normal force on top geometry.

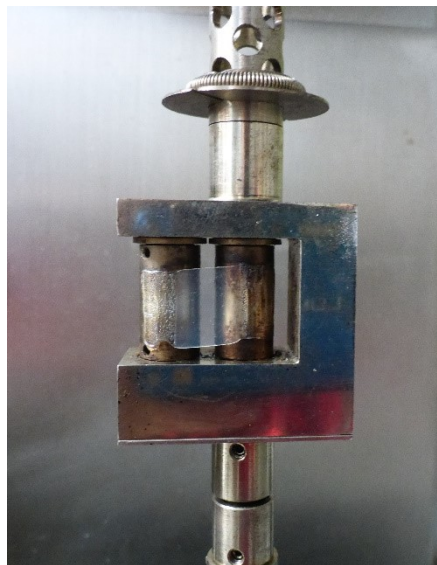


Figure 18: *Attaching the sample to geometry*

### 6.1.2 High pressure capillary viscometry

The Göttfert RG25-50 capillary rheometer, presented in Figure 19, was used to measure the shear/elongation viscosity at high shear/elongation strain rates of polymers.



Figure 19: *Capillary rheometer Göttfert RG25-50*

#### 6.1.2.1 *Shear viscosity measurements*

The pressure required for generation of shear stress is exerted by the piston. The measured characteristic values are the pressure drop along the length of the capillary, the temperature and the volume flow. The calculated shear stress and shear rate are usually corrected with Bagley (correction of the entrance pressure drop) and Rabinowitsch (correction of non-Newtonian behaviour) correction. [29]

The pressure drop is defined as the pressure difference at the beginning of the capillary corrected to the capillary entrance pressure using zero-length capillary and the atmospheric pressure at the end of the capillary.

### 6.1.2.2 Elongation viscosity determination via entrance flow simulation

Capillary rheometer is beside evaluation of the shear viscosity able also to determined the elongation viscosity. In such case the Cogswell model based on the principle of transferring the measured material from a wide cylinder to a narrow capillary and evaluating the pressure at the inlet to the capillary could be employed. [29]

### 6.1.2.3 Elongation viscosity measurements using extensional tester

Rheological behaviour is different for shear and elongation loads. In elongation stress, the velocity gradient is in the direction of flow. The Rheotens method is used for description of the elongation viscosity based on resistance of polymer melt extruded from the reservoir through the capillary to its extension by the rotating wheels that are part of the balance located under the capillary, as displayed in Figure 20. With increasing piston velocity the melt force applied to the balance is recorded and the elongation viscosity is calculated based on the resistance force development during the melt elongation acceleration. [29]

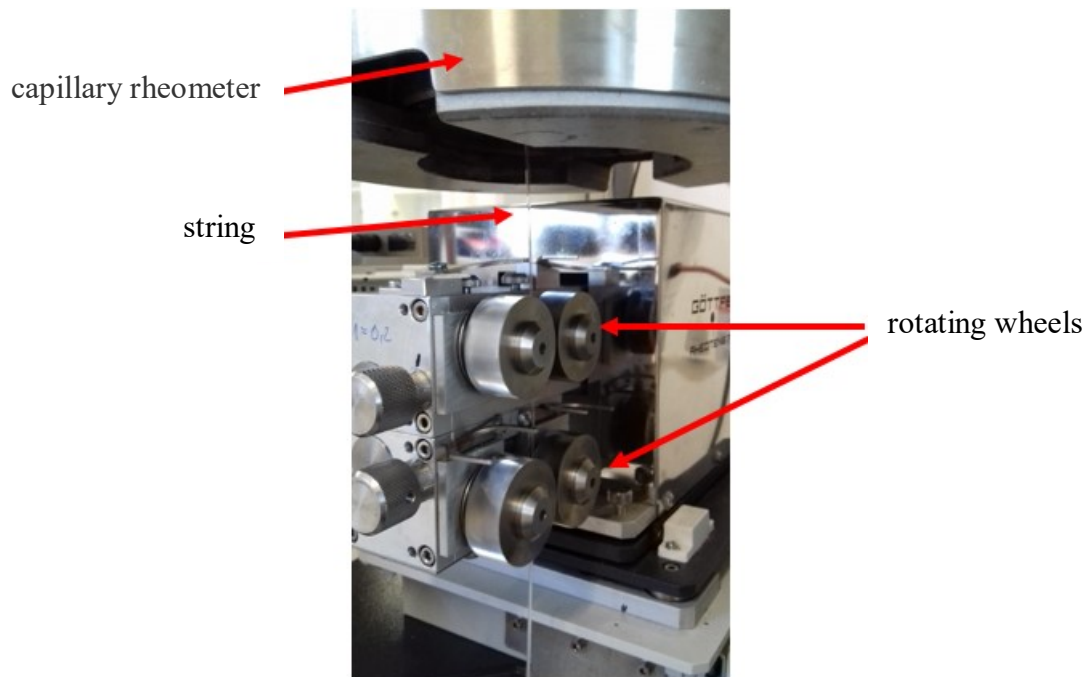


Figure 20: *Capillary rheometer Göttfert with Rheotens device*



## 6.2 Thermal analysis

The thermal analysis are utilised for description of the properties of materials that change with temperature. Many methods can be used, one of them is differential scanning calorimetry.

### 6.2.1 DSC

The DSC method is based on comparison of heating of the crucible with encapsulated sample and the empty reference one. The sample is heated in the furnace applying the same heating flow. Then, when the thermal transition region of the material are reached, for example, the endothermic, the temperature lag in the crucible with sample occur comparing to the reference pan since the endothermic transition consumes more energy. Therefore, the principle of the DSC method is to measure the difference in temperatures between the sample and the reference crucible. Most often are measured the melting temperature, the recrystallization temperature, the glass transition temperature and also the heat capacity. Mettler Toledo DSC 1/700 (see Figure 21) was used for measurement. [30]



Figure 21: *Mettler Toledo DSC 1/700*

## 7 EXPERIMENTAL SETUP/PROCEDURE

This chapter will describe the workflow, setup of the devices and commentary of the results.

### 7.1 Materials employed

- PLA - Ingeo 4043D (NatureWorks LLC, USA)
- Plasticizer PES – (Preluna, Germany)

Compound of PLA and plasticizer (with 1, 3 and 6 wt.%) were obtained as granules prepared in advanced using twin-screw extruder.

### 7.2 Material drying

PLA, plasticizer and PLA/plasticizer granules were dried at 60 °C for 4 h. The drying procedure was applied prior to compounding, DSC experiments, pressing and capillary viscometer characterisation.

### 7.3 DSC measurement

Samples for DSC were prepared from the supplied granules. The aim was to determine the melting temperature of the individual materials. The melting temperature was important for setting of instruments in the next experimental steps. In Charts 1-2 thermal behaviour of pure PLA and plasticizer is presented, while PLA compounds containing 1, 3, and 6 wt.% of plasticizer is shown in Charts 3-5, respectively. For the experiments two following heating/cooling scans in the region 25-230 °C was employed. Whereas the first heating and the last cooling scans were set with the temperature rate of 50 °C.min<sup>-1</sup>, for the second heating and first cooling scans the rate of 10 °C.min<sup>-1</sup> was chosen.

Further, PLA for pure PLA, PLA 1 for PLA with 1 wt.% plasticizer and so on will be used in the descriptions.

