

NONWOVEN FABRICS BASED ON BIODEGRADABLE MATERIALS

Bc. Nikol Polášková

Master's thesis
2021



Tomas Bata University in Zlín
Faculty of Technology



Univerzita Tomáše Bati ve Zlíně

Fakulta technologická

Ústav inženýrství polymerů

Akademický rok: 2020/2021

ZADÁNÍ DIPLOMOVÉ PRÁCE

(projektu, uměleckého díla, uměleckého výkonu)

Jméno a příjmení: **Bc. Nikol Polášková**
Osobní číslo: **T19436**
Studijní program: **N0722A130001 Inženýrství polymerů**
Studijní obor: **Inženýrství polymerů**
Forma studia: **Kombinovaná**
Téma práce: **Netkané textilie z biorozložitelných materiálů**

Zásady pro vypracování

Vypracovat literární rešerši s důrazem kladeným na biorozložitelné polymery obsahující změkčující aditiva s následným zpracováním pomocí procesů zvlákňování z taveniny.

Příprava a charakterizace netkaných textilií z pohledu jejich měkkosti a mechanických vlastností.

Diskutovat výsledky s vedoucím práce.

Forma zpracování diplomové práce: **tištěná/elektronická**
Jazyk zpracování: **Angličtina**

Seznam doporučené literatury:

- S.J. Russell. Handbook of nonwovens. 2007. ISBN 9781855736030.
Lee Tin Sin, Bee Soo Tuen. Polylactic Acid. A Practical Guide for the Processing, Manufacturing, and Applications of PLA. 2nd Edition. 2019. ISBN 9780128144725
S.K. Batra, B. Pourdeyhimi. Introduction to nonwovens technology. 2012. ISBN 9781605950372.
O. Jirsák, K. Kalinová. Netkané textilie. 2003. ISBN 80-7083-746-2.

Vedoucí diplomové práce: **Ing. Roman Kolařík, Ph.D.**
Centrum polymerních systémů

Datum zadání diplomové práce: **1. února 2021**
Termín odevzdání diplomové práce: **14. května 2021**

L.S.

prof. Ing. Roman Čermák, Ph.D.
děkan

Ing. Jana Navrátilová, Ph.D.
ředitel ústavu

PROHLÁŠENÍ AUTORA DIPLOMOVÉ PRÁCE

Beru na vědomí, že:

- diplomová práce bude uložena v elektronické podobě v univerzitním informačním systému a dostupná k nahlédnutí;
- na moji diplomovou práci se plně vztahuje zákon č. 121/2000 Sb. o právu autorském, o právech souvisejících s právem autorským a o změně některých zákonů (autorský zákon) ve znění pozdějších právních předpisů, zejm. § 35 odst. 3;
- podle § 60 odst. 1 autorského zákona má Univerzita Tomáše Bati ve Zlíně právo na uzavření licenční smlouvy o užití školního díla v rozsahu § 12 odst. 4 autorského zákona;
- podle § 60 odst. 2 a 3 autorského zákona mohu užít své dílo – diplomovou práci nebo poskytnout licenci k jejímu využití jen s předchozím písemným souhlasem Univerzity Tomáše Bati ve Zlíně, která je oprávněna v takovém případě ode mne požadovat přiměřený příspěvek na úhradu nákladů, které byly Univerzitou Tomáše Bati ve Zlíně na vytvoření díla vynaloženy (až do jejich skutečné výše);
- pokud bylo k vypracování diplomové práce využito softwaru poskytnutého Univerzitou Tomáše Bati ve Zlíně nebo jinými subjekty pouze ke studijním a výzkumným účelům (tj. k nekomerčnímu využití), nelze výsledky diplomové práce využít ke komerčním účelům;
- pokud je výstupem diplomové práce jakýkoliv softwarový produkt, považují se za součást práce rovněž i zdrojové kódy, popř. soubory, ze kterých se projekt skládá. Neodevzdání této součásti může být důvodem k neobhájení práce.

Prohlašuji,

- že jsem diplomové práci pracoval samostatně a použitou literaturu jsem citoval. V případě publikace výsledků budu uveden jako spoluautor.
- že odevzdaná verze diplomové práce a verze elektronická nahraná do IS/STAG jsou obsahově totožné.

Ve Zlíně dne: 14.5.2021

Jméno a příjmení studenta:

Nikol Polášková

.....
podpis studenta

ABSTRAKT

Netkané textilie se skládají z nekonečných vláken nebo z krátkých vláken spojených různými druhy pojení. Nejvíce používaná technologie pro netkané textilie vyrobené z nekonečných vláken jsou zvláště technologie Spunbond a Meltblown. Tyto netkané textilie se používají převážně v hygienickém, zdravotnickém a technickém průmyslu. Největší využití nachází netkané textilie v hygienickém průmyslu (převážně v aplikaci dětských plen, vlhčených ubrousků, dámských hygienických potřeb, inkontinenčních pomůckách). Jedna z nejvíce používaných a stále se rozvíjejících technologií výroby netkaných textilií je technologie Spunbond. Tento proces pracuje s granulovaným polymerem, kterým byl historicky převážně polypropylen a zvláknuje ho z taveniny. Kvůli vzrůstajícím nárokům na redukci odpadu v oblasti průmyslu netkaných textilií se vývoj soustředí na materiály z přírodních zdrojů (biobased) a na materiály v přírodě rozložitelné (biodegradable). Praktická část práce se soustředí na biologicky rozložitelný materiál s přídavkem Poly(butylene succinate), PBS, které bylo použito jako aditivum pro získání více flexibilního a měkkého materiálu. Bylo vyrobeno několik funkčních prototypů s různým složením bikomponentního vlákna pro dané procesní podmínky. Během extruze byla vyhodnocena stabilita zvláknování. Materiály byly testovány několika metodami pro vyhodnocení mechanických vlastností stejně jako vyhodnocení měkkosti.

Klíčová slova: Spunbond technologie, bikomponentní vlákna, polymery z obnovitelných zdrojů, netkané textilie, polymerní taveniny, biologicky rozložitelné polymery

ABSTRACT

Nonwovens are fiber structures that are formed by joining of endless filaments or stapled fibers by various bonding techniques. The most commonly used nonwoven technologies for endless filaments are especially Spunbond and Meltblown technology. Products made from nonwovens are for hygiene, medical, technical or other industry. The greatest utilization of nonwoven textiles is focused on hygiene needs (baby diapers, wet napkins, feminine care, incontinent care). One of the most widely used and still developing technologies of nonwoven production is Spunbond technology. During this production spinning takes place directly from the polymer which has historically been polypropylene. Increasing trends of reducing use of polymers based from non-renewable sources in the nonwovens industry started the focus on biobased and biodegradable material with similar or better properties of nonwovens based on polypropylene. The practical part of this work was focused on biodegradable materials with Poly(butylene succinate), PBS, as additive to gain more flexible and soft material. Several samples were produced with different compositions of bicomponent fibers for given processing conditions. Process stability during extrusion process was evaluated. Materials were tested by several different analytic method in order to evaluate mechanical properties and softness.

Keywords: Spunbond technology, bicomponent fibres, biobased polymers, nonwoven textiles, polymer melts, biodegradable polymers

ACKNOWLEDGMENT

Throughout the writing of this Master thesis I have received a great deal of support and assistance.

First of all, I would like to thank my supervisor, Ing. Roman Kolařík, Ph.D, whose expertise was invaluable in formulating the research questions and methodology. Your insightful feedback pushed me to sharpen my thinking and brought my work to a higher level.

I would like to acknowledge my colleagues from PFNonwovens for their wonderful collaboration. I would particularly like to thank you to R&D manager Ing. Zdeněk Mečl for his patient support, to Peter Zajackowski, B.Tech. for pieces of advice and guiding, to John Parsons, M.S. for text revision, Tonny DeBeer, Ph.D. and dipl. Ing. Michael Kauschke for providing support and advices.

In addition, I would like to thank my parents for their wise counsel and sympathetic ear. You are always there for me.

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

CONTENT

INTRODUCTION	13
1 NONWOVENS	15
1.1 NONWOVEN DEFINITION	15
1.2 NONWOVEN INDUSTRY	15
2 SPUNMELT.....	18
2.1 MONOCOMPONENT FILAMENT	20
2.2 MULTICOMPONENT FIBERS.....	20
2.3 BONDING.....	20
2.4 APPLICATIONS.....	22
2.4.1 HYGIENE	22
2.4.3 AUTOMOTIVE	24
2.4.4 TECHNICAL APPLICATIONS	25
3 BIOMATERIALS	26
3.1 POLY(BUTYLENE SUCCINATE).....	26
3.2 POLY(LACTIC ACID)	27
3.3 MISCIBILITY OF PLA/PBS MIXTURE.....	27
4 THE DEFINITIONS OF FREQUENT TERMS IN USE.....	29
4.1 DIFFERENCE BETWEEN BLEND AND COMPOUND	29
4.2 HOMOGENEITY OF BLEND OR COMPOUND	29
4.3 MISCIBILITY OF TWO OR MORE POLYMERS/SUBSTANCES	29
4.4 EVALUATION OF HOMOGENEITY AND MISCIBILITY	29
4.5 MECHANICAL AND PHYSICAL PROPERTIES.....	32
4.6 RHEOLOGY	32
4.7 LABORATORY EQUIPMENT.....	32
4.7.1 LABORATORY LINE.....	32
4.7.2 DRYING.....	33
4.7.3 LABORATORY HOT PRESS	33
4.7.4 COMPOUNDING MACHINE	33
4.7.5 SCANNING ELECTRON MICROSCOPY	34
4.7.6 DIFFERENTIAL SCANNING CALORIMETRY	34
4.7.7 HIGH PRESSURE CAPILLARY VISCOMETRY	34
4.7.8 EVALUATION OF MISCIBILITY ON PLATES	36
4.7.9 TENSILE TESTER	36
4.7.10 HANDLE-O-METER	36

4.7.11 SOFTNESS PANEL TEST.....	36
5 TARGETS.....	38
5.1 NONWOVEN PRODUCTION	38
5.2 INVESTIGATION OF CAUSE OF SPINNING PROBLEMS.....	38
6 PREPARATION OF NONWOVENS	39
6.1 DRYING OF MATERIAL	39
6.2 CHOSEN GRADES	39
6.2.1 CORE.....	39
6.2.2 SHEATH.....	39
6.2.3 ADDITIVE	39
6.3 PRODUCED COMBINATIONS	40
6.4 PREPARATION OF BLENDS AND COMPOUNDS	41
6.5 PROCESS DESCRIPTION.....	41
6.6 PRODUCTION PROBLEMS	43
7 MEASUREMENT METHODS DESCRIPTION.....	44
7.1 MECHANICAL PROPERTIES	44
7.1.1 DETERMINING MASS PER UNIT AREA.....	44
7.1.2 TENSILE STRENGTH AND ELONGATION OF NONWOVEN.....	44
7.2 SOFTNESS OF MATERIAL	44
7.2.1 HANDLE – O – MATTER.....	44
7.2.2 SOFTNESS PANEL TEST.....	44
7.3 DIFFERENTIAL SCANNING CALORIMETRY.....	44
7.4 RHEOLOGY	45
7.4.1 SHEAR VISCOSITY.....	45
7.4.2 EXTENSIONAL VISCOSITY	45
8 RESULTS.....	46
8.1 MECHANICAL PROPERTIES OF PRODUCED NONWOVENS	46
8.2 DIFFERENTIAL SCANNING CALORIMETRY.....	48
8.3 RHEOLOGY EVALUATION	51
8.4 EVALUATION OF VISIBLE ASPECT OF PLATES	54
8.4.1 PLA WITHOUT PBS.....	55
8.4.2 PLA WITH PBS	56
8.5 SEM EVALUATION	57
CONCLUSION	58
BIBLIOGRAFIE.....	58

LIST OF ABBREVIATIONS62
LIST OF FIGURES63
LIST OF TABLES65

INTRODUCTION

The current trend is to find more eco-friendly plastic materials which will help us to protect our environment. Every year more than 3 000 000 tons of nonwoven fabric are produced in Europe and just a small part of it is recycled (1).

All medical products are burned as toxic waste, and there is no space for biodegradable materials.

Furniture and filtration are also big consumerists of nonwoven materials, but they usually use recycled materials.

The agriculture industry usually needs some aging tests, and there is a paramount question price of final nonwoven. Biodegradable materials are more expensive than commonly used materials, and because of that, they are not the main focus for developing biodegradable nonwovens fabric in this area.

All hygiene product ends in standard bins, and part of it is burned, part of it is landfilled, and some amount ends in water (sea or rivers). This sector is where compostable materials can have a future, and there is the main focus of big world producers of nonwovens.

This work is focused on finding cheap solution to increase softness of Poly(lactic acid) based nonwovens. Drapability and softness are one of the most important properties in hygiene industry where the problem with the recycling of waste is the most urgent.

I. THEORY

1 NONWOVENS

1.1 Nonwoven definition (2)

“A nonwoven is an engineered fibrous assembly, primarily planar, which has been given a designed level of structural integrity by physical and/or chemical means, excluding weaving, knitting or paper making.”

1.2 Nonwoven industry (3) (4) (5) (6)

“Nonwovens are unique, innovative, high-tech, engineered class of textile material formed from fibers that are bonded together through various means to form a coherent structure.”

(3) Bonding can be thermal (for example, air-through-bonding, calender-bonding, ultrasonic bonding), chemical (for example, using glue), mechanical (for example, hydro-entanglement), or by their combination (for example, calender and hydro-entanglement). A nonwoven is a manufactured sheet or web of directionally or randomly oriented fibers that are first formed into a batt and then consolidated together by friction, cohesion, adhesion, and bonding. The fibers may be of natural or man-made origin and may be stapled, or continuous filaments or are formed in situ. Commercially available fibers have diameters ranging from less than about 0.001 mm to more than about 0.2 mm. They come in several different forms: short fibers (known as a staple or chopped), continuous single fibres (filaments or monofilaments), untwisted bundles of continuous filaments (tow), and twisted bundles of continuous filaments (yarn). Nonwoven fabrics can be formed by many processes, including but not limited to melt-blown process, spun-bond process, spunmelt process, solvent spinning, electrospinning, carding, film fibrillation, melt-film fibrillation, air-laying, dry-laying, wet-laying with staple fibers, and combinations of these processes as known in the art. (4) (5)

Nonwovens are used in a wide range of consumer and industrial products. They are designed from thin to strong, robust nonwovens either in combination with other materials or alone. One of the main influences is the primary material. Nonwovens are usually based on polypropylene or polyethylene terephthalate with polyethylene in combination. Nonwovens are frequently treated to improve their hydrophobic or hydrophilic properties. For many nonwovens fabric, it is possible to apply finishing treatments, such as printing, embossing, laminating, etc., allowing to deliver high-performance products.

The practical part is focused only to spunmelt production concretely to Spunbond method. Spunbond method is high effective production process with possibility to implement one or more Meltblown layers. Spunmelt products are cheaper than carded materials but there are some limitations for example in one layer of product can be just one type of fiber with specific properties. Carded production is able to combine more than two types of different fibres (for example different polymers, cross sections, fiber diameter, etc.)

Different fibre layering is visible on following figures. Nonwoven composition Spunmelt – Meltblown – Spunmelt (SMS) is presented in Figure 1.

