T.R.
EGE UNIVERSITY
Graduate School of Applied and Natural Science

MODIFICATION OF PLA BASED PLASTICS AND NONWOVEN PRODUCTS MADE OF THEM

MSc Thesis

Name SURNAME: Melis ÖZKAYA

Material Science and Engineering

İzmir
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Name SURNAME: Melis ÖZKAYA

Supervisor : Assoc. Prof. Lütfiye ALTAY
Supervisor : doc. Ing. Tomáš Sedláček, Ph.D.

Material Science and Engineering
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By Melis ÖZKAYA as Master thesis, this work full of ‘’Modification of PLA Based Plastics and Nonwoven Products Made of Them