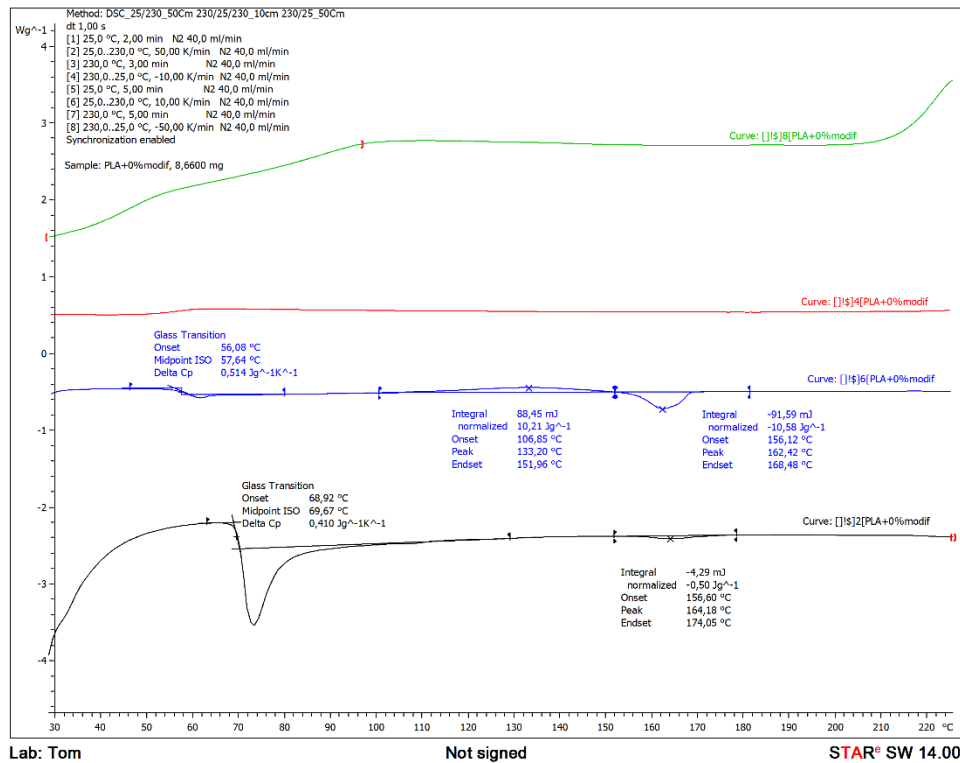


Chart 1: DSC evaluation for PLA

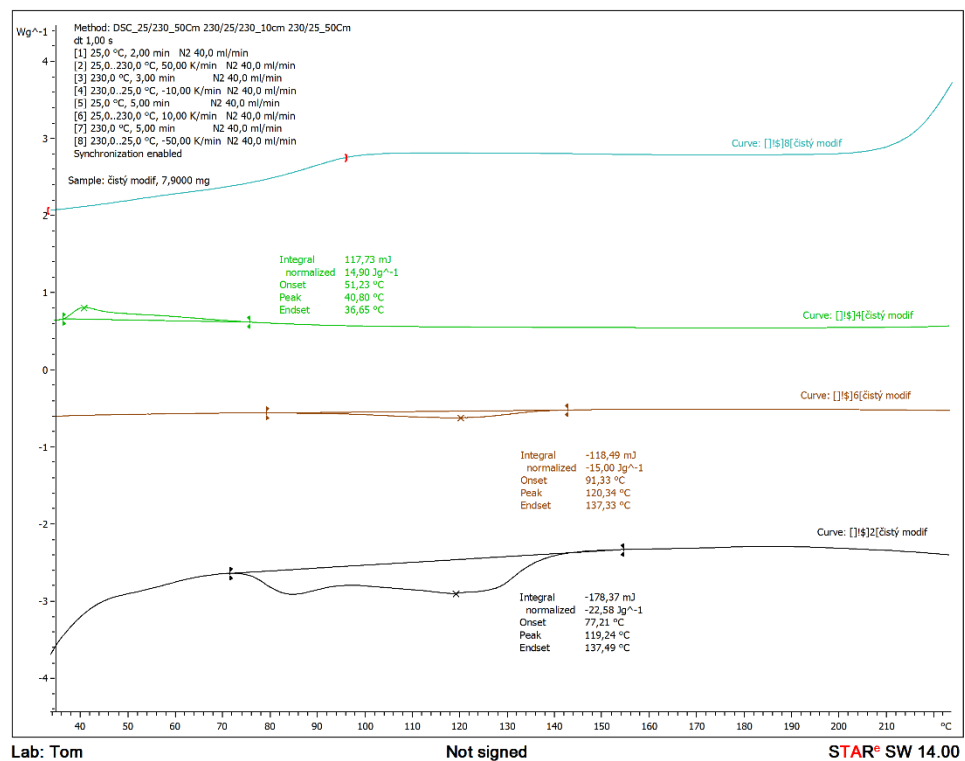


Chart 2: DSC evaluation for plasticizer

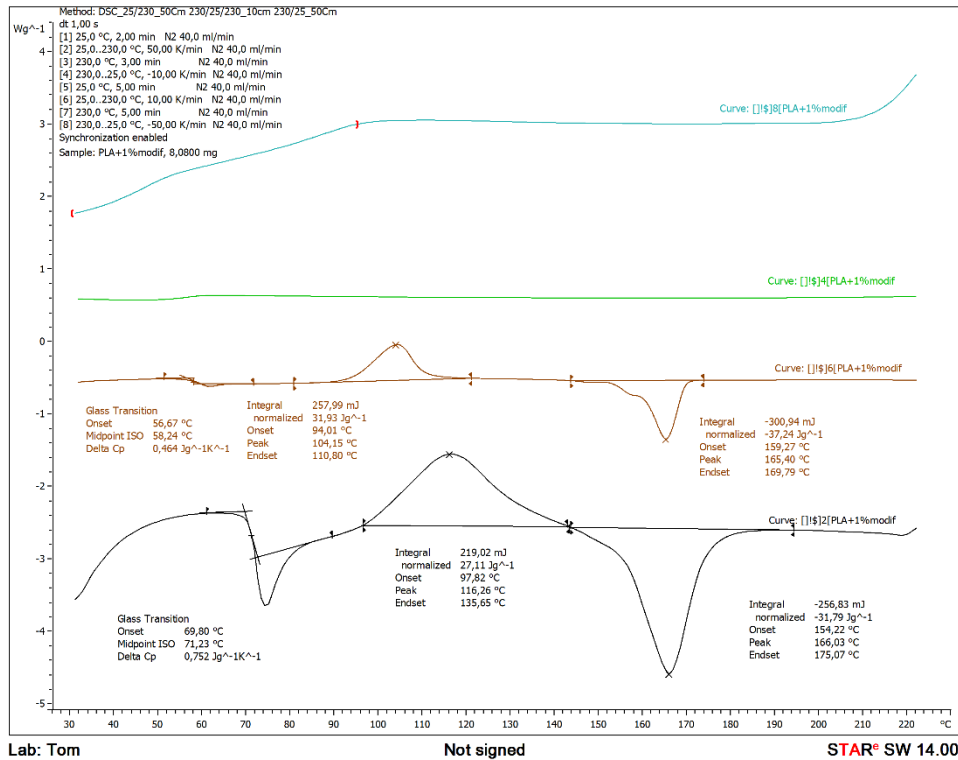


Chart 3: DSC evaluation for PLA 1

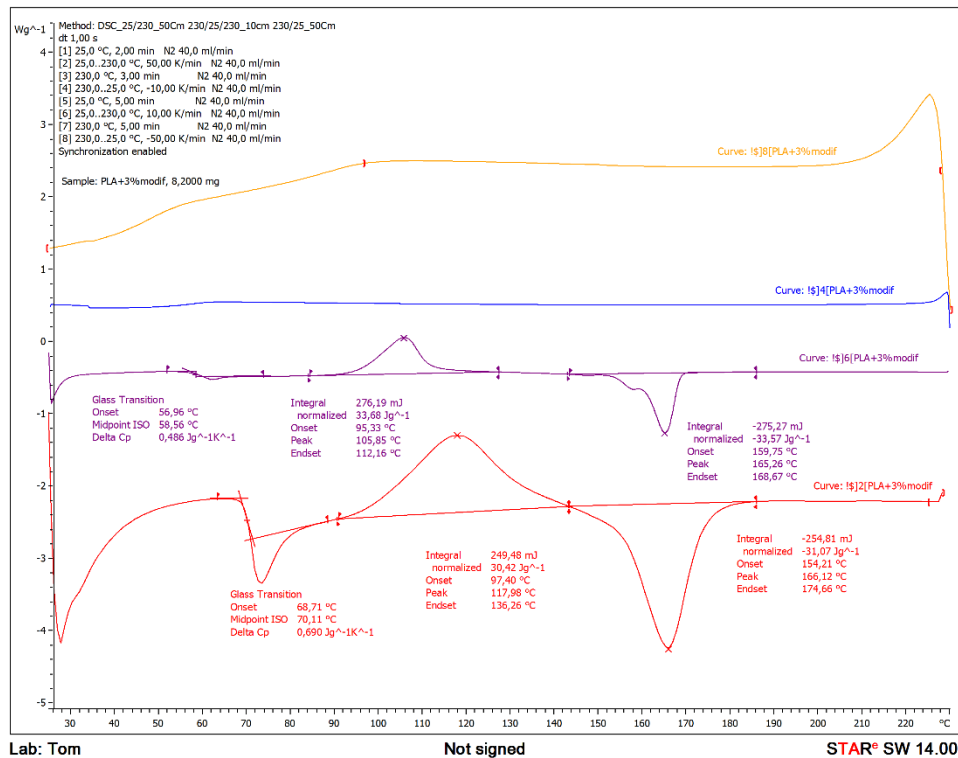


Chart 4: DSC evaluation for PLA 3

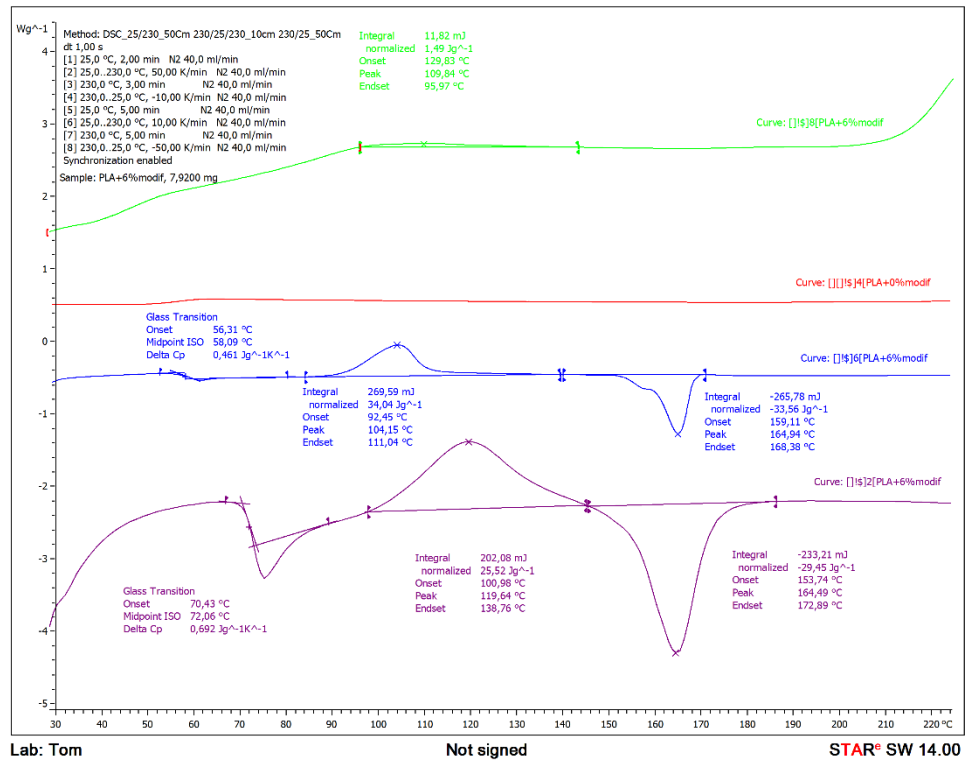


Chart 5: DSC evaluation for PLA 6

7.3.1 Discussion of results

Table 3: Characteristic temperature evaluated from the second heating scan

Material	Glass transition temperature [°C]	Cold crystallization temperature [°C]	Melting temperature [°C]
Pure PLA	58	133	162
Plasticizer	-	-	120
PLA 1	58	104	165
PLA 3	59	106	165
PLA 6	58	104	165

Table 3 shows characteristic temperatures for individual materials. Melting point for pure PLA is 162 °C and for compounded PLA 165 °C and for pure plasticizer 120 °C. From this we deduced temperature settings for other processes. For example, a temperature of 175 °C was set to characterize rheological properties.

#### 7.4 Manual pressing of testing plates

The testing specimens with dimensions of 150x150x0.5 mm for rotational rheometry characterisation were prepared from granules by the help of manual presses, presented in Figure 22. While the melting press was heated to the temperature 210 °C, the other one used for melted pressed specimens cooling was tempered with cold water of the temperature 15 °C. Four plates of each material were prepared (pure PLA, PLA with 1 %, 3 % and 6 % of plasticizer). The prepared plates were kept in a desiccator throughout the further experimental process.



Figure 22: *Hand presses*

## 7.5 Rotational rheometry with SER geometry

The elongation viscosity was evaluated on an ARES 2000 instrument. Small samples of dimensions 20x12.5x0.5 mm were cut out of the prepared plates. The measurement was carried out at 175 °C in a nitrogen atmosphere. Elongation strain rates were 20 s<sup>-1</sup>, 10 s<sup>-1</sup>, 5 s<sup>-1</sup>, 3 s<sup>-1</sup>, 1 s<sup>-1</sup>, 0.5 s<sup>-1</sup> for each material. Because the elongation viscosity calculated using equations suggested by Sentmanat [31] did not return in realistic values (see large increase in elongation viscosity in Chart 6 the raw measured torque data is used for farther comparison of extensional behaviour. Observed incoherent rise of elongation viscosity is likely caused by an impropriety of original calculation formula for the PLA melt strength. While each tested material was measured at least three times, in Charts 7-12 the most coherent values of the torque-time dependency are displayed.