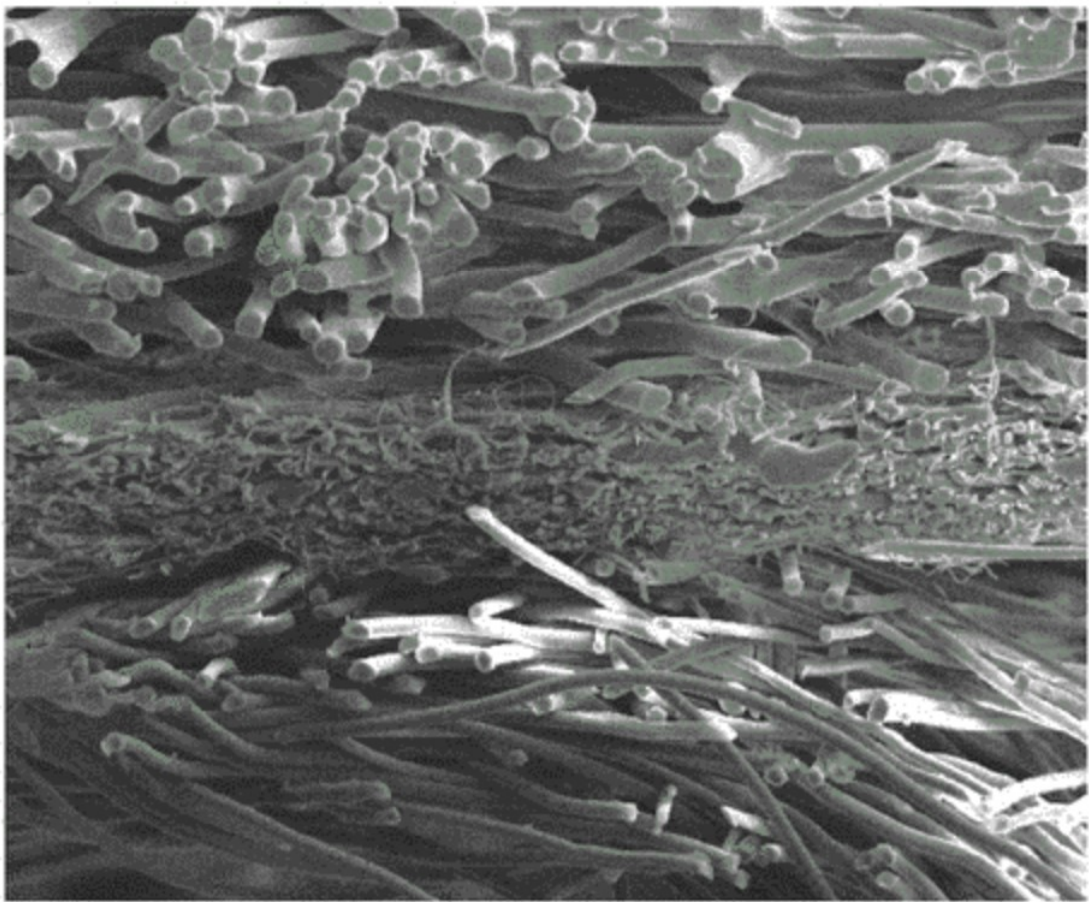


Figure 1 Cross section SMS spunmelt material (7)

Carded nonwoven material formed by short fibres is shown in Figure 2.

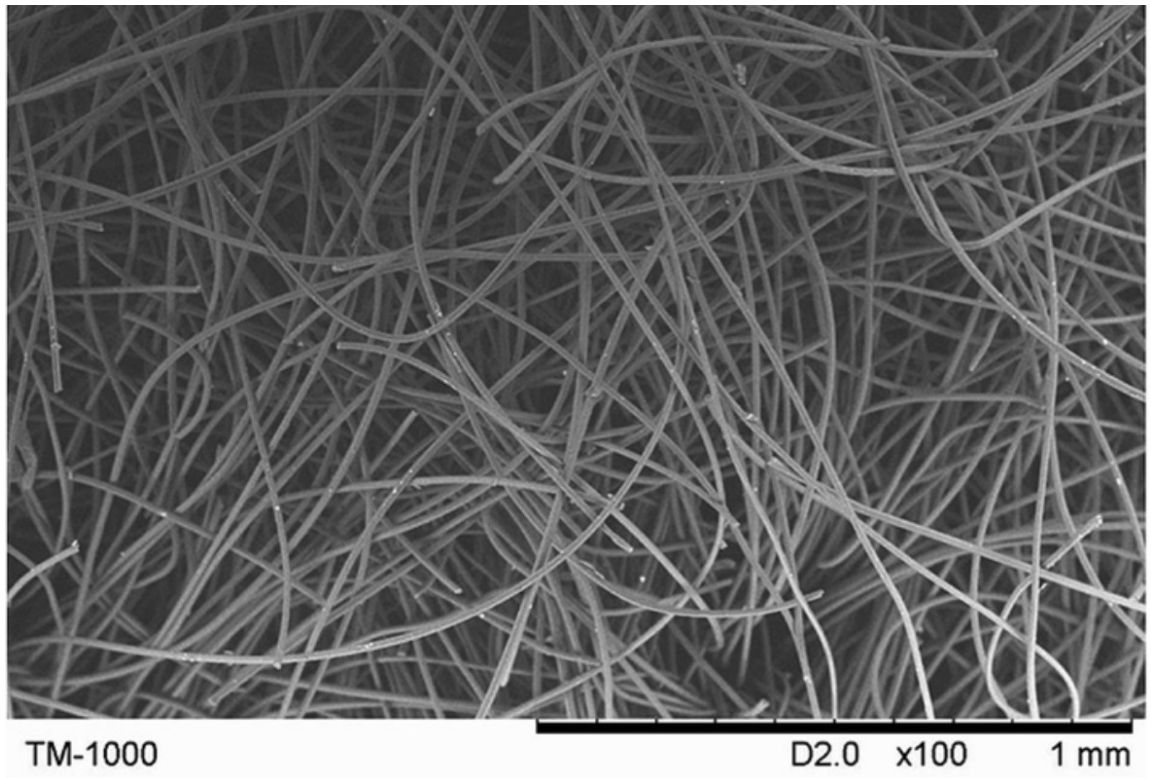


Figure 2 Carded nonwoven (8)

Figure 3 shows nonwoven material form by endless filament thermal bonded by calender.



Figure 3 Spunbond nonwoven thermally bonded by calender

2 SPUNMELT (9) (10) (11) (12)

The most extensive nonwovens technology offers high speed, uniformity, and a value proposition unmatched by competing technologies. Spunmelt is the material used in hygiene and medical applications and provides a more cost-efficient manufacturing process.

Usually, layered nonwoven textile contains one or more layers of filaments, where the layers of filaments have continuous filaments containing one or more base polymer and the first bonding polymer when continuous filaments are bicomponent composition. One of the crucial properties of nonwoven textile is bulkiness, and the other is thickness. We are using several known methods to achieve thicker material – namely utilizing selecting suitable polymers, modification of the filament shape (variously and using various methods of crimped or curled filaments), and by the bonding method – whether thermal (e.g., calender with a suitable emboss pattern, air-laying, ultrasound bonding, etc.), mechanical (e.g., by water-laying, needle punching, etc.) or by combining several bonding methods together.

The term “spunmelt” includes Spunbond and melt-blown technology, which have more detailed descriptions below.

The term "Spunbond technology" or “Spunbond fibers" refers to fibers made by an extrusion process where a molten thermoplastic material is formed as filaments from a plurality of fine, typically circular holes of a spinneret.

The process starts with crystallization and drying of polymer material if it is needed. The dry polymer material is delivered to the hopper. The extruder is usually formed by three or more extrusion zone (feed zone, compressing zone, metering zone). Zones are heated by one of many types of heat elements (for example, oil heating, electrical heating) and also cooling because, during the melting process, mechanical energy is transformed into thermal energy. Set temperatures are usually significantly higher than polymer’s melting temperatures. Molten polymer passes through the screen filter and is forced by the gear pump into the spin beam. The gear pump is used to have stable pressure in the spin beam. The inside spin beam is a system of plates that distribute polymer melt to all holes of the spinneret. More than one extruder can be part of one spin beam. When filament leaves spinneret, a draw tension is applied on it. The filaments can be drawn mechanically or pneumatically (for example, mechanically wrapping the filaments around a draw roll or entraining the filaments in an airstream). The filaments may be quenched by an air stream before or while being drawn.

The filaments are usually laid down to a running belt to form a web of randomly arranged substantially continuous filaments, which can be bonded together to form a nonwoven fabric.

The term "Meltblown" and "Meltblown fibers" means fibers made by process where typically a polymer material is extruded under pressure through spinneret or die. High-velocity hot air flow entrains the filaments as they exit the die to form filaments that are elongated and reduced in diameter, and seemingly end fibers are produced but with knowledge of the technology, we can say that they are endless. This differs from a spunbond process whereby the continuity of the filaments is preserved along their length.

Commercial line where Spunbond and Meltblown technology are combined are shown in Figure 4 and Figure 5.

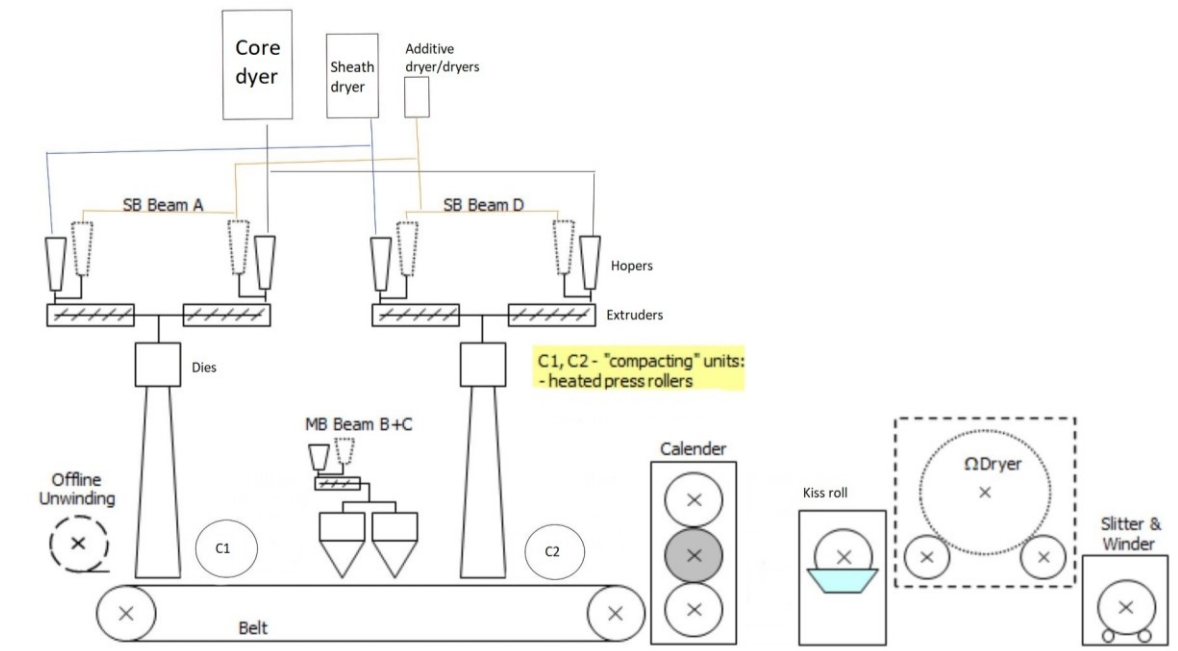


Figure 4 Scheme of spinnmelt machine with dryers

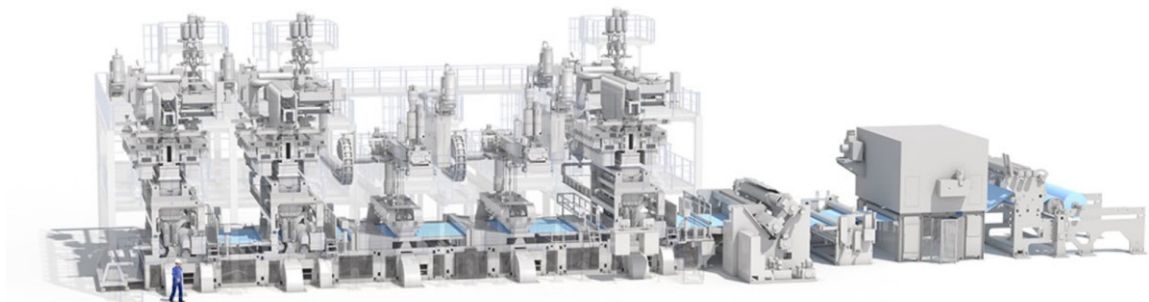


Figure 5 Reifenhäuser Reicofil RF5 Composite Line (13)

2.1 Monocomponent filament

The term "monocomponent filament" means a filament formed of a single polymer or polymer blend, usually with a round shape, extruded by a single extruder.

2.2 Multicomponent fibers (14) (4) (10)

"Multicomponent filament" refers to a fiber including more than one polymer component. A cross-section of the die is not simple, but the machine must be equipped with at least two extruders. "Multicomponent fiber" includes, but is not limited to, "bi-component fiber." A multicomponent fiber may have an overall cross-section divided into subsections of the different components of any shape or arrangement, including, for example, coaxial subsections, core-and-sheath subsections, side-by-side subsections, radial subsections, islands-in-the-sea, etc. as it is visible in Figure 6.




















FAMILY	BICOMPONENT FIBERS					
	VARIANTS					
CORE & SHEATH	 50/50	 20/80	 ECCENTRIC	 TRILOBAL	 CONDUCTIVE	
SIDE BY SIDE	 50/50	 20/80	 MIXED VISCOSITY	 ABA	 TRILOBAL OR OTHERS	 CONDUCTIVE
TIPPED	 TRILOBAL	 CROSS				
MICRO-DENIER	 SEGMENTED PIE	 ISLANDS-IN-A-SEA		 STRIPED		
MIXED FIBERS	 COLORS		 DENIERS, COMPONENTS, CROSS-SECTIONS		 BICOMPONENT/HOMOFILAMENT	

Figure 6 Different types of bicomponent fibers (14)

Bi-component fibers are nowadays the most expanding technology because these fibers combine best cost estimate with the best customer desired properties. By using bi-component technology it is possible to achieve many different properties by using same base polymer and different second polymer.

2.3 Bonding (10) (11)

For spun melt technologies the most commonly used process is thermal bonding, especially calender bonding. The calender is a roll with specific pattern formed by embossing lands

with a particular shape. We use one smooth roll and one with the pattern as is visible in Figure 7.

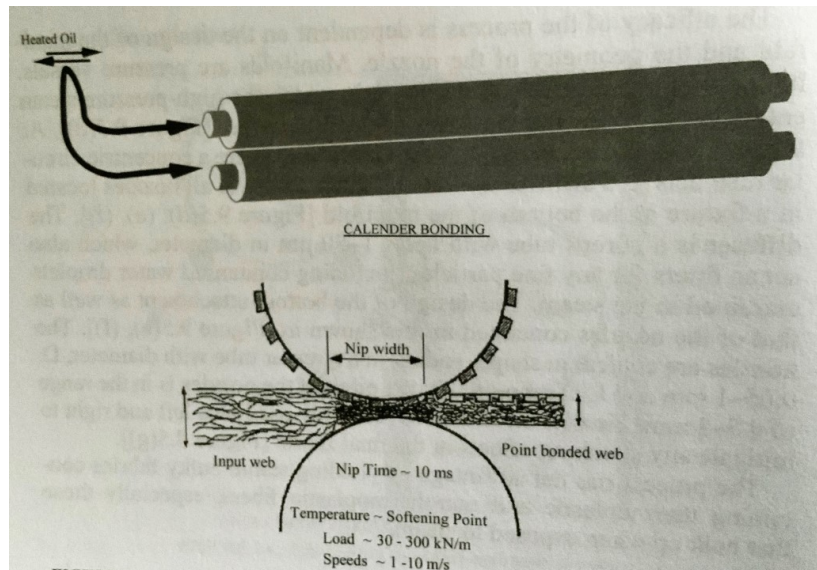


Figure 7 Thermal bonding with calender (11)

Another type of thermal bonding is bonding by hot air. This is commonly used in carded industry and it is new in spun melt industry. Hot air passes through the nonwoven and softens the bonding polymer (Figure 8).

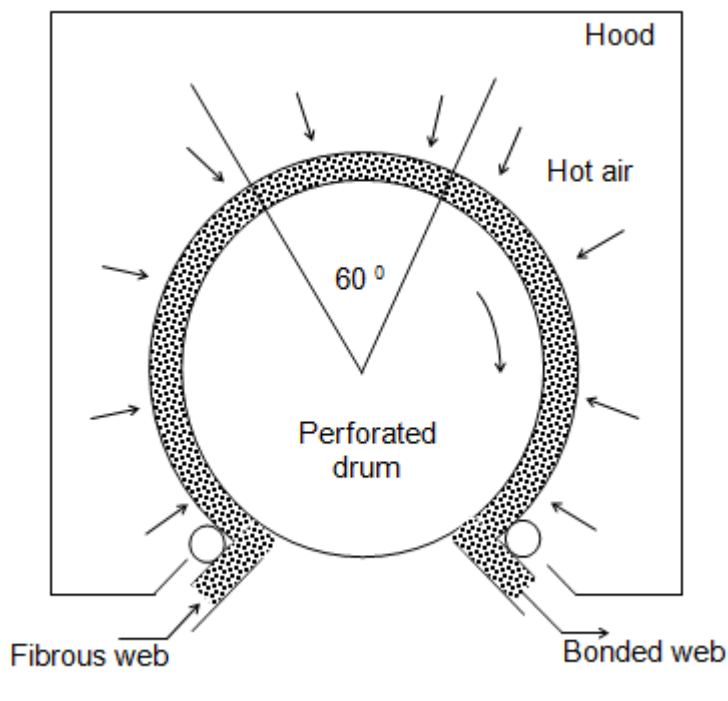


Figure 8 Principle of bonding with hot air (15)

Hydroentanglement bonding is also suitable for spun melt industry. Pressurized water needles are applied with an injector to the nonwoven to entangle the fibers together Figure 9. This type of bonding provides soft touch nonwovens. These nonwovens have similar topical softness as cotton.