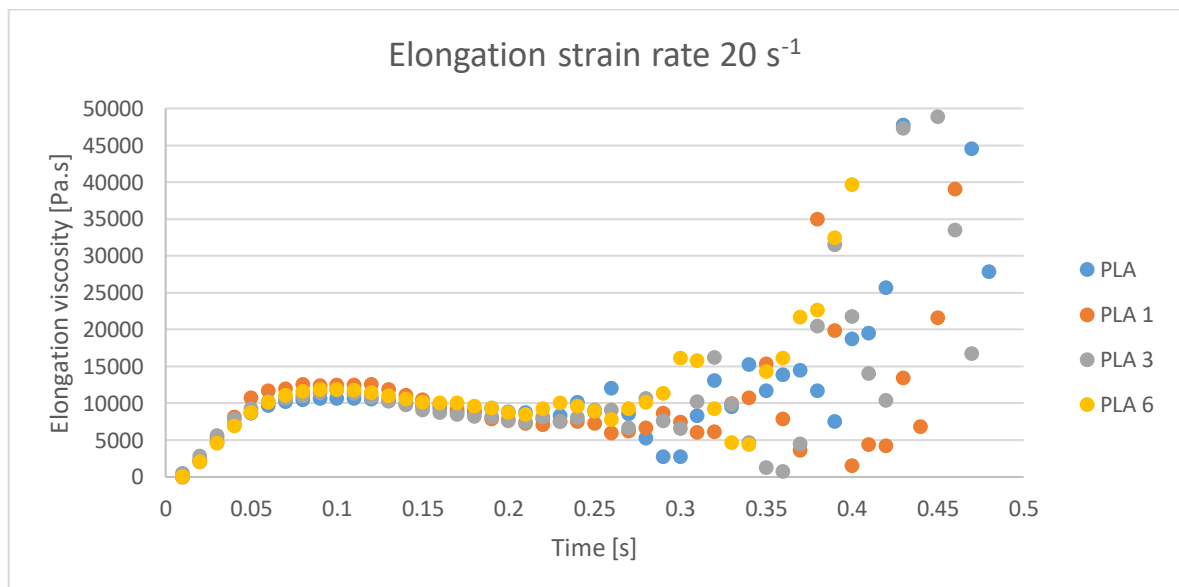


Chart 6: *Elongation viscosity dependence on time for elongation strain rate 20 s<sup>-1</sup>*