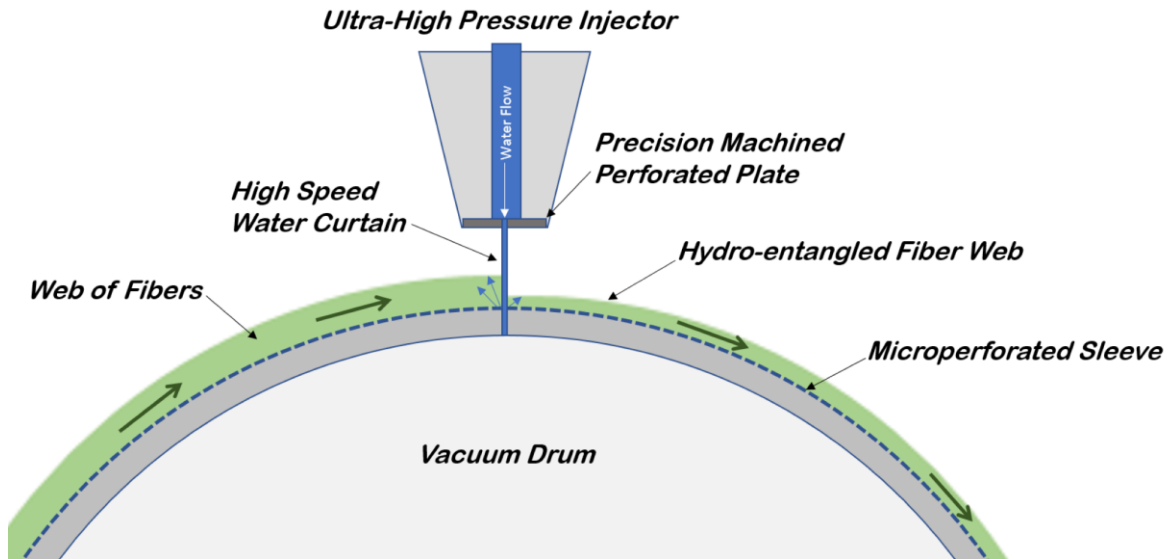


Figure 9 Scheme of hydroentanglement bonding (16)

Hydroentanglement can be also used for 3D patterning. In this case nonwoven has benefit in lofty, bulky 3D soft structure.

2.4 Applications (17)

Nonwoven's textile is one of the most enlarged products. It is crucial material for hygiene and other industry. Due to pandemic of SARS-CoV-2 (2019-nCoV or Covid 19) there was significantly increase of production in Spunbond and Meltblown materials for hygiene and medical industry.

2.4.1 Hygiene

Baby diapers, ladies' hygiene products, dry and wet pads, incontinence products, operation drapes, gowns and packs, face masks, respirators, swabs, etc.

For example, Edana says that "Around 33 billion nappies and diapers are sold every year in Europe." (1)

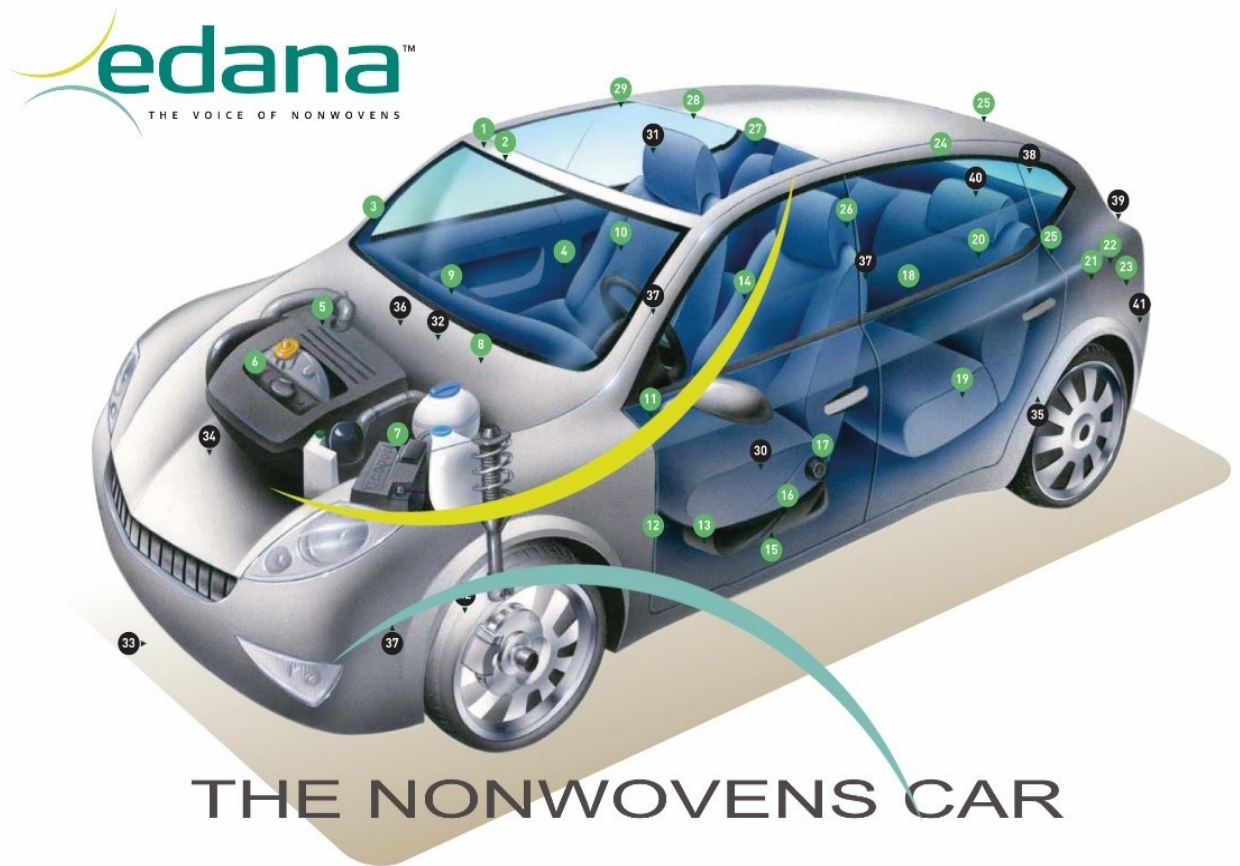


Figure 10 Baby diaper composition

Figure 10 describes basic diaper composition: A) Top Sheet – soft nonwoven, B) Acquisition Layer – open structure nonwoven or cellulose, C) Backsheet – laminate of film and nonwoven, D) Core – Absorbing materials, E) Fasteners – elastic parts combine with nonwoven, F) Elastics – Composite with nonwoven

2.4.3 Automotive

Boot liners, shelf trim, oil and cabin air filters, airbags, tapes and lot of others application as shown in Figure 11.



- | | | | | | |
|----|----------------------------------|----|----------------------------------|---------------------------------------|------------------------------------|
| 1 | Covering material for sun-visors | 16 | Covering for seat belt anchorage | Acoustic absorber applications | |
| 2 | Padding for sun-visors | 17 | Covering for seat belt | 30 | Doors |
| 3 | A, B, C, column padding | 18 | Decorative fabric | 31 | Headliner |
| 4 | Door trim pads | 19 | Polyurethane coated backing | 32 | Inner & outer dashboard insulation |
| 5 | Fuel filters | 20 | Seat slip agents | 33 | Under engine shield |
| 6 | Oil filters | 21 | Boot (trunk) liners | 34 | Moulded bonnet liner |
| 7 | Battery separators | 22 | Moulded fuel tanks | 35 | Rear wheel arch liner |
| 8 | Cabin air filters | 23 | Bodywork parts | 36 | Cowl |
| 9 | Loudspeaker cover | 24 | Window frames | 37 | Pillar trim panels |
| 10 | Covering for moulded seats | 25 | Headliner facings | 38 | Parcel shelf |
| 11 | Transmission tunnel | 26 | Upholstery backing | 39 | Trunk trims |
| 12 | Carpet & carpet reinforcement | 27 | Loudspeaker housing | 40 | Rear seat strainer |
| 13 | Car mats | 28 | Sunroof | 41 | Air extractor |
| 14 | Vinyl backing for seat covers | 29 | Saloon roof | 42 | Wheel arch liners |
| 15 | Backing for tufted carpeting | | | | |

Figure 11 Nonwoven parts inside cars

2.4.4 Technical applications

Roofing and tile underlays, thermal and noise insulation, filtration air and gas, Hevac, Hepa, Ulpa filters (Figure 12), wet cleaning wipes and dusters, tea and coffee bags, dryer fabric softeners, food wraps, geotextiles asphalt overlay, soil stabilization (Figure 13), drainage, etc.



Figure 12 Nonwoven filters (18)



Figure 13 Practical use of geotextile (19)

3 BIOMATERIALS

Due to European Union restrictions to plastic production and discussions about environmental problems caused by petrochemical-based polymers, the future developments is focused to the use of Poly(lactic acid) (PLA) or other bio polymers. The use of PLA has been already growing, for example, in the general consumer market and in biodegradable packaging. (20) Total Corbion announced that they will build new production capacity therefore the production volume of PLA will increase and the manufacturing process will be improved. A new plant will start production in 2024 in Europe and therefore pricing should be more competitive in comparison with polyolefins. (21)

One of the issues of Poly(lactic acid) is the stiffness of the fibers. Amorphous material is less stiff on the other side drying takes 24 hours which requires significant drying capacities. There are several generally known additives for softening polylactic acid. The Poly(butylene succinate) seems to be promising option and it was subject of this research.

3.1 Poly(butylene succinate)

Poly(butylene succinate) (PBS) is aliphatic polyester produced from polymerization of bio-based succinic acid and 1,4-butanediol. Poly(butylene succinate) is a white semi - crystalline material which is hygroscopic and it therefore is necessary to dry this material. This polymer is in general an industrial compostable material and some of its grades are home compostable. Chemical structure is visible in Figure 14.

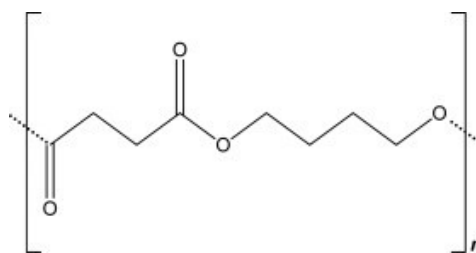


Figure 14 Chemical structure of Poly(butylene succinate)

3.2 Poly(lactic acid)

Poly(lactic acid) or polylactide (PLA) is a thermoplastic aliphatic polyester derived from renewable resources, such as corn starch (in the United States), tapioca roots, chips, or starch (mostly in Asia), or sugarcane (in the rest of the world). Poly(lactic acid) is a slightly yellow crystalline, semi-crystalline or amorphous material. Morphology can be controlled stereochemically. Poly(lactic acid) is a hygroscopic material and it is necessary to dry this material. Poly(lactic acid) is industrial compostable material. Melt temperature is between 150 – 180°C. Poly(lactic acid) has high strength and stiffness, but low impact strength. “Degradation of PLA occurs primarily through hydrolysis of the ester bond, and is highly dependent on temperature, moisture, microbial environment, morphology, as well as thickness and geometry of the article.” (22) Chemical structure of PLA is shown in Figure 15.

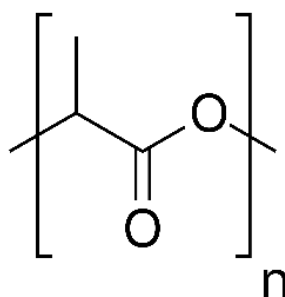


Figure 15 Chemical structure of Poly(lactic acid)

3.3 Miscibility of PLA/PBS mixture

“In the case of blending of PBS and PLA, the extent of miscibility is not entirely clear. Park and Im (23) investigated phase behavior and morphology of melt blended PLA and PBS and calculated the Flory–Huggins interaction parameter, X , to be -0.15. The negative value of X indicates that PLA and PBS are fully miscible, although these authors also reported that at a PBS content in excess of 40% there was significant crystallization-induced phase separation. Bhatia et al. (24) used modulated DSC to measure T_g and reported that the T_g of PLA did not change with addition of PBS, and hence concluded that the blends were immiscible, although they found that rheological results showed compatibility when the PBS content was below 20 wt%. On the other hand, Jompang et al. (25) investigated morphology of PLA/PBS blends by scanning electron microscopy (SEM) from which they concluded that PBS was miscible with PLA up to an addition level of 10 wt%.” (26)

Conclusion of research summarize in article from JOMPANG and collective “Crystallinity of PLA in the blends increased when increasing PBS contents. On the contrary, crystallinity of PBS was suppressed when adding high PLA contents. From the results, it was considered that PBS would act as nucleation site for PLA in order to crystallization while PLA inhibited PBS crystallization.” (25)

Overall based on online literature search positive impact of PBS was expected.

4 THE DEFINITIONS OF FREQUENT TERMS IN USE

4.1 Difference between blend and compound

“A polymer blend is a mixture of two or more polymers that have been blended together to create a new material with different physical properties.” (27) Compound means: “Upgrading or adding value of polymers or polymer systems through melt blending and mixing of additives into a polymer matrix or melt mixing two or more polymers together to make an alloy.” (28) In conclude: Blend are two types of granules mixed straight in extruder of spinning machine while compounds are formed by granules which are first mixed together in compounder (machine with single or twin screw) there we gain new homogenous granules which includes two types of substances. Then we use compounded material at spinning machine (we dose just one material into hopper).

4.2 Homogeneity of blend or compound

“Homogeneity mixture - a mixture in which the composition is uniform throughout the mixture. Mixture - consists of multiple substances put together. Substance - it has a uniform and definite composition.” (29) Homogeneity of a mixture (blend or compound) is a basic assumption for achieving spinnability, process stability, and homogenous mechanical properties. Homogeneous mixture essential for one peak of glass transition temperature and homogenate rheological properties. Homogenate mixture produces fibers without any physical defect with uniform mechanical properties.

4.3 Miscibility of two or more polymers/substances

Miscibility is essential for achieving a homogenate mixture. Usually, two polymers are miscible in a specific process window. Two substances are miscible when the final solution is a homogenate mixture.

4.4 Evaluation of homogeneity and miscibility

For the understanding of the behavior of polymers mixtures, evaluation of miscibility can be used. Differential scanning calorimetry (DSC) is one of the standard evaluation methods. Based on glass transition temperature it is possible to evaluate if the mixture is miscible or not (see There are four basic types of miscibility (see Figure 17). When mixture has two

glass transitions, we can suppose that mixture is not miscible. In Figure 16 miscible mixture is A while non-miscible mixture is B.

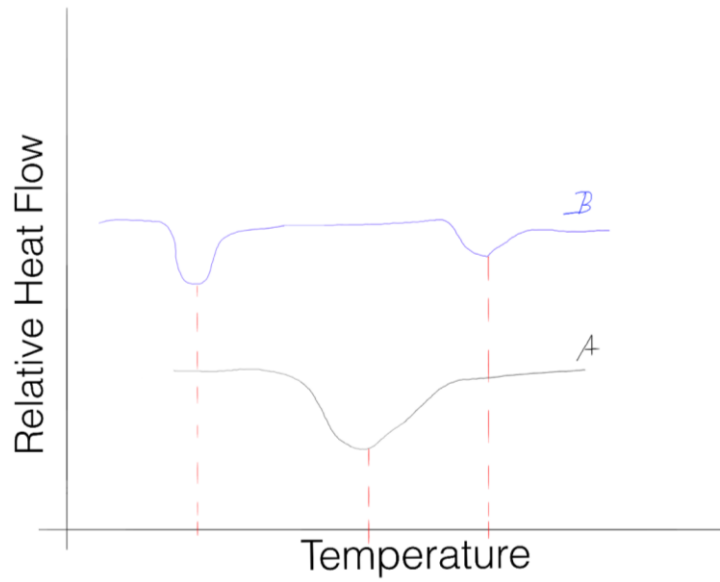


Figure 16 DSC evaluation

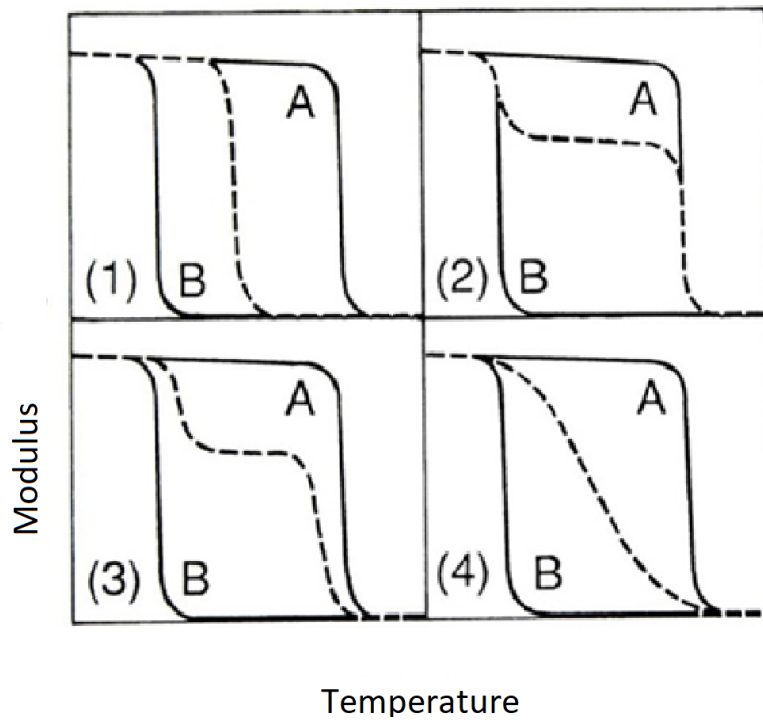


Figure 17 DMA evaluation of different miscibility

“Dynamic mechanical analysis (DMA) is one of the most important techniques in thermal analysis. It can be used to study the viscoelastic properties and behavior of a wide range of materials as a function of temperature or frequency.” (30)

In Figure 17 DMA evaluation of different miscibility Figure 17 is picture (1) describes a fully miscible mixture. Picture (2) describes a non-miscible mixture. Picture (3) describes a partly-miscible mixture. Picture (4) describes a non-miscible mixture with dispersion and a wide area of the glass transition temperature.

The miscibility of a mixture can also be evaluated by Scanning electron microscopy (SEM). “SEM use an electron beam to image samples with a resolution down to nanometer scale. The electrons are emitted from source of electrons and collimated into beam in the electron source.” The beam is then focused on the sample surface where is interaction between electron and sample, producing various signals. These signals can be used to obtain information about topography or composition. In case of SEM analysis, pictures were evaluated. Trained skill person is able to evaluate homogeneity based on the given photo as you can see in Figure 18.

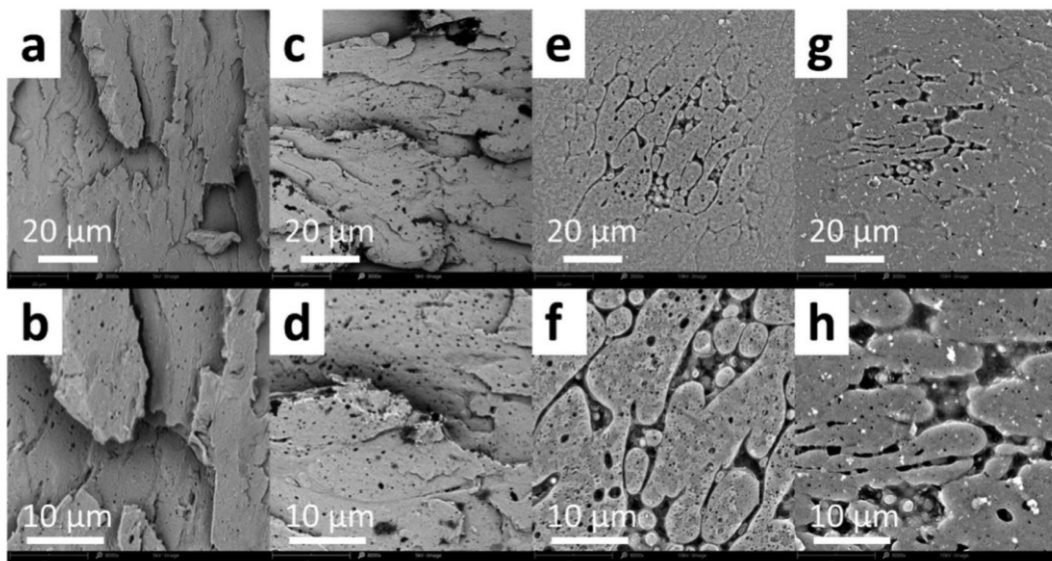


Figure 18 SEM pictures - Example of non-miscible and particularly miscible mixture

Fourier transforms infrared spectrometry (FTIR) is based on interaction of infrared light with sample. The most common Michelson interferometer where the intensity of the interference light is recorded in an interferogram, with the optical path difference recorded along the horizontal axis. FTIR can be used for evaluation type of polymer or other unknown material.

FTIR can be used for determination the quality or consistency and for examination the amount of substances in mixtures. (31)

Visible evaluation of miscibility two kinds of polymers is also possible. If the polymers have different color is possible to evaluate their miscibility on prepared plate.

4.5 Mechanical and physical properties

Tensile strength and elongation are one of essential mechanical properties. For follow-up application is usually necessary to know this for setting up process correctly.

Biobased materials are stiffer, less drape than standard polyolefin version.

Stiffness is evaluated by Handle-o-Meter, this machine combine resistance as result of surface friction and stiffness in the bend of sheet material which passing through a limited gap.

4.6 Rheology

“Rheology is the scientific field that encompasses the flow phenomena of matter (solids, liquids, and gases) and notably involves time-dependent behavior under the influence of stresses.” (32) “Rheological measurements are performed on polymers in order to assess for their behavior during processing.” (33) “Rheological characterization can be used to fix the optimum process.” (33)

4.7 Laboratory equipment

4.7.1 Laboratory line

The required experiments were performed using polymer melt filament laboratory line Hills LBS-300. This line has been used for bicomponent Spunbond technology. As visible in Figure 19 laboratory line is equipped with kiss-roll and drier. All experiments were hold without using kiss-roll and drier.

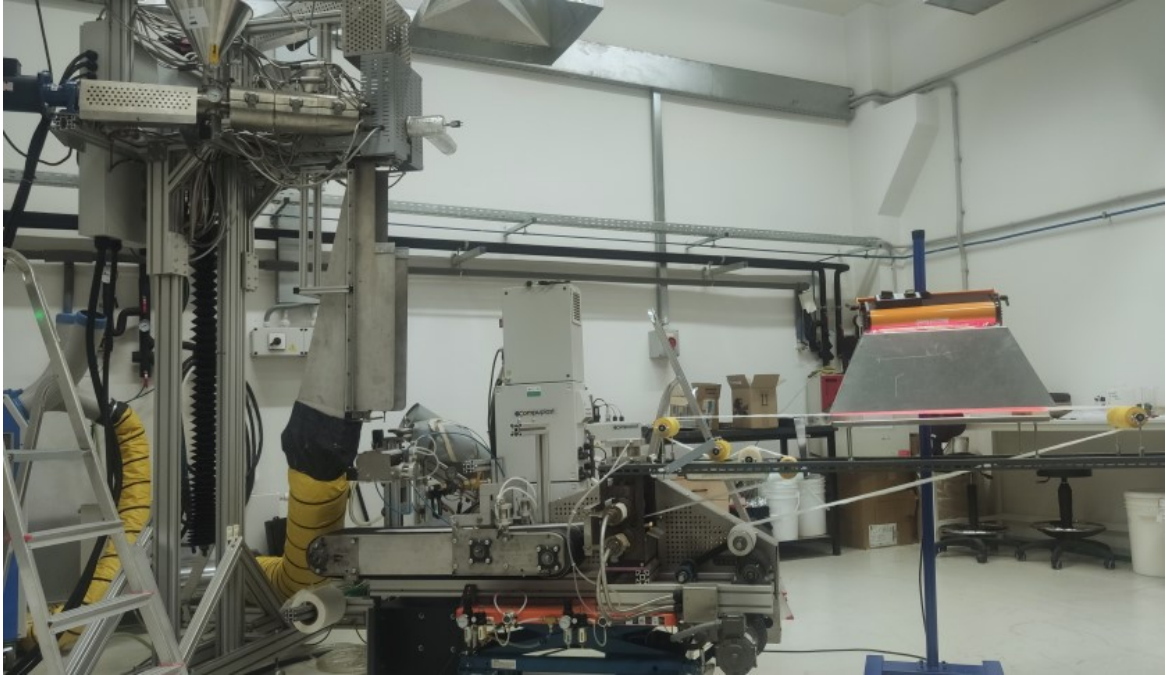


Figure 19 Laboratory line Hills LBS-300

4.7.2 Drying

For drying PLA a Moreto Frahe model CNS45 dryer was used. For drying of Poly(butylene succinate) a laboratory dryer Memmer VO400 was utilized. All materials were dried by air under atmospheric pressure.

4.7.3 Laboratory hot press

For preparing of plastic plate was used laboratory hot press. Form (frame) 120 mm x 120 mm x 1mm was used for getting final shape of plate. PET foil was placed from each side of frame. Both sides of hot press were heated and form was placed between them. The polymer pellets were melted and shape was given by the form and applied press for certain time.

4.7.4 Compounding machine

Blends were prepared by scientific twin-screw extruder with co-rotating screws of 26 mm in diameter and length 48D. In principle twin-screw compounder consist of two intermeshing, co-rotating screws mounted on splined shafts in a closed barrel. Twin screw extruder is able to ensure transporting, compressing, mixing very effectively.

4.7.5 Scanning electron microscopy

For analysis of plastic plates was used Scanning electron microscopy type Vega 3 Tescan.

4.7.6 Differential scanning calorimetry

Analysis of granules were performed by Differential Scanning Calorimetry using a Mettler Toledo DSC 1/700 device (Figure 20).

“The DSC method detects endothermic and exothermic transitions like the determination of transformation temperatures and enthalpy of solids and liquids as a function of temperature.” (34) Most common quantities are the melting temperature, the recrystallization temperature, the glass transition temperature and also the heat capacity. 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 by linearly increases temperature, which is function of time. The principle of the DSC method is to measure the difference in temperatures (heat flow) between the sample and the reference. (17) (34)



Figure 20 Differential scanning calorimeter

4.7.7 High pressure capillary viscometry

In order to characterize flow and viscoelastic properties of polymer melts at high strain rates, the Göttfert Rheograph RG25-50 high pressure capillary viscometer was used (Figure 21).



Figure 21 The Göttfert Rheograph RG25-50

4.7.7.1 *Shear viscosity determination*

In order to characterize the shear flow properties, the pressure is required. Thus, the piston is used for generation of shear stress. The measured characteristic values are the pressure drop along the length of the capillary, the temperature and the volumetric flow. The calculated shear stress and shear rate are usually corrected with Bagley (correction for capillary entrance and exit effects) and Weissenberg-Rabinowitsch (correction of non-Newtonian behavior) corrections. (35) 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. Then, shear viscosity is obtained. (17)

4.7.7.2 *Elongational viscosity determination using Rheotens device*

The uniaxial elongational viscosity can be characterized using Rheotens device (Figure 22). During the experiment, polymer melt string is extruded through a capillary at constant piston speed. Such extruded melt string is then drawn by a pair of rotating wheels with a corrugated surface which are fixed to a very sensitive balance system. Then, the drawdown velocity is linearly increased from an initial speed with a constant acceleration rate until the extended melt string breaks at certain speed. After that, drawdown force as a function of drawdown velocity is reached and such experiment is then repeated several times. Finally, uniaxial elongational viscosity is evaluated according to the Wagner model (36).

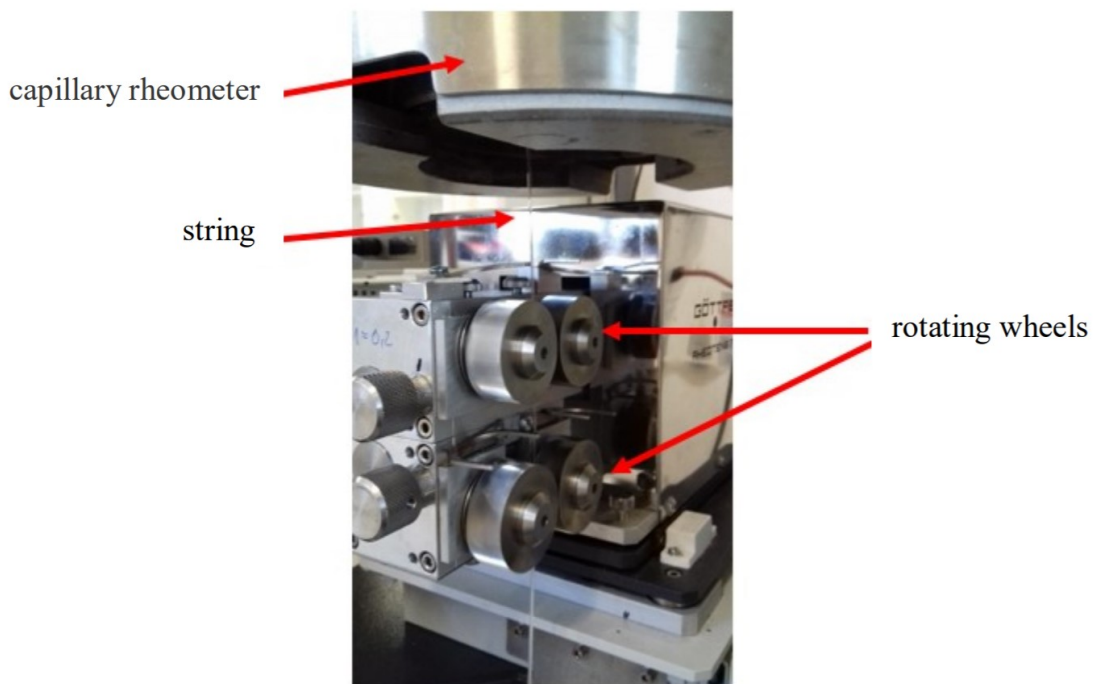


Figure 22 Rheotens device

4.7.8 Evaluation of miscibility on plates

Plates were prepared on with hot press. 16 grams of polymer blend or compound was used for each plate. Prepared plate was placed on black background, then visible aspects were evaluated. Miscible mixture should be without any shadow while non-miscible blends or compounds contain shadows. This evaluation is possible because PBS is white while PLA is transparent.

4.7.9 Tensile tester

Nonwoven textiles were analyzed on tensile tester Zwick.

4.7.10 Handle-O-Meter

Nonwoven textile was analyzed by Thwing-Albert Handle-O-Meter. The nonwoven is bend into defined gap. Then, the force which is necessary for bending the material to the sensor throw gap is evaluated.

4.7.11 Softness panel test

Nonwoven textile was cut to 15 cm long pieces and was evaluated by 10 train and skill people. Following aspects were evaluated – topical softness, drape ability, softness of whole nonwoven by gentle pressing the material by fingertips.

II. ANALYSIS

5 TARGETS

5.1 Nonwoven production

One of the targets was to produce nonwoven based on PLA with certain amount of additive which will provide softer touch, more drape able and flexible material. PBS FZ78TM was chosen as the process additive.

5.2 Investigation of cause of spinning problems

Spinning problems occur during the production. There was effort to analyze the cause of the unstable spinning. Therefore, DSC analysis, SEM analysis and rheological behavior were investigated.

6 PREPARATION OF NONWOVENS

6.1 Drying of material

PLA and PBS polymers and their compounds were dried in dryers during a day at 65°C at least for 6 hours or more.

6.2 Chosen grades

6.2.1 Core

Poly(lactic acid) used in core was Ingeo 6100D from company NatureWorks. This grade is used for spinning endless filaments. Melt temperature of this polymer is 165 -180°C and melt flow rate is 24 g/10 min at 210°C/2.16kg. Ingeo 6100D is a crystalline polymer with food contact approval regarding U.S. Food and Drug Administration (FDA).

6.2.2 Sheath

Poly(lactic acid) used in sheath was Ingeo 6752D from NatureWorks. This grade is used for spinning endless filaments. Melt temperature of this polymer is 145 - 160°C and melt flow rate is 15 g/10 min at 210°C/2.16 kg.

6.2.3 Additive

Poly(butylene succinate) used as additive was FZ78TM from MCPP Mitsubishi Chemical company. This grade is semi-crystalline polyester and is suitable for spinning filaments. Melt temperature of this polymer is 115°C and melt flow rate is 22 g/10 min at 190°C/2.16kg. This grade is certified as Home Compostable therefore is promising for future wider application. Used grade is also food contact approved, therefore is possible to use it in other sensitive applications.

6.3 Produced combinations

All the performed experiments (see Table 1) were done in ratio 80/20 at Core/Sheath configuration.