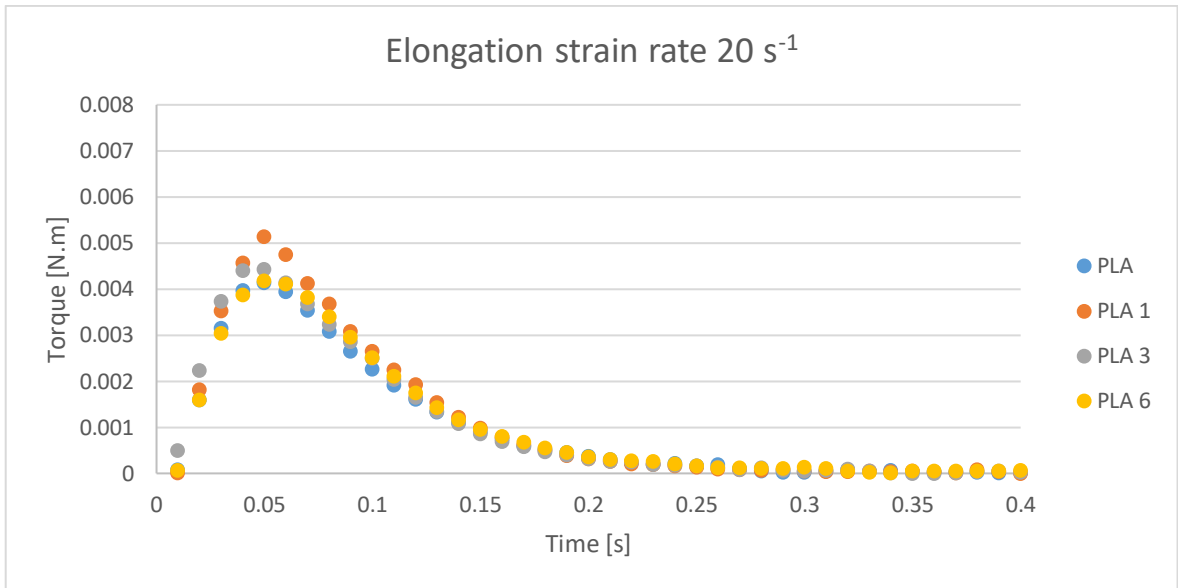


Chart 7: Torque dependence on time for elongation strain rate 20 s<sup>-1</sup>

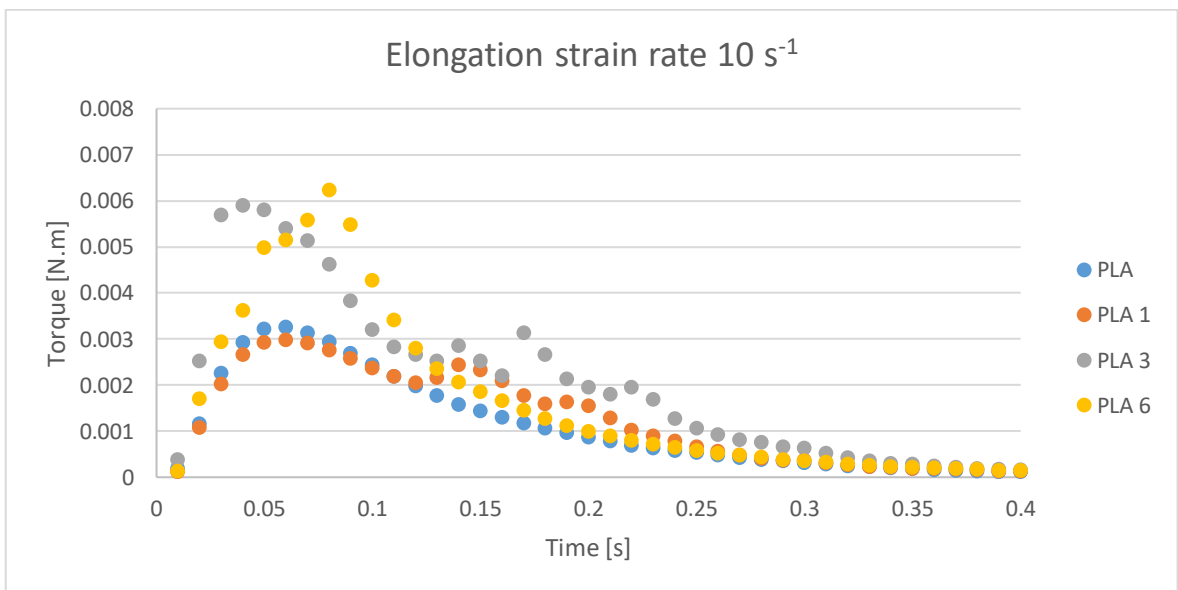


Chart 8: Torque dependence on time for elongation strain rate 10 s<sup>-1</sup>



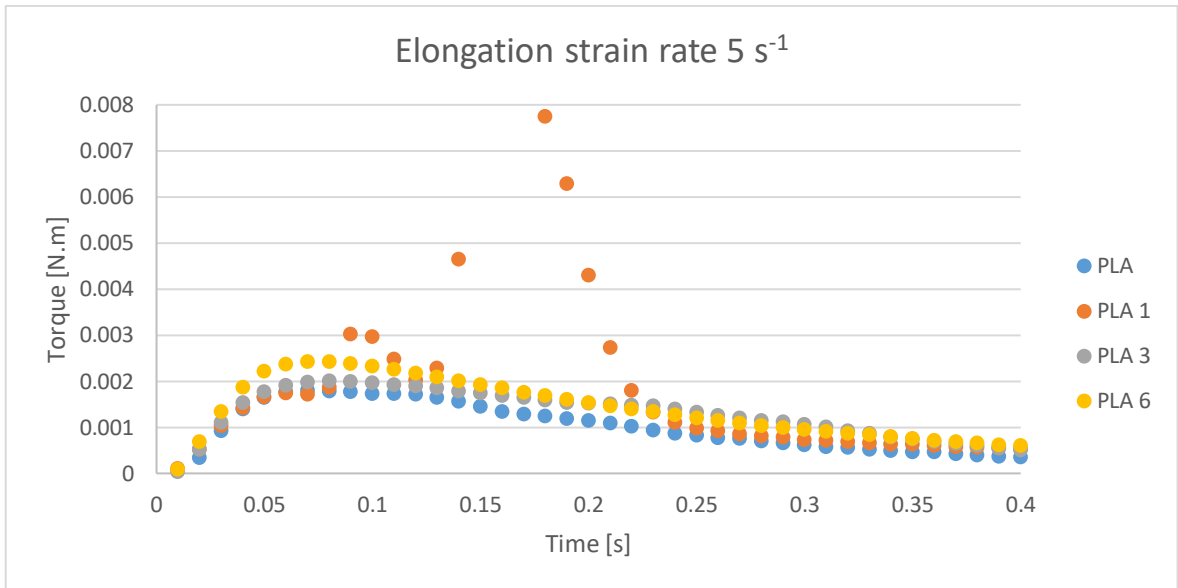


Chart 9: Torque dependence on time for elongation strain rate 5 s<sup>-1</sup>

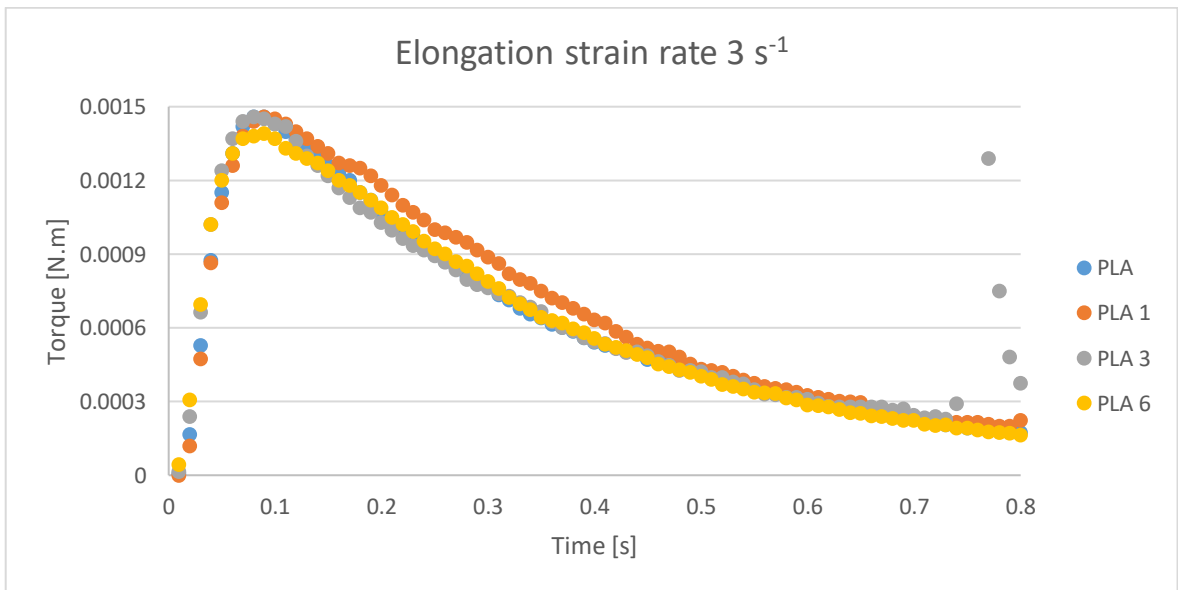


Chart 10: Torque dependence on time for elongation strain rate 3 s<sup>-1</sup>

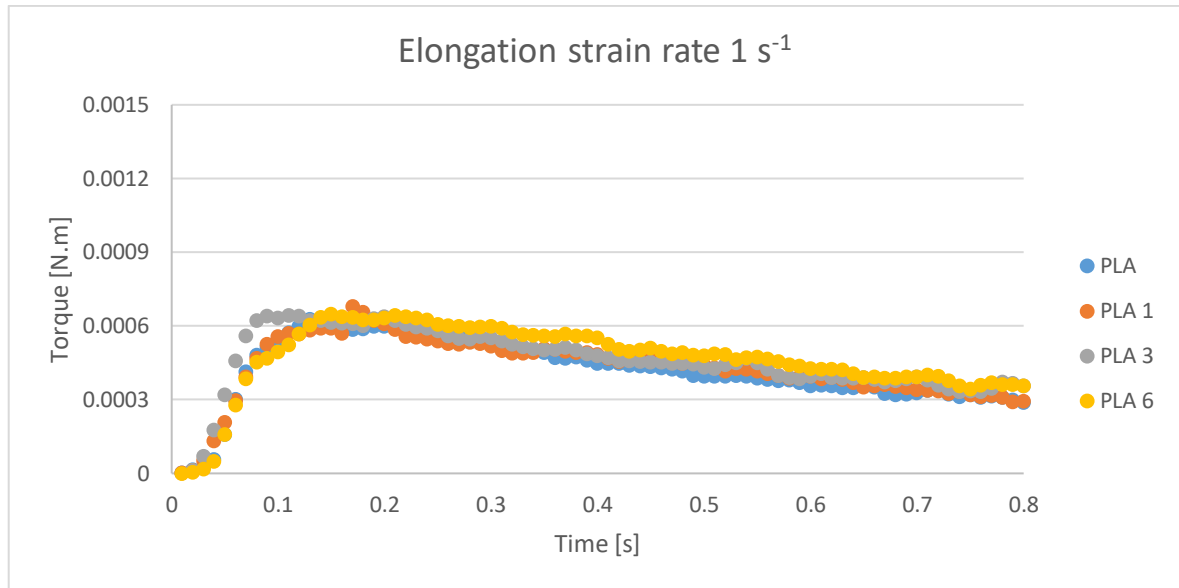


Chart 11: *Torque dependence on time for elongation strain rate  $1 \text{ s}^{-1}$*

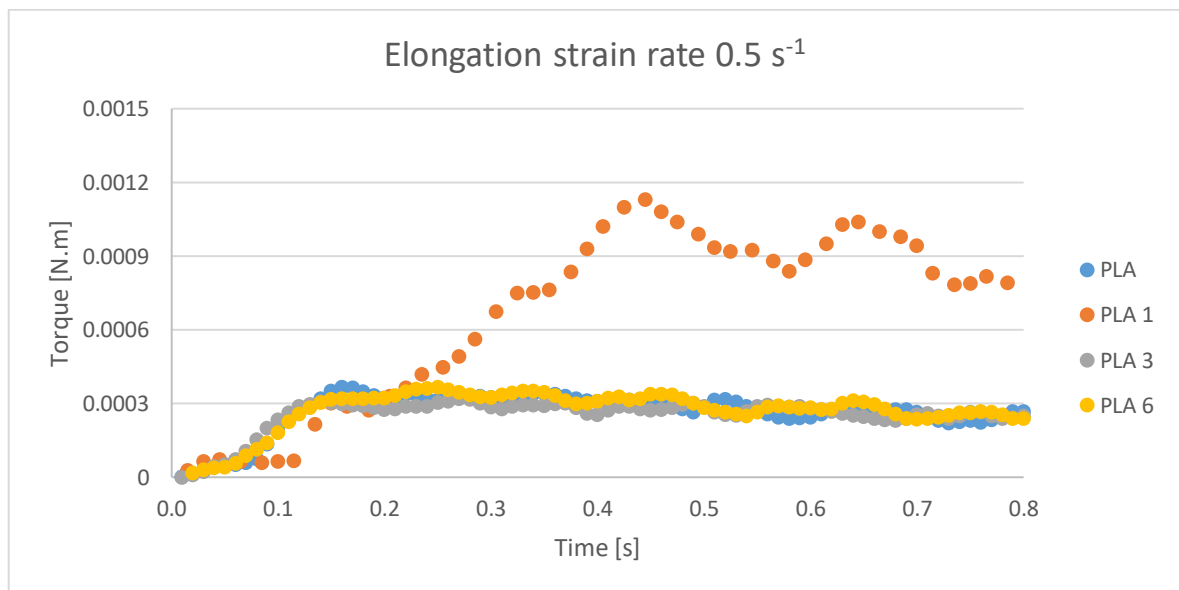


Chart 12: *Torque dependence on time for elongation strain rate  $0.5 \text{ s}^{-1}$*

### 7.5.1 Discussion of results

The measurement results were often inconclusive and the measurements had to be done multiple times but the measured data still did not produce smooth curves in some cases. However, it appears from the graphs that none of tested PLA materials display significant difference in extensional behaviour. Based on this finding it can be concluded that these materials seems to have the similar extensional strength favourable for melt spinning process.

## 7.6 Elongation viscosity measurements using extensional tester

The molten granules of tested materials were pressed out from capillary rheometer Göttfert RG25-50 with the constant piston speed of  $0.32 \text{ mm}\cdot\text{s}^{-1}$ . The extruded string was pulled by the four wheels of the Rheotens device. After starting the measurement, the take-off speed was gradually increased up to the speed when the string was broken. Multiple curves were measured and they are overlapped in the Chart 13.

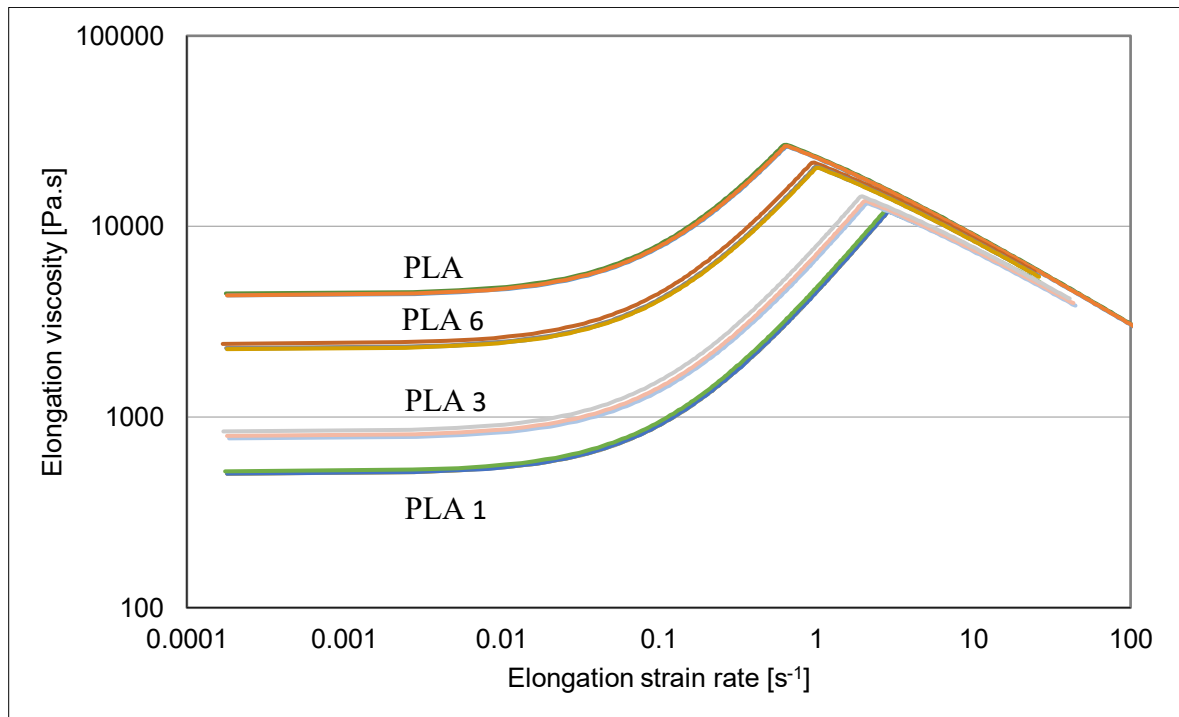


Chart 13: *Elongation viscosity dependence on elongation strain rate*

### 7.6.1 Discussion of results

It can be seen in the Chart 13, that PLA 3 and PLA 1 have a lower values of elongation viscosity comparing to PLA and PLA 6. However, the peaks of strength hardening of PLA 1 and PLA 3 was observed at the higher values of elongation strain rate. In connection to the results of nonwoven textile manufacturing when PLA 1 and 3 proved to be better for spinning, seems to be the strength hardening the crucial property defining ability of polymeric material for fibre production. It is also worth pointing out that this measurement process is closest to practical spinning.

## 7.7 Elongation viscosity determination via entrance flow simulation

The measurements of viscosity data was taken for each material in a series of defined apparent shear rates from 35 to 2000  $\text{s}^{-1}$ . The measured data was corrected by Bagley and Rabinowitsch corrections. Corrected shear viscosity as a function of corrected shear rate is shown in the Chart 14, while elongation viscosity calculated via Cogswell analysis as a function of extensional strain rate is depicted in the Chart 15.