Table 1 Codes of produced samples

Code of sample	Core	Sheath
#A	PLA Ingeo 6100D	Aspun 6834
#B	PLA Ingeo 6100D	PLA Ingeo 6752D
#C	PLA Ingeo 6100D + 5% PBS FZ78TM	PLA Ingeo 6752D
#D	PLA Ingeo 6100D + 10% PBS FZ78TM	PLA Ingeo 6752D
#E	PLA Ingeo 6100D + 15% PBS FZ78TM	PLA Ingeo 6752D
#F	PLA Ingeo 6100D + 20% PBS FZ78TM	PLA Ingeo 6752D
#G	PLA Ingeo 6100D	PLA Ingeo 6752D +20% PBS FZ78TM
#H	PBS FZ78TM	PBS FZ78TM

Reference settings #A (nonwoven available on market) containing PLA Ingeo 6100 in core and PE Aspun 6834 in sheath was prepared in ratio 80/20 with die configuration Core/Sheath.

As comparison nonwoven with PLA/PE; 100% Poly(lactid acid) was prepared. PLA Ingeo 6100D was used in core and PLA Ingeo 6752D was used in a sheath of the fiber.

To gain more drape-able and soft material samples containing PBS were prepared. As first 5% of PBS FZ78TM were added to PLA Ingeo 6100D and pure PLA Ingeo 6752D was used in sheath. Than amount of Poly(butylene succinate) was risen up to 10%. Next step was addition of 15% Poly(butylene succinate) – this occurs as top border for process stability. Compound PLA Ingeo 6100 + 20% PBS FZ78TM was not possible to spin.

Compound PLA Ingeo 6752 + 20% PBS FZ78TM was prepared as comparison of process stability with mixture PLA Ingeo 6100. With composition 6100/6752+20%PBS was possible to spin this mixture without problems.

Pure Poly(butylene succinate) was used for production of nonwoven. This laboratory line is not suitable for this type of polymer. During spinning were no problems detected but was not possible to stretch fibres properly.

6.4 Preparation of blends and compounds

Compounds of PLA Ingeo 6100D + 20 % of PBS FZ78TM and PLA Ingeo 6752D + 20 % PBS FZ78TM were prepared on twin screw compound machine.

Table 2 Produced compounds:

Compound code	Composition
Compound A	Ingeo 6100D + 20 % PBS FZ78TM
Compound B	Ingeo 6752D + 20 % PBS FZ78TM

From Compound A 100 g of several blends was prepared as described in Table 3:

Table 3 Used blends

Blend code	Composition	Final amount of PBS [%]
Blend A	15 g (Ingeo 6100D+ 20% PBS) + 85 g Ingeo 6100D	3
Blend B	25 g (Ingeo 6100D+ 20% PBS) + 75 g Ingeo 6100D	5
Blend C	50 g (Ingeo 6100D+ 20% PBS) + 50 g Ingeo 6100D	10
Blend D	75 g (Ingeo 6100D+ 20% PBS) + 25 g Ingeo 6100D	15

6.5 Process description

The extrusion machine was heated up to desired temperature described in Table 4. Production was started with pure Poly(lactic acid) as benchmark. Capillary output was set to 0,22 g/min for fiber configurations Core/Sheath with given ratio 80 % to 20 %. For stretched fibers, setting of Aspirator was same for all produced samples. Following values were set - Aspirator height above belt was 250 mm; die height above Aspirator was 940 mm; air intensity inside Aspirator was 80 kPa; space between Aspirator parts was 2 mm as thickness and 150 mm in width. This setting was kept for all experiments. Surface density of samples was kept between 40 g/m² and 80 g/m². Nonwovens were calendered by heated calender.

It should be noted, that after calendering, there was observed Neck in effect (narrowing of the material caused by high shrinkage of material or high drawing of winding machine). Therefore, belt speed had to be changed due to increase of basis weight of the nonwoven sample.

Table 4 Setting of spinning machine

Product C/S	Extruder A			Extruder B			Spinning die				
	Zone 1 - hopper	Zone 2	Zone 3	Zone 1 - hopper	Zone 2	Zone 3	Melt pump A	Melt pump B	Die	Pack well	
	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	
#A	212	220	211	180	190	200	200	200	200	200	200
#B	180	190	200	185	195	205	200	200	200	200	200
#C	180	190	200	185	195	205	200	200	200	200	200
#D	180	190	200	185	195	205	200	200	200	200	200
#E	165	190	200	185	195	205	200	200	200	200	200
#F	180	190	200	185	195	205	200	200	200	200	200
#G	212	220	211	180	190	200	200	200	200	200	200
#H	212	220	211	180	190	200	200	200	200	200	200

Table 5 Setting of Extruder and Winder machine

Extrusion											Winding	
Exp.	Extruder A pressure	Extruder B pressure	Melt pump A	Melt pump B	Output (72 cap.)	Pressure measured behind melt pump A	Pressure measured behind melt pump B	Motor load A	Motor load B	Belt speed	Calender speed	Bonding temp. Upper/lower
	bar	bar	rpm	rpm	g/min	bar	bar	%	%	m/min	m/min	°C
#A	25	25	6	4	16.0	78	54	31	14	3	3	100/100
#B	25	25	2	8	20.3	80	99	22	32	6.2	6.2	100/100
#C	25	25	2	8	20.3	80	103	22	32	6.2	6.2	100/100
#D	25	25	2	8	20.3	80	101	11	32	6.2	6.2	102/101
#E	25	25	2	8	20.3	100	100	18	28	6.2	6.2	102/101
#G	25	25	2	8	20.3	60	90	8	31	6.2	6.2	97/106
#H	25	25	2	8	20.3	59	65	6	33	6.2	6.2	85/85

6.6 Production problems

During laboratory production, several problems occurred.

1. Neck in after calendering caused different basic weight with same spinning conditions and fiber diameter.
2. It was not possible to spin PLA/PBS blend in core when blend contain more than 15% PBS. To define this phenomenon, SEM analysis were performed on polymer plates prepared by using hot press. In order to evaluate homogeneity of each sample, DSC analysis were done.
3. Nonwoven production of 100% PBS material was complicated. There were performed several settings presented in Figure 23 and Figure 24 than was obtain final laydown.

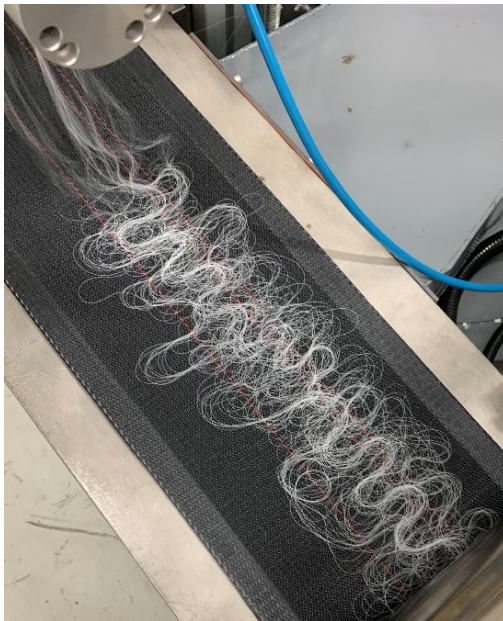


Figure 23 PBS structure before calendering

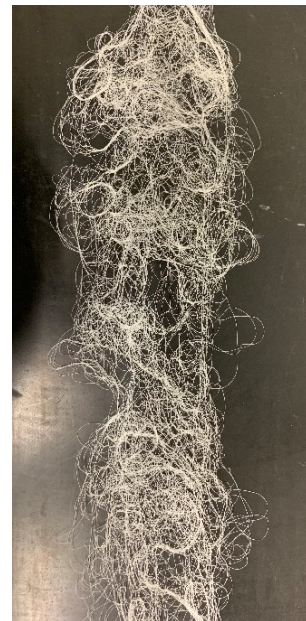


Figure 24 PBS structure after calendering.

7 MEASUREMENT METHODS DESCRIPTION

7.1 Mechanical Properties

All measurements were done at laboratory temperature $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$, RH $50\% \pm 5\%$. Prior to performing the tests, temper the samples at laboratory conditions for a period of at least 2 hours.

7.1.1 Determining Mass per Unit Area ČSN EN 29073, part 1 a WSP 130.1.R4 (12)

Tested samples were cut to diameter 20x100 mm. Scale was reset before each weighing action. 10 samples were measured.

7.1.2 Tensile strength and Elongation of NW in MD ISO 9073-3:1999, WSP 110.4.R4 (12)

Test conditions were following: Used pretension 0.5N, load speed increment 200 mm/min. The clamps of the tearing machine were set to a clearance of 100 mm. Sample 50x200 mm. 10 samples were measured.

7.2 Softness of material

7.2.1 Handle – o – matter

The tests were done under WSP 090.3.R4 (12) the 20 mm wide gap was used for all measurements. 5 measurements for each sample were done.

7.2.2 Softness panel test

A consistent skilled panel test was used to evaluate all materials using standard fabric references (PLA/PE). 5 measurements for each sample were done.

7.3 Differential scanning calorimetry

The subjects of analysis were small pieces of PLA/PBS blend samples (8-10 mg). The characterization of the thermal properties was performed to define the melting/crystallization heat (J/g) and the characteristic melting/crystallization temperature (peaks in $^{\circ}\text{C}$) on polymer pellet samples. Two heating scans were chosen for determination of characteristic properties. The record from the second heating was used for evaluation, ie after deleting the temperature

history of the sample. The analysis was carried out under inert atmosphere of nitrogen flow of 40 ml/min. Tests were running from -50°C up to 250°C with step 10°C per minute.

7.4 Rheology

7.4.1 Shear viscosity

In order to evaluate and compare a shear flow behavior of the tested materials, the shear viscosity was investigated using a Rheograph RG 25-50 high-pressure capillary viscometer at 200°C. The shear rates were determined from 2000 1/s to 35 1/s. For the flow curve, 10 shear rates were measured in the indicated range. The experiments were performed for a capillary with a length of 20 mm and a diameter of 1 mm.

7.4.2 Extensional viscosity

Extensional viscosity of the prepared samples was characterized using a high-pressure capillary rheometer Göttfert Rheograph RG 50 with a Rheotens device (scale with rollers) at 200°C. The distance between the end of the capillary and the center of wheels describes a string length that was set to 100 mm for all the performed experiments. During the experiment, when polymer melt string was extruded through a capillary with a length of 20 mm and a diameter of 2 mm at constant piston speed $0.20 \text{ mm} \cdot \text{s}^{-1}$, rollers were accelerating from an initial speed 30 mm/s to higher speeds until polymer strand broke.

8 RESULTS

All results from mechanical and physical measurements and evaluations are described in this chapter.

8.1 Mechanical properties of produced nonwovens

Final results of mechanical properties of produced nonwoven samples are summarized in Table 6. As shown in Table 6 positive impact on tensile strength was observed with 20% PBS in sheath on the other side adding PBS into core decrease tensile. Regarding softness the best soft touch was observed with usage pure PBS and similar touch feeling was observed with PE in sheath. Regarding stiffness of produced nonwovens adding PBS material into sheath has positive effect on stiffness. On the other side adding PBS into core shows similar behavior as bicomponent nonwoven without additive.

Table 6 Mechanical properties of produced nonwovens

sample	Basis weight	STT	Fiber diameter	Relative Tensile Strength @ MD	Relative Elongation @ Peak - MD	Softness panel test	Relative Stiffness MD gap 20mm
	g/m ²	s	um	g/m ²	(N/2,54cm)		mN*m ² /g
#A	41.63	< 50	24.93	0.84	0.44	1.9	2.95
#B	83.2	19.82	33.1	0.95	0.53	6.5	15.83
#C	82.05	10.01	33.17	0.49	0.04	6.0	16.97
#D	71.25	12.28	32.55	0.42	0.05	4.3	9.79
#E	67.06	5.43	31.43	0.19	0.03	4.7	19.62
#F	Not possible to spin						
#G	38.65	12.49	26.89	1.35	0.87	3.5	4.42
#H	42.69	3.08	24.93	0.7	0.93	1.1	0.72

8.2 Differential scanning calorimetry

DSC analysis of the investigated samples was evaluated from the second heating scan (Figure 25). DSC analysis of pure PBS (Figure 26) and PLA (Figure 27) were measured as a reference and for comparison of the systems.

Glass transition temperature for pure PLA was found to be 58.49 °C and decreased to 57.64 °C, 58.46 °C and 58.76 °C with addition of 3 %, 5 % and 10 % of PBS, respectively. The slight drop can represent some limited miscibility of the materials or their low molecular weight parts, or PBS can act as a plasticizer when amorphous part of PBS could interact with amorphous part of PLA (26). With further increase in PBS content (15 % and 20 %), the glass transition temperatures were found 60.14 °C and 60.43 °C, it means they even exceeded the value for neat PLA (58.49 °C). Interestingly, the melting enthalpy for PLA crystals was the highest for the sample with 3 % PBS (54.95 J/g) and further decreased with its increasing amount, however, in all cases was higher than the melting enthalpy for neat PLA (34.36 J/g). Droplets of PBS itself or its impurities can act as nucleating agent and significantly accelerate crystallization of PLA (37). Unfortunately, it was not possible to calculate crystallization enthalpy for individual PLA or PBS in the blends due to their close crystallization temperatures and thus it was not possible to evaluate their crystallization any further. Nevertheless, it is assumed, that in their blends crystallinity of both PLA and PBS increases compared to neat materials (26).

According to the literature, it is not possible to clearly state whether PLA and PBS are miscible materials or not. While in some studies it was stated that PLA and PBS are immiscible polymers, in many studies it has been found that they are miscible at low content of PBS in the blend (lower than 20 %) or at least miscibility of their low molecular weight parts (38). According to the DSC analysis, where two separate melting peaks can be found and the fact that glass transition temperature changed only slightly, could be stated that the miscibility of PLA and PBS in this study occurred only at low level which could be confirmed by slight shift in glass transition temperatures at low PBS concentration and low melting enthalpy of the system with 3 % of PBS for PBS (only 0.31 J/g).