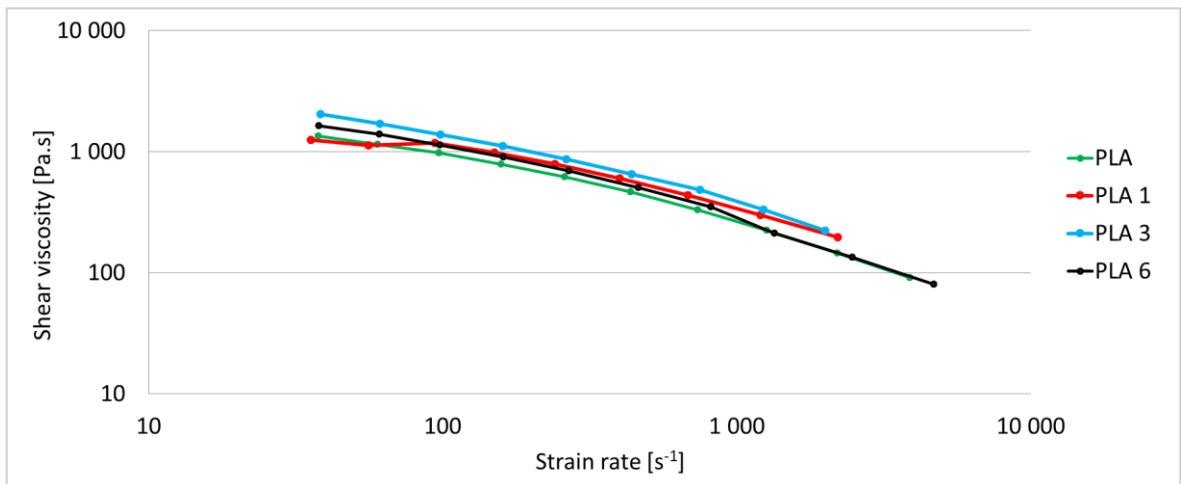


Chart 14: *Shear viscosity dependence on strain rate*

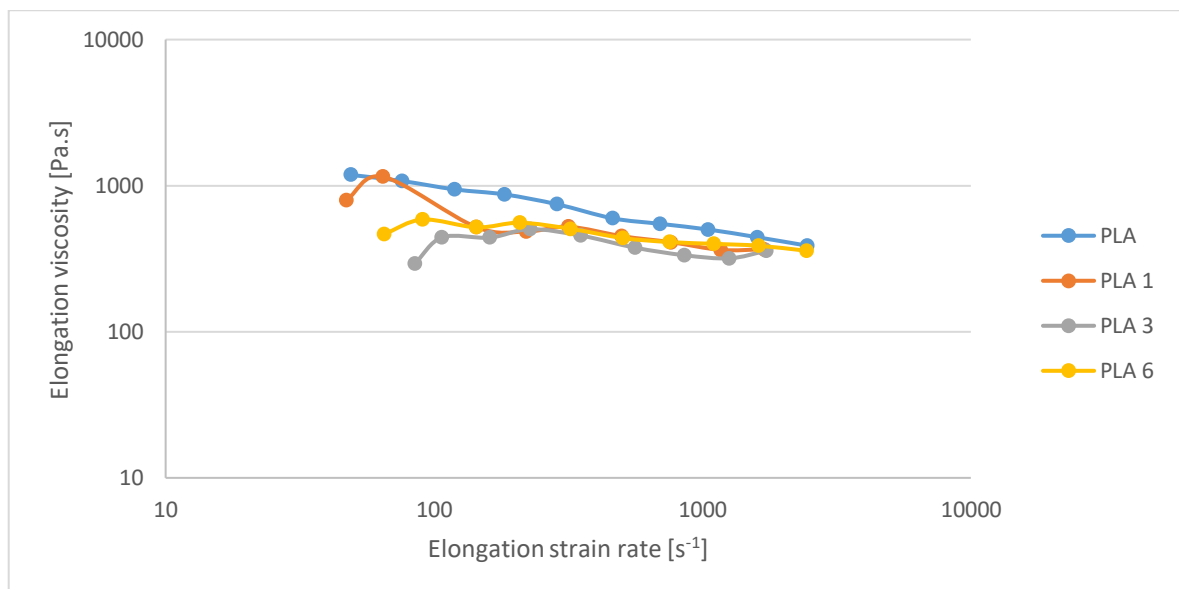


Chart 15: *Elongation viscosity dependence on elongation strain rate*

### 7.7.1 Discussion of results

It can be seen in the Chart 14 that whereas the lowest shear viscosity was determined for pure PLA, increase in shear viscosity due to the presence of plasticizer is not significant. The highest value was observed for PLA compounded with 3 wt.% of plasticizer, while further addition of plasticizer induced viscosity decrease. From the comparison of results of shear and elongation viscosity presented in the Chart 14 it could be noted that values elongation viscosity are below the level of shear viscosity for low strain rates. Such behaviour which is not in agreement with a theory, defining that the elongation viscosity in Newtonian plateau region is triple of the shear one, could be connected to the low entrance pressure of PLA melt. The highest elongation viscosity in measured region of strain rates was determined for pure PLA melt. Elongation viscosity values of PLA 1, PLA 3 and PLA 6 follow roughly the same trend and level so unique influence of plasticizer addition could not be evaluated via this method. Such behaviour does not correspond to practical observations during nonwoven textile production.

## CONCLUSION

Finally, it can be said that the measured data on the ARES 2000 instrument were not coherent and we cannot draw any conclusive conclusion for melt spinning process.

Elongation viscosity measurements using the extensional tester have proven to be very good characteristics for melt spinning, where strength hardening appears to be an important characteristic for melt spinning. It was seen here that the PLA 1 and PLA 3 materials are suitable for the production of nonwovens, which also confirmed practical observation.

In the measurement of elongation viscosity, it is strange that it does not coincide with theory defining that the elongation viscosity in Newtonian plateau region is triple of the shear one. Elongation viscosity values of PLA 1, PLA 3 and PLA 6 follow roughly the same trend and level so unique influence of plasticizer addition could not be evaluated via this method.

In conclusion, elongation viscosity measurements using the extensional tester have been found to be the best method for evaluating melt spinning process and production of nonwoven textiles.

**BIBLIOGRAPHY**

- [1] NARAYANAN, ROYCHOUDHURY and SRIVASTAVA, L (+) lactic acid fermentation and its product polymerization. *Electronic Journal of Biotechnology* [online]. 7(2) [cit. 2019-01-23]. DOI: 10.2225/vol7-issue2-fulltext-7. ISSN 0717-3458. Retrieved from: <http://www.ejbiotechnology.info/content/vol7/issue2/full/7/index.html#article>
- [2] PEREPELKIN, 2002. Poly lactice Fibres: Fabrication, Properties, Use, Prospects. *Fibre Chemistry* [online]. 34(2), 85-100 [cit. 2019-01-23]. DOI: <https://doi.org/10.1023/A:1016359925976>. ISSN 1573-8493. Retrieved from: <https://link.springer.com/article/10.1023/A:1016359925976#citeas>
- [3] LASPRILLA et al., 2012. Polylactic acid synthesis for application in biomedical devices. *Biotechnology Advances* [online]. 30(1), 321-328 [cit. 2019-01-24]. ISSN 0734-9750. Retrieved from: <https://www.sciencedirect.com/science/article/pii/S0734975011000954?via%3Dihub>
- [4] DEOPURA, ALAGIRUSAMY and GUPTA, 2008. Polyesters and Polyamides [online]. Woodhead Publishing [cit. 2019-01-24]. ISBN 978-1-84569-298-8. Retrieved from: <https://www.sciencedirect.com/book/9781845692988/polyesters-and-polyamides>
- [5] HAMAD and KASEEM, 2018. Polylactic acid blends: The future of green, light and tough. *Progress in Polymer Science* [online]. 85, 83-127 [cit. 2019-01-31]. DOI: <https://doi.org/10.1016/j.progpolymsci.2018.07.001>. ISSN 0079-6700. Retrieved from: <https://www.sciencedirect.com/science/article/pii/S0079670018300212>
- [6] LEE TIN SIN, RAHMAT a RAHMAN, 2013. Polylactic Acid [online]. William Andrew [cit. 2019-01-30]. ISBN 978-1-4377-4459-0. Retrieved from: <https://doi.org/10.1016/C2010-0-65966-9>
- [7] SUNG-BINPARK et al., 2017. Biopolymer-based functional composites for medical applications. *Progress in Polymer Science*[online]. 68, 77-105 [cit. 2019-02-17]. DOI: <https://doi.org/10.1016/j.progpolymsci.2016.12.003>. ISSN 0079-6700