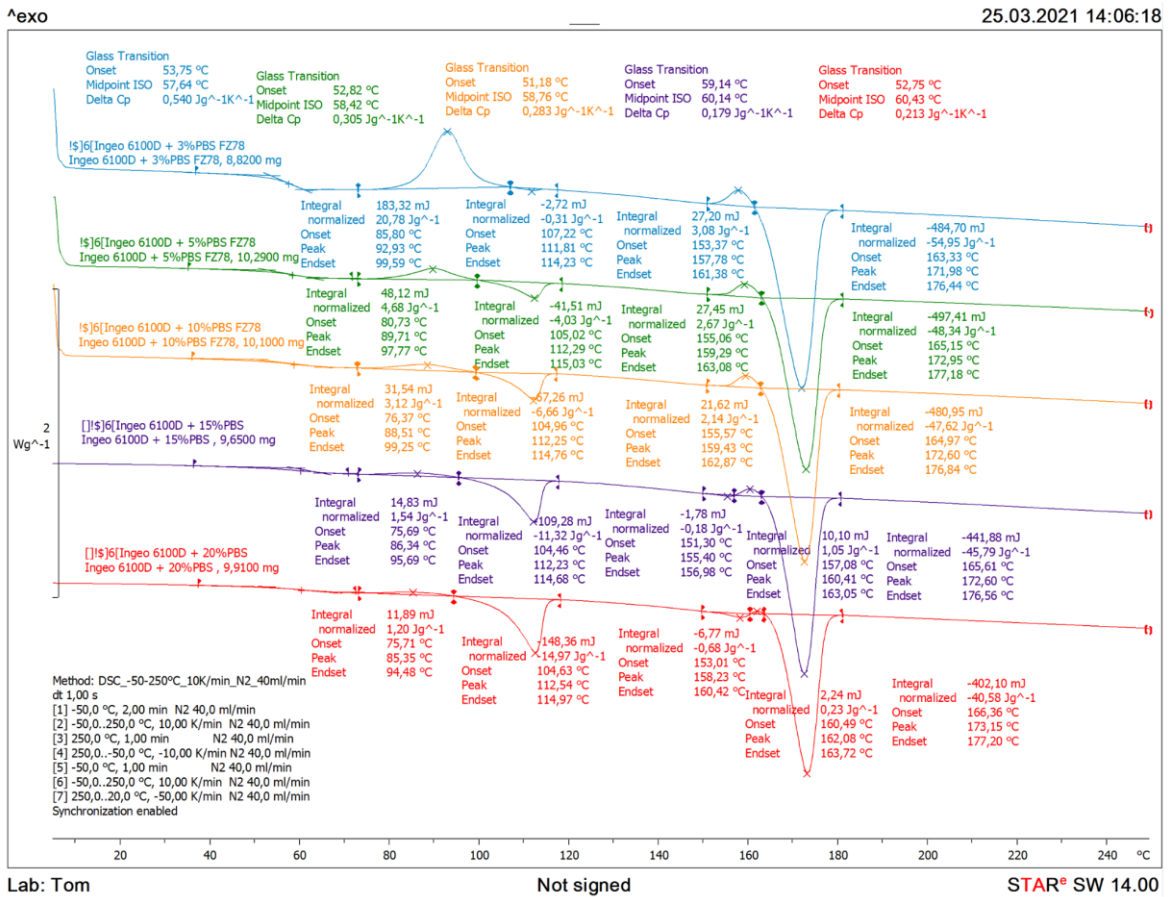


Figure 25 DSC evaluation of mixtures PLA + PBS

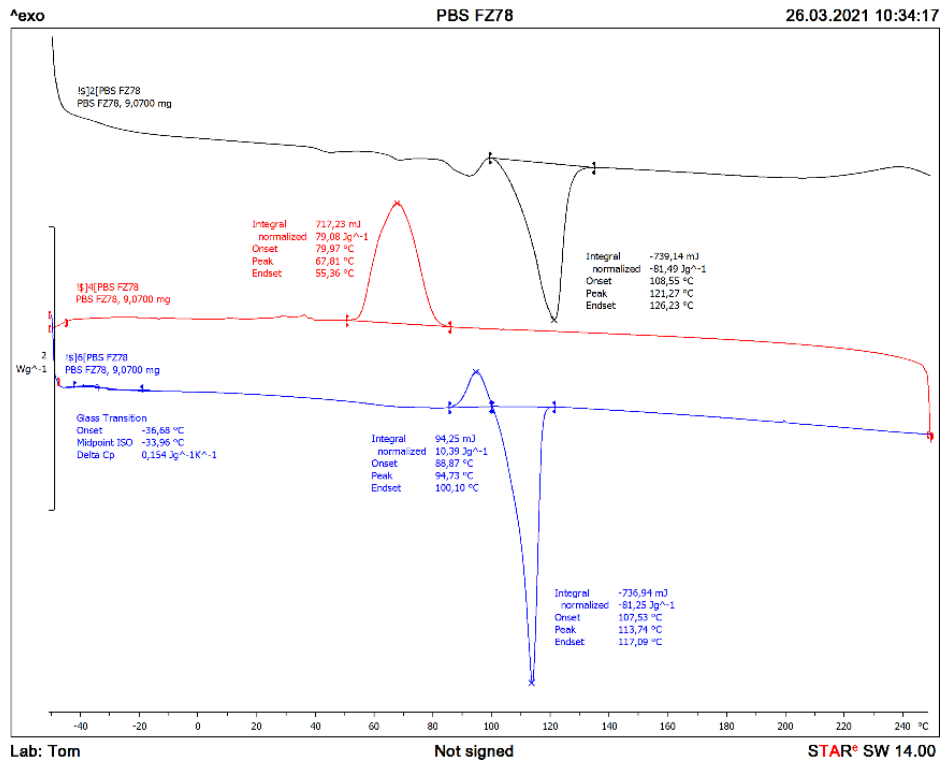


Figure 26 DSC evaluation of PBS FZ78TM

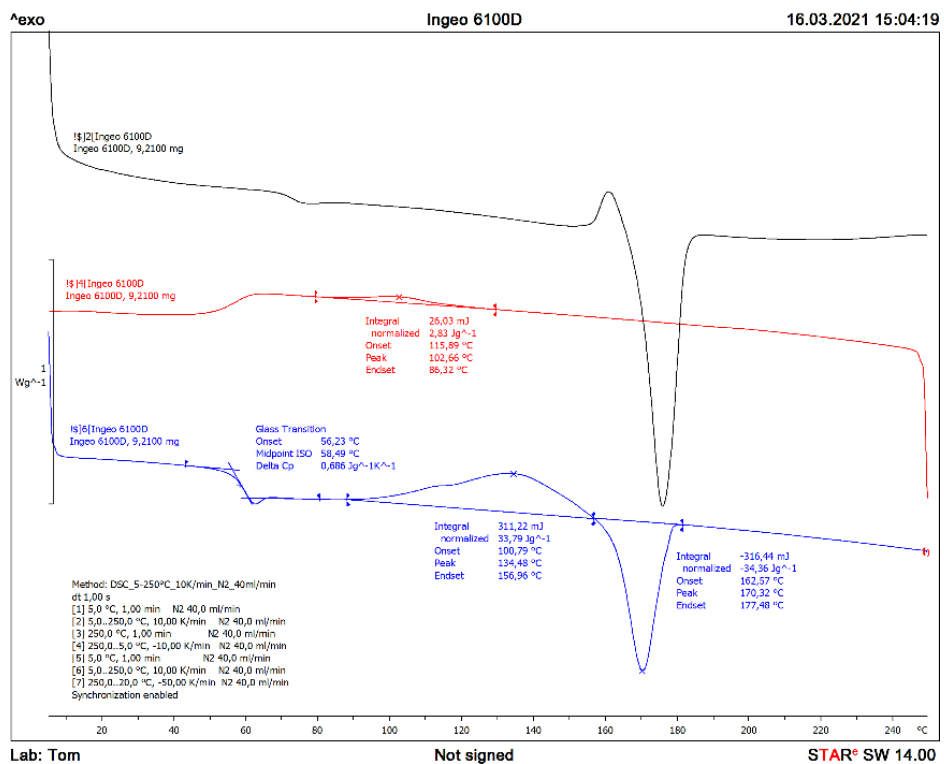


Figure 27 DSC evaluation of PLA Ingeo 6100D

8.3 Rheology evaluation

Strain rate dependent shear viscosity has been determined at 200°C for both pure PLA types and their compounds with PBS from 3 to 20 % as well as for pure PBS (Figure 28). It is clear that the lowest shear viscosity is observed in case of pure PBS. On the other hand, the highest viscosity is observed in case of PLA 6752. As can be seen in Figure 28, shear viscosity increases with decreasing amount of PBS.

It should be noted that processing window of PLA 6752 samples belongs to higher shear viscosities than in case of PLA 6100 samples. During the spinning process (shear rate inside a capillary equal to 10^3 1/s), PLA6100 mixture with 15% of PBS represented an unstable process, even more, with 20% of PBS was not possible to spin. On the other side, PLA 6752 mixture with 20% was spinnable without any significant problems. It seems, that shear viscosity of PLA 6752 + 20% of PBS in area around 10^3 1/s represents a border for spinnability of these materials.

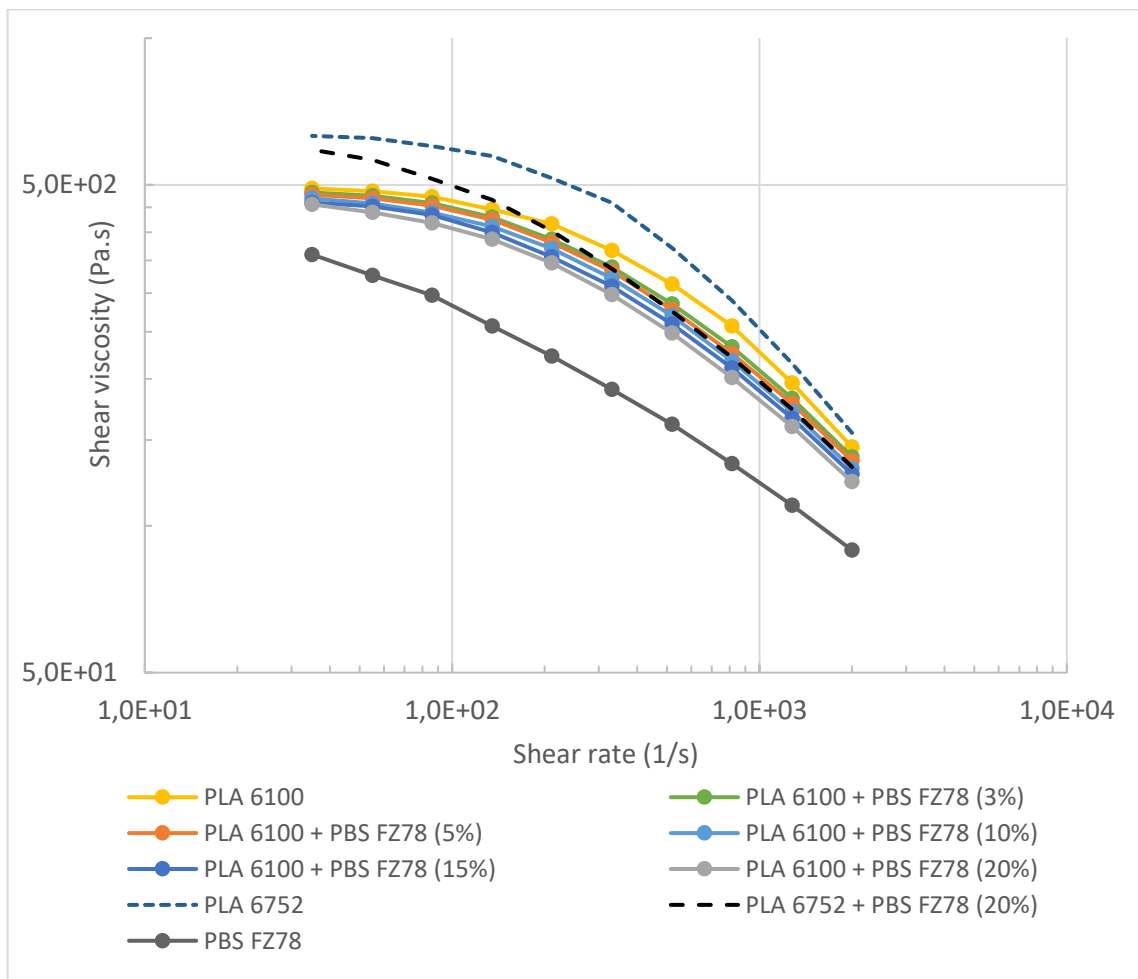


Figure 28 Shear viscosity dependence on shear rate at 200°C

Further, the uniaxial elongational viscosity of the prepared samples has been studied. Thus, the melt strength is given according to the maximum force during a break of the polymer string which shows also a drawability of the samples.

Typical drawdown force dependence on drawdown velocity can be seen in Figure 29 as well as in Figure 30 as a data fitted according to the Wagner model (35). Then, using software evaluation, the uniaxial extensional viscosity is obtained (Figure 31).

As can be seen in Figure B and C, in case of 15% and 20% of PBS included in PLA 6100, the drawability is significantly reduced. As was already mentioned, this effect was also observed during a sample preparation by spinning process when processing of this compound was very problematic (15 % of PBS) or even not possible (20 % of PBS).

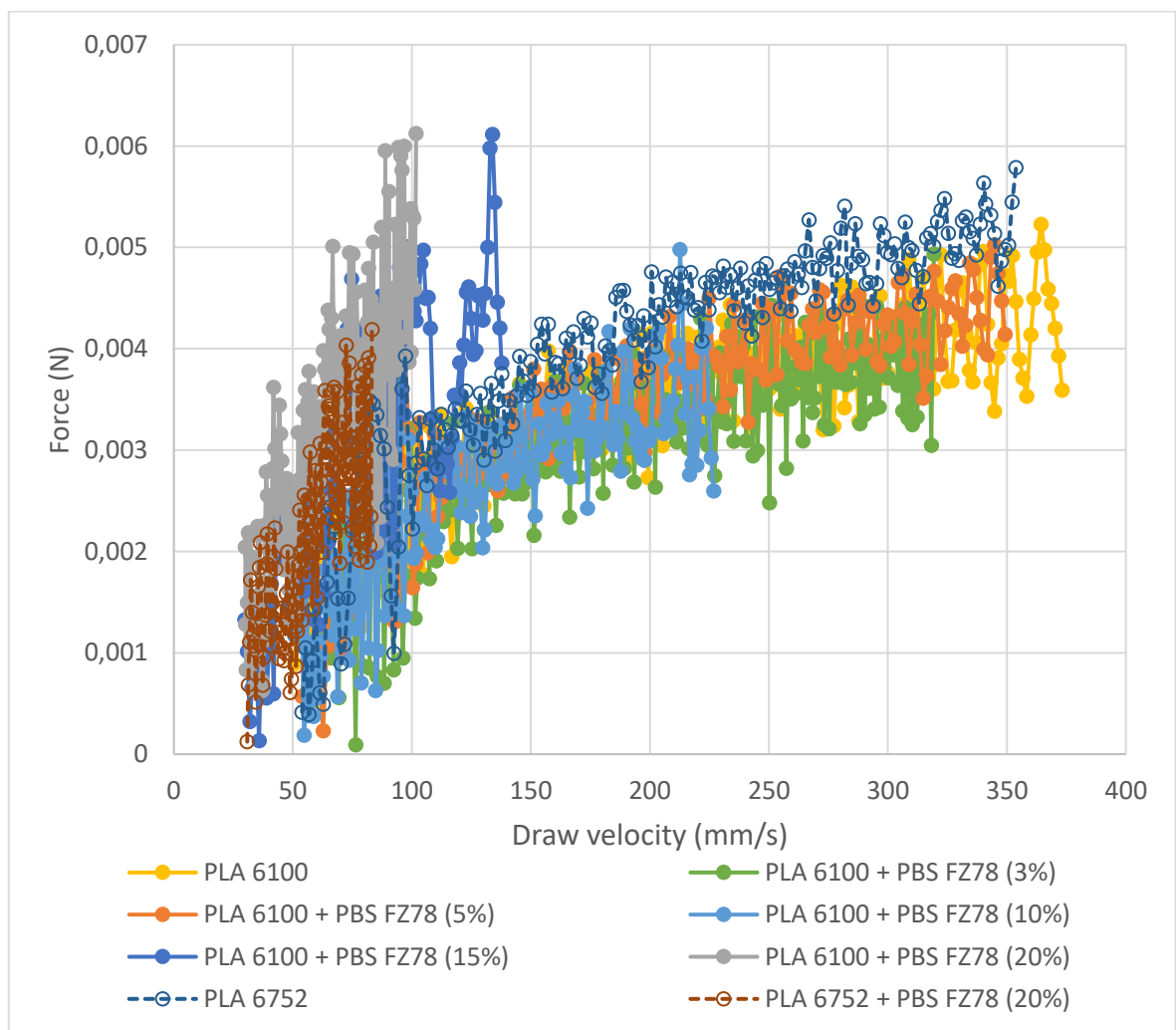


Figure 29 Drawdown force dependence on drawdown velocity

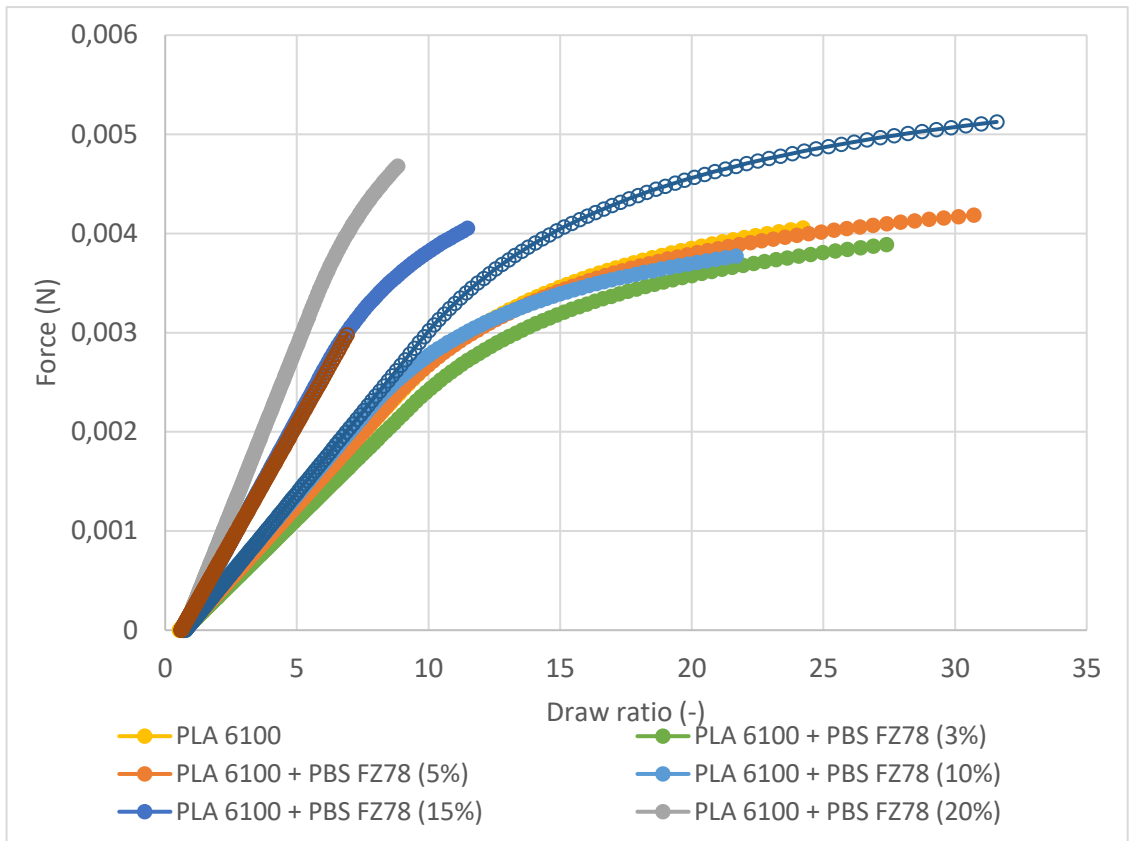


Figure 30 Wagner model fit

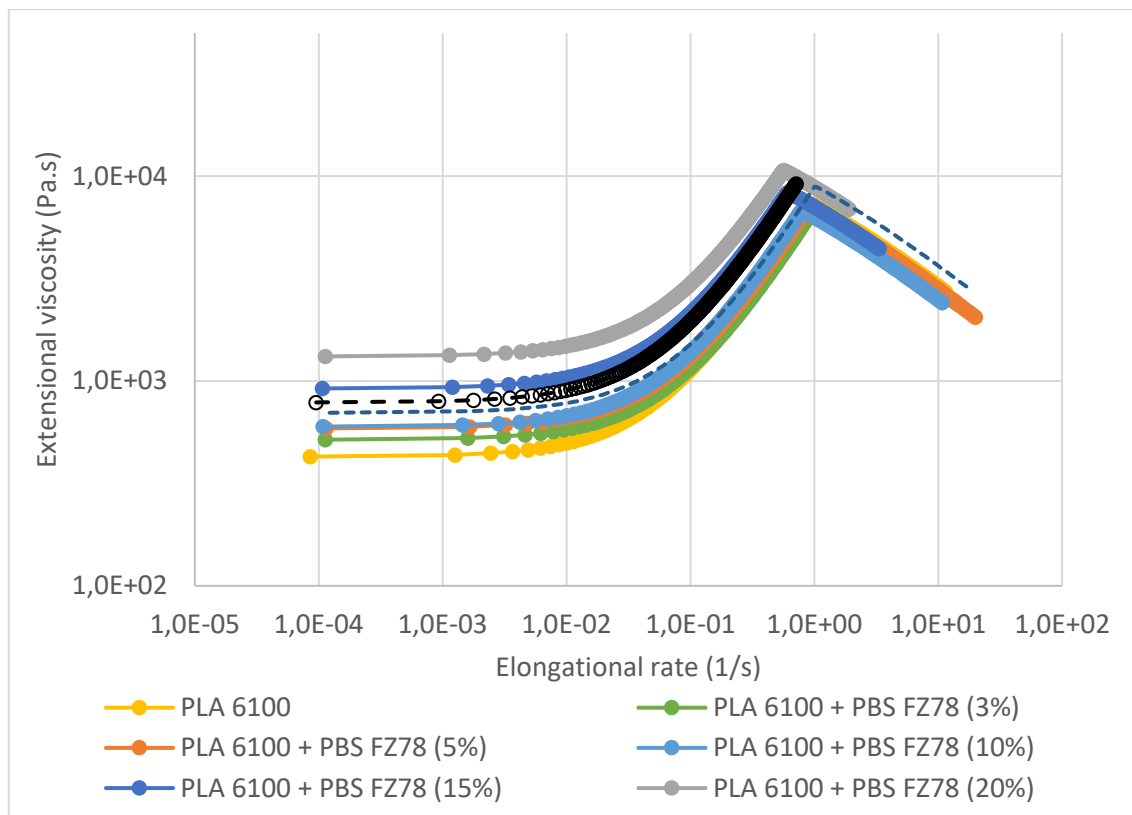


Figure 31 Extensional viscosity dependence on extensional rate at 200°C

As can be seen in Figure 31, the extensional viscosity in Newtonian plateau region steadily increases with PBS content which is opposite in case of shear viscosity (Figure 28). It should be noted, that elongational behavior is more various than in case of shear behavior. It can be also seen that if strain hardening is too significant, as in case of samples with 15 and 20% PBS, processing of these compounds is not possible.

8.4 Evaluation of visible aspect of plates

Black background was use for evaluation of visual appearance. Pictures were taken 10 cm high over the sample with iPhone XR without any magnification.

8.4.1 PLA without PBS

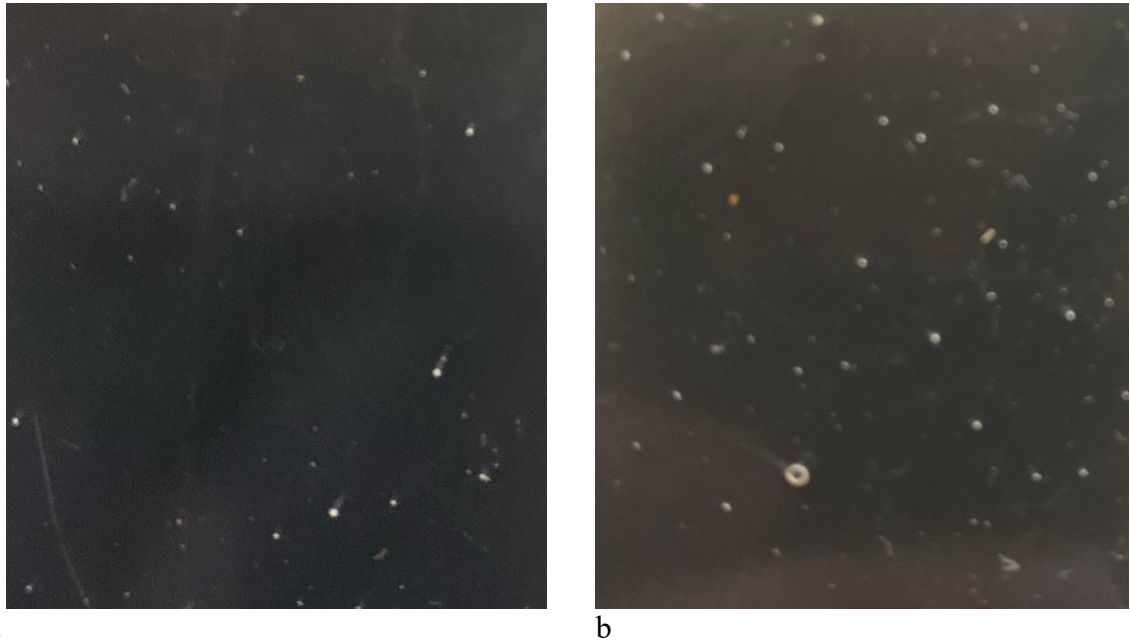


Figure 32 Pure PLA plates

As visible on Figure 32 pure Ingeo 6100D (a) contain small white parts. These parts can be not melted polymer or air bubbles in compare Ingeo 6752D (b) contains visible air bubbles. Based on presence of air bubbles is possible that material was not dried properly.

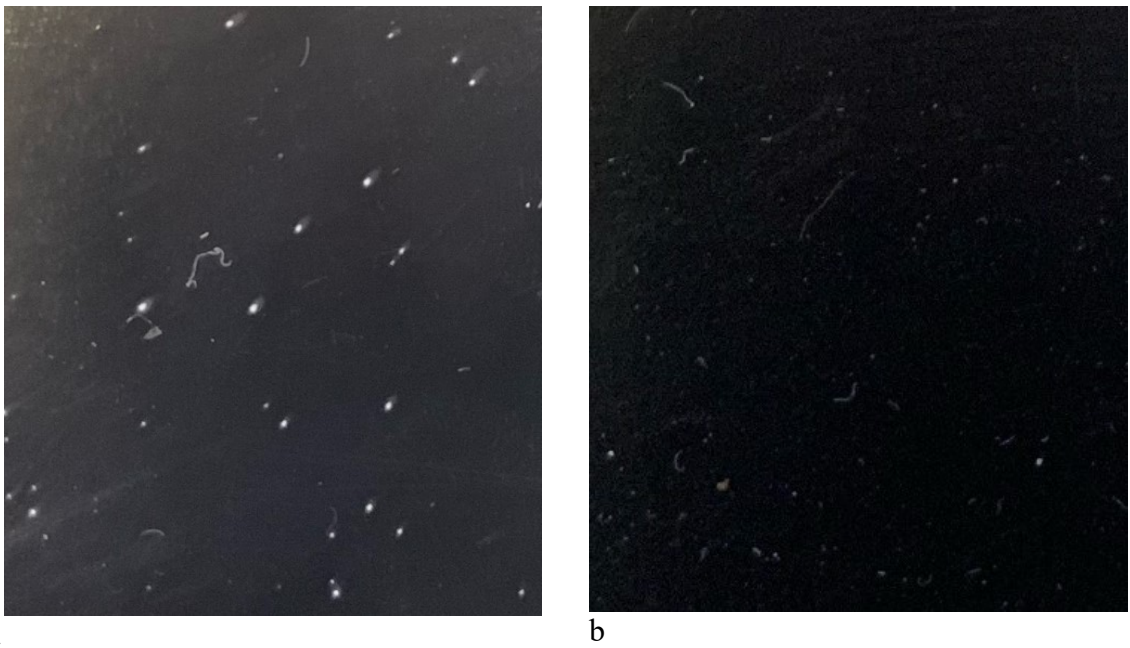


Figure 33 Visual comparison PLA/PLA plate - compound and blend

In Figure 33 picture a is PLA Ingeo 6100 D + PLA Ingeo 6752 blend while picture b is PLA Ingeo 6100 D + PLA Ingeo 6752 D compound. White pieces are visible in the left picture. These pieces are probably a) not melted part of 6100 or b) not miscible part of 6752.

Figure 32 support theory of not-melted parts. In compare on right picture is PLA/PLA compound where plate was transparent with small white defects. These defects were smaller than blended mixture. Therefore, I suppose that white pieces on left picture were not mixed PLA Ingeo 6100D.

8.4.2 PLA with PBS

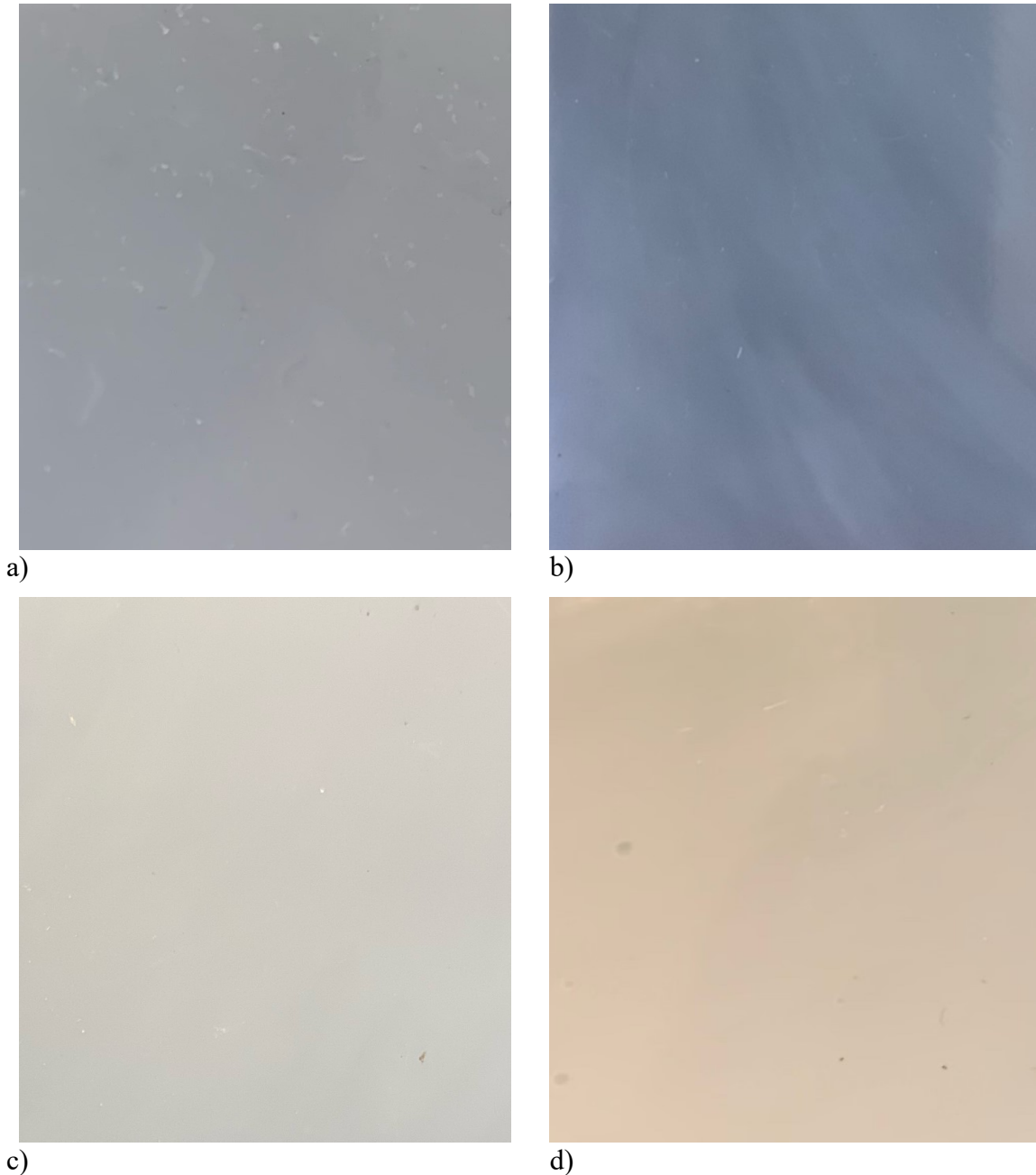


Figure 34 a) Ingeo 6752D + 20% PBS; b) Ingeo 6100D + 3% PBS ; c) Ingeo 6100D + 5% PBS; d) Ingeo 6100D + 20% PBS

PBS changed color of produced plates. As visible in Figure 34 when is PBS mixed with Ingeo 6100D material is more yellowish (beige) on the other side with same amount of PBS

compounded with 6752 material was whiter. In Figure 33 is also visible that blend Ingeo 6100D + 3% FZ78TM was not properly mixed during production plates – this was probably caused by different viscosity.

8.5 SEM evaluation

In Figure 35 is shown that our mixture behavior is similar as described in Deng and Thomas (26) where phase separation is visible in both mixtures. PLA phase (dark one) is disintegrated into PBS matrix.