- [8] BELGACEM and GANDINI, 2008. Monomers, Polymers and Composites from Renewable Resources [online]. Elsevier Science [cit. 2019-02-17]. ISBN 978-0-08-045316-3. Retrieved from: <https://www.sciencedirect.com/book/9780080453163/monomers-polymers-and-composites-from-renewable-resources>
- [9] EICHHORN et al., 2009. Handbook of Textile Fibre Structure: Fundamentals and Manufactured Polymer Fibres [online]. Woodhead Publishing [cit. 2019-02-22]. ISBN 978-1-84-569650-4. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpHTFSVFMQ/handbook-textile-fibre/handbook-textile-fibre>
- [10] GUPTA and KOTHARI, 1997. Manufactured fibre technology. Chapman & Hall. ISBN 978-94-010-6473-6
- [11] FAKIROV a STOYKO, 2017. Fundamentals of Polymer Science for Engineers [online]. John Wiley [cit. 2019-02-27]. ISBN 978-1-5231-1526-6. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpFPSE0035/fundamentals-polymer/fundamentals-polymer>
- [12] MATHER, WARDMAN a ROGER, 2011. Chemistry of Textile Fibres [online]. Royal Society of Chemistry [cit. 2019-02-27]. ISBN 978-1-62198-202-9. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpCTF00001/chemistry-textile-fibres/chemistry-textile-fibres>
- [13] ASHTER a SYED ALI, 2016. Introduction to Bioplastics Engineering [online]. Elsevier [cit. 2019-03-09]. ISBN 978-0-323-39407-9. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpIBE00013/introduction-bioplastics/introduction-bioplastics>
- [14] TONG a JIAN, 2017. Fundamentals of Electrospinning & Electrospun Nanofibers [online]. DEStech Publications [cit. 2019-03-18]. ISBN 978-1-5231-1638-6. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpFEEN0004/fundamentals-electrospinning/fundamentals-electrospinning>



- [15] HORROCKS et al., 2016. Handbook of Technical Textiles: Volume 1 - Technical Textile Processes [online]. 2nd Edition. Elsevier [cit. 2019-03-18]. ISBN 978-1-78242-481-9. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpHTTVTTPA/handbook-technical-textiles/handbook-technical-textiles>
- [16] CHAPMAN, 2010. Applications of Nonwovens in Technical Textiles [online]. Woodhead Publishing [cit. 2019-03-21]. ISBN 978-1-84-569974-1. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpANTT0002/applications-nonwovens/applications-nonwovens>
- [17] PEREIRA, 2016. Filtration efficiency of meltblown webs. Braga. Master thesis. University of Minho
- [18] MIAO et al., 2018. Engineering of High-Performance Textiles [online]. Elsevier [cit. 2019-03-21]. ISBN 978-0-08-101273-4. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpEHPT0003/engineering-high-performance/engineering-high-performance>
- [19] DANIELCZYK a STADNICKI, 2015. Optimisation of Selected Components of a Roller Carding Machine in the Aspect of Improving their Cooperation Quality. FIBRES & TEXTILES in Eastern Europe [online]. 23(6), 159-165 [cit. 2019-04-29]. DOI: 10.5604/12303666.1167436. Retrieved from: [https://www.researchgate.net/publication/284897812\\_Optimisation\\_of\\_selected\\_components\\_of\\_a\\_roller\\_carding\\_machine\\_in\\_the\\_aspect\\_of\\_improving\\_their\\_cooperation\\_quality](https://www.researchgate.net/publication/284897812_Optimisation_of_selected_components_of_a_roller_carding_machine_in_the_aspect_of_improving_their_cooperation_quality)
- [20] HORROCKS a ANAND, 2000. Handbook of Technical Textiles [online]. Woodhead Publishing [cit. 2019-03-21]. ISBN 978-1-85-573896-6. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpHTT00001/handbook-technical-textiles/handbook-technical-textiles>
- [21] ALBRECHT, FUCHS a KITTELMANN, 2003. Nonwoven Fabrics. Weinheim: WILEY-VCH. ISBN 978-3-527-30406-6

- [22] PEACOCK et al., 2006. Polymer Chemistry: Properties and Applications [online]. Hanser Publishers [cit. 2019-03-25]. ISBN 978-1-61344-300-2. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpPCPA0002/polymer-chemistry-properties/polymer-chemistry-properties>
- [23] BARTELS, 2011. Handbook of Medical Textiles [online]. Woodhead Publishing [cit. 2019-03-25]. ISBN 978-0-85-709369-1. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpHMT00004/handbook-medical-textiles/handbook-medical-textiles>
- [24] EDANA: FACTS AND FIGURES [online], [cit. 2019-04-30]. Retrieved from: <https://www.edana.org/>
- [25] WULFHORST et al., 2006. Textile Technology [online]. Hanser Publishers [cit. 2019-04-30]. ISBN 978-1-61344-306-4. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpTT000012/textile-technology/textile-technology>
- [26] BLACKBURN, 2006. Biodegradable and Sustainable Fibres [online]. Woodhead Publishing [cit. 2019-04-30]. ISBN 978-1-85573-916-1. Retrieved from: <https://www.sciencedirect.com/book/9781855739161/biodegradable-and-sustainable-fibres>
- [27] KHODDAMI a AVINC, OVERVIEW OF POLY(LACTIC ACID) (PLA) FIBRE. Fibre Chemistry [online]. 41(6), 391-401 [cit. 2019-04-30]. DOI: 10.1007/s10692-010-9213-z. ISSN 0015-0541. Retrieved from: [https://www.researchgate.net/publication/263554234\\_Overview\\_of\\_Polylactic\\_acid\\_PLA\\_Fibre\\_Part\\_I\\_Production\\_Properties\\_Performance\\_Environmental\\_Impact\\_and\\_End-use\\_Applications\\_of\\_Polylactic\\_acid\\_Fibres](https://www.researchgate.net/publication/263554234_Overview_of_Polylactic_acid_PLA_Fibre_Part_I_Production_Properties_Performance_Environmental_Impact_and_End-use_Applications_of_Polylactic_acid_Fibres)
- [28] QIAN et al., 2011. Advanced Textile Materials, Part 1 [online]. Trans Tech Publications [cit. 2019-04-30]. ISBN 978-1-61344-690-4. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpATMP000C/advanced-textile-materials/advanced-textile-materials>

- [29] MALKIN et al., 2012. Rheology - Concepts, Methods, and Applications [online]. 2nd. ChemTec Publishing [cit. 2019-05-01]. ISBN 978-1-61344-990-5. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpRCMAE001/rheology-concepts-methods/rheology-concepts-methods>
- [30] GAISFORD et al., 2016. Principles of Thermal Analysis and Calorimetry [online]. 2nd Edition. Royal Society of Chemistry [cit. 2019-05-01]. ISBN 978-1-5231-1946-2. Retrieved from: <https://app.knovel.com/hotlink/toc/id:kpPTACE001/principles-thermal-analysis/principles-thermal-analysis>
- [31] SENTMANAT, 2004. Miniature universal testing platform: from extensional melt rheology to solid-state deformation behavior. Rheologica Acta [online]. 43(6), 657-669 [cit. 2019-05-14]. DOI: 10.1007/s00397-004-0405-4. ISSN 0035-4511. Retrieved from: [https://www.researchgate.net/publication/226330968\\_Miniature\\_universal\\_testing\\_platform\\_from\\_extensional\\_melt\\_rheology\\_to\\_solid-state\\_deformation\\_behavior](https://www.researchgate.net/publication/226330968_Miniature_universal_testing_platform_from_extensional_melt_rheology_to_solid-state_deformation_behavior)

**LIST OF ABBREVIATIONS**

PLA	Polylactic acid
MPa	Megapascal
US	United States
MD	Machine direction
CD	Cross-machine direction
PP	Polypropylene
PET	Polyethylene terephthalate
HDPE	High density polyethylene
PA	Polyamides
LLDPE	Linear polyethylene of low density

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## **APPENDICES**