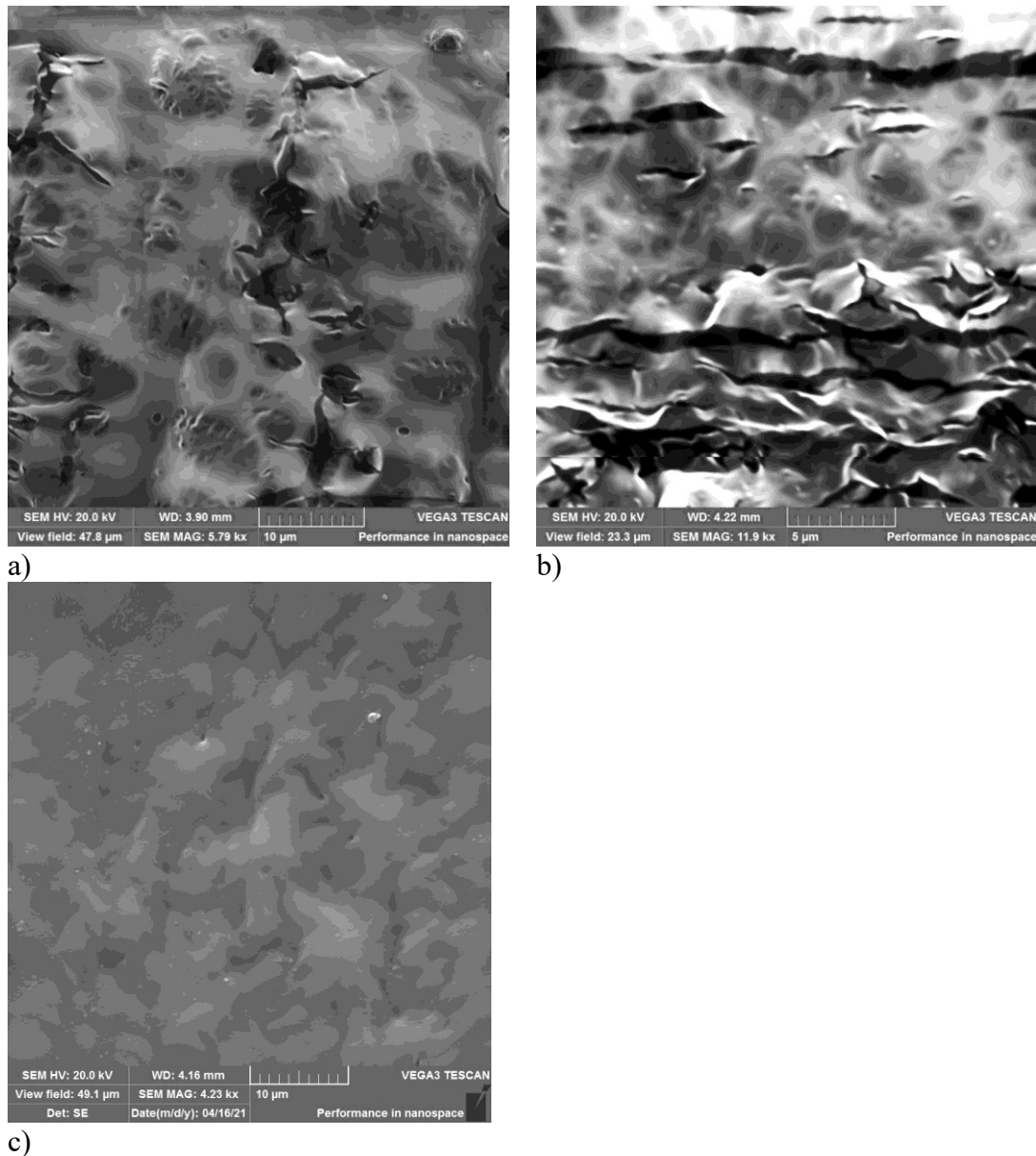


Figure 35 SEM evaluation of produced plates - a) PLA Ingeo 6752 + 20% PBS FZ78TM; b) PLA Ingeo 6100 + 20% PBS FZ78TM; c) pure PBS FZ78TM

CONCLUSION

This work is focused on finding cheap solution to increase softness of Poly(lactic acid) based nonwovens. Thus, several samples was produced with different material compositions of bicomponent fibers for given processing conditions.

During the spinning process it was discovered that laboratory line Hills LBS-300 is not able to stretch pure PBS fibres. Therefore, it was complicated to produce 100% PBS nonwoven samples.

Further, it was observed that PLA Ingeo 6100 + 20% PBS composition (Compound A) is not possible to spin in contrast with tested PLA Ingeo 6752 +20% PBS composition (Compound B) which was stable during the processing. In order to find out these spinnability problems, several analyses were done. Based on these analyses it is visible, that shear viscosity of Compound A is lower than shear viscosity of Compound B having similar values as Blend C (PLA Ingeo 6100 + 10% PBS). Therefore, one of the theory is that shear rate of Blend C represents border limit for stable spinning of the material.

In order to evaluate the miscibility of the mixtures, DSC measurements were done. It was found that all mixtures are miscible.

Further, with the help of SEM analysis performed on polymer plates, it was observed that homogeneity of the blends is not stable.

Although several measurements and expertise were done the main cause was not defined. Further investigation is needed.

9 BIBLIOGRAPHY

- (1) European nonwovens production grows by over 7%. *Nonwovens Trends* [online]. [cit. 2021-04-07]. Dostupné z: <https://www.nonwoventrends.com/news/research-institutes-education/Edana-European-nonwovens-production-grows-by-over-7--23813>
- (2) *ISO 9092:2019(en) Nonwovens — Vocabulary*. 3. 2019-03.
- (3) *What are nonwovens?* [online]. [cit. 2020-09-10]. Dostupné z: <https://www.edana.org/nw-related-industry/what-are-nonwovens>
- (4) JAROSLAV KOHUT, ZDENEK MECL, FRANTISEK KLASKA. *Batt comprising crimped bi- or multi-component fibres*. wo2014108106. Uděleno 2013.
- (5) ZDENĚK MEČL, JAROSLAV KOHUT, PAVLINA KASPARKOVA. *Nonwoven web with enhanced barrier properties*. 2018. EP3313343A1. Zapsáno 2018.
- (6) Polylactic acid blends: The future of green, light and tough. *Progress in Polymer Science*. **2018**(85), 83-127.
- (7) DIPAYAN, Das a Behnam POURDEYHIMI. *Composite Nonwoven Materials - Structure, Properties and Applications*. [online]. UK: Elsevier, 2014 [cit. 2021-03-14]. ISBN 978-0-85709-775-0. Dostupné z: <https://app.knovel.com/hotlink/toc/id:kpCNMSPA04/composite-nonwoven-materials/composite-nonwoven-materials>
- (8) YU, Bin, Xiaoming ZHAO, Yuening ZENG a Dongyue QI. The influence of process parameters on needle punched nonwovens investigated using image analysis. *RSC Advances* [online]. 2017, **7**(9), 5183-5188 [cit. 2021-03-23]. ISSN 2046-2069. Dostupné z: doi:10.1039/C6RA25474H
- (9) BHAT, G. a D.V. PARIKH, R.A. CHAPMAN, ed. 3 - Biodegradable materials for nonwovens. *Applications of Nonwovens in Technical Textiles*. Woodhead Publishing, 2010, s. 46-62. ISBN 978184569437.
- (10) RUSSELL, S.J., ed. *Handbook of Nonwovens*. Woodhead Publishing, 2007, 544 s. ISBN 9781855736030.
- (11) BATRA, Subhash, a Behnam POURDEYHIMI. *Engineering with fibers - Introduction to Nonwovens Technology*. Pennsylvania, USA: DEStechPublication, Inc., 2012. ISBN 978-1-60595-037-2.
- (12) ALBRECHT, Wilhelm, Hilmar FUCHS a Walter KITTELMANN, ed. *Nonwoven Fabrics*. 2002. ISBN 9783527304066.
- (13) RF5 Composite. *Reifenhäuser* [online]. Germany [cit. 2021-04-07]. Dostupné z: <https://reifenhauser.com/en/lines-components/extrusion-lines/nonwoven-lines/rf5-composite>
- (14) MULTI-COMPONENT FIBER TECHNOLOGY FOR MEDICAL AND OTHER FILTRATION APPLICATIONS. *Hills inc.* [online]. USA [cit. 2020-09-13]. Dostupné z: <http://www.hillsinc.net/assets/pdfs/multi-component-fiber-medical.pdf>
- (15) HOSSAIN, M., M. ACAR a W. MALALASEKERA. Modelling of the Through-air Bonding Process. *Journal of Engineered Fibers and Fabrics* [online]. 2009, **4**(2) [cit. 2021-04-07]. ISSN 1558-9250. Dostupné z: doi:10.1177/155892500900400202
- (16) Hydro-entangled nonwovens. *Bondex* [online]. [cit. 2021-03-20]. Dostupné z: <https://www.bondexinc.com/hydro-entangled-non-wovens/>

- (17) VILÉM, Rostislav. *Nonwoven Textiles Based on PLA*. Zlín, 2019. Bakalářská práce. Univerzita Tomáše Bati ve Zlíně. Vedoucí práce Doc., Ing., Sedláček Tomáš, Ph.D.
- (18) *Why use nonwovens in filtration?* [online]. [cit. 2021-05-13]. Dostupné z: <https://www.edana.org/nw-related-industry/nonwovens-in-daily-life/filtration>
- (19) *ACF environmental: Nonwoven Geotextile Fabric* [online]. [cit. 2021-05-13]. Dostupné z: <https://acfenvironmental.com/products/geosynthetics/geotextile/nonwoven/>
- (20) SIN, Lee, Abdul RAHMAT a Wan RAHMAN. *Polylactic acid: PLA biopolymer technology and applications*. Amsterdam: William Andrew is an imprint of Elsevier, 2013. PDL handbook series. ISBN 978-1-4377-4459-0. Dostupné také z: <https://www.sciencedirect.com/book/9781437744590/polylactic-acid?via=ihub=>
- (21) *The latest news from the world of Bioplastics* [online]. [cit. 2021-03-07]. Dostupné z: <https://www.total-corbion.com/news/total-corbion-pla-announces-the-first-world-scale-pla-plant-in-europe/>
- (22) HARRIS, Angela a Ellen LEE. Improving mechanical performance of injection molded PLA by controlling crystallinity. *Journal of Applied Polymer Science* [online]. 2008, **107**(4), 2246-2255 [cit. 2021-03-14]. ISSN 00218995. Dostupné z: doi:10.1002/app.27261
- (23) PARK, Jun Wuk a Seung Soon IM. Phase behavior and morphology in blends of poly(L-lactic acid) and poly(butylene succinate). *Journal of Applied Polymer Science* [online]. 2002, **86**(3), 647-655 [cit. 2021-05-14]. ISSN 0021-8995. Dostupné z: doi:10.1002/app.10923
- (24) BHATIA, A., R.K. GUPTA, S.N. BHATTACHARYA a H.J. CHOI. Compatibility of biodegradable poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) blends for packaging application. *Korea Australia Rheology Journal*. 2007, **19**(3), 125-131.
- (25) JOMPANG, Lalita, Supaphorn THUMSORN, Jessada Wong ON et al. Poly(Lactic Acid) and Poly(Butylene Succinate) Blend Fibers Prepared by Melt Spinning Technique. *Energy Procedia* [online]. 2013, **34**, 493-499 [cit. 2021-05-14]. ISSN 18766102. Dostupné z: doi:10.1016/j.egypro.2013.06.777
- (26) DENG, Y. a N.L. THOMAS. Blending poly(butylene succinate) with poly(lactic acid): Ductility and phase inversion effects. *European Polymer Journal* [online]. 2015, **71**, 534-546 [cit. 2021-05-14]. ISSN 00143057. Dostupné z: doi:10.1016/j.eurpolymj.2015.08.029
- (27) MARKOVIC, G. a P.M. VISAKH. Polymer blends. *Recent Developments in Polymer Macro, Micro and Nano Blends* [online]. Elsevier, 2017, s. 1-15 [cit. 2021-04-20]. ISBN 9780081004081. Dostupné z: doi:10.1016/B978-0-08-100408-1.00001-7
- (28) *Polymer Compounding Basics* [online]. [cit. 2021-04-20]. Dostupné z: <https://www.fostercomp.com/polymer-compounding-basics/>
- (29) Chemistry for Non-Majors. *Homogenous and Heterogenous Mixtures* [online]. [cit. 2021-03-04]. Dostupné z: <https://courses.lumenlearning.com/cheminter/chapter/homogenous-and-heterogenous-mixtures/>
- (30) DMA Principles and Basic Applications. *Mettler Toledo* [online]. [cit. 2021-05-12]. Dostupné z: https://www.mt.com/int/en/home/library/on-demand-webinars/lab-analytical-instruments/Dynamic_Mechanical_Analysis.html
- (31) EBWELE, Robert O. *Polymer science and technology*. 1. Florida, USA: CRC Press LLC, 2000. ISBN 0849389399.

- (32) ELIADES, T., S. ZINELIS, D.-G. KIM a W. BRANTLEY. Structure/property relationships in orthodontic polymers. *Orthodontic Applications of Biomaterials* [online]. Elsevier, 2017, s. 39-59 [cit. 2021-03-14]. ISBN 9780081003831. Dostupné z: doi:10.1016/B978-0-08-100383-1.00002-3
- (33) TAGUET, Aurélie. Rheological characterization of compatibilized polymer blends. *Compatibilization of Polymer Blends* [online]. Elsevier, 2020, s. 453-487 [cit. 2021-03-14]. ISBN 9780128160060. Dostupné z: doi:10.1016/B978-0-12-816006-0.00016-5
- (34) Differential Scanning Calorimetry. *Linseis GmbH* [online]. [cit. 2021-04-12]. Dostupné z: <https://www.linseis.com/en/methods/differential-scanning-calorimetry-dsc/>
- (35) HAN, Chang Dae. *Rheology and processing of polymeric materials*. New York: Oxford University Press, 2007. ISBN 9780195187830.
- (36) WAGNER, M., V. SCHULZE a A. GÖTTFERT. Rheotens-mastercurves and drawability of polymer melts. *Polymer Engineering & Science* [online]. 1996, **36**(7), 925-935 [cit. 2021-04-12]. ISSN 00323888. Dostupné z: doi:10.1002/pen.10480
- (37) YOKOHARA, Tadashi a Masayuki YAMAGUCHI. Structure and properties for biomass-based polyester blends of PLA and PBS. *European Polymer Journal* [online]. 2008, **44**(3), 677-685 [cit. 2021-05-14]. ISSN 00143057. Dostupné z: doi:10.1016/j.eurpolymj.2008.01.008
- (38) SU, Shen, Rodion KOPITZKY, Sengül TOLGA a Stephan KABASCI. Polylactide (PLA) and Its Blends with Poly(butylene succinate) (PBS): A Brief Review. *Polymers* [online]. 2019, **11**(7) [cit. 2021-05-14]. ISSN 2073-4360. Dostupné z: doi:10.3390/polym11071193

LIST OF ABBREVIATIONS

Etc.	Et cetera
SMS	Spunbond – Meltblown – Spunbond nonwoven
e.g.	For Example
3D	three-dimensional
Covid – 19	Coronavirus disease
PLA	Poly (lactic acid)
PBS	Poly (butylene succinate)
°C	degree Celsius (unit)
DSC	Differential scanning calorimetry
DMA	
SEM	Scanning electron microscopy
FTIR	Fourier infrared spectroscopy
cm	centimeter
%	percentage
mm	millimeter
kPa	kilopascal
g/m ²	gram per square meter
rpm	revolutions per minute
cap.	capillaries
ml	milliliter
RH	relative humidity
l/s	liter per second
s	second
µm	micron
@	at

LIST OF FIGURES

Figure 1 Cross section SMS spinnmelt material (7)	16
Figure 2 Carded nonwoven (8)	17
Figure 3 Spunbond nonwoven thermally bonded by calender	17
Figure 4 Scheme of spinnmelt machine with dryers.....	19
Figure 5 Reifenhäuser Reicofil RF5 Composite Line (13).....	19
Figure 6 Different types of bicomponent fibers (14).....	20
Figure 7 Thermal bonding with calender (11).....	21
Figure 8 Principle of bonding with hot air (15).....	21
Figure 9 Scheme of hydroentanglement bonding (16)	22
Figure 10 Baby diaper composition.....	23
Figure 11 Nonwoven parts inside cars.....	24
Figure 12 Nonwoven filters (18)	25
Figure 13 Practical use of geotextile (19).....	25
Figure 14 Chemical structure of Poly(butylene succinate).....	26
Figure 15 Chemical structure of Poly(lactic acid)	27
Figure 16 DSC evaluation.....	30
Figure 17 DMA evaluation of different miscibility.....	30
Figure 18 SEM pictures - Example of non-miscible and particularly miscible mixture	31
Figure 19 Laboratory line Hills LBS-300.....	33
Figure 20 Differential scanning calorimeter	34
Figure 21 The Göttfert Rheograph RG25-50.....	35
Figure 22 Rheotens device.....	36
Figure 23 PBS structure before calendaring	43
Figure 24 PBS structure after calendaring.	43
Figure 25 DSC evaluation of mixtures PLA + PBS	49
Figure 26 DSC evaluation of PBS FZ78TM	50
Figure 27 DSC evaluation of PLA Ingeo 6100D.....	50
Figure 28 Shear viscosity dependence on shear rate at 200°C	51
Figure 29 Drawdown force dependence on drawdown velocity	52
Figure 30 Wagner model fit.....	53
Figure 31 Extensional viscosity dependence on extensional rate at 200°C.....	53
Figure 32 Pure PLA plates.....	55
Figure 33 Visual comparison PLA/PLA plate - compound and blend.....	55

Figure 34 a) Ingeo 6752D + 20% PBS; b) Ingeo 6100D + 3% PBS ; c) Ingeo 6100D + 5% PBS; d) Ingeo 6100D + 20% PBS 56

Figure 35 SEM evaluation of produced plates - a) PLA Ingeo 6752 + 20% PBS FZ78TM; b) PLA Ingeo 6100 + 20% PBS FZ78TM; c) pure PBS FZ78TM 57

LIST OF TABLES

Table 1 Codes of produced samples	40
Table 2 Produced compounds:.....	41
Table 3 Used blends.....	41
Table 4 Setting of spinning machine	42
Table 5 Setting of Extruder and Winder machine	42
Table 6 Mechanical properties of produced nonwovens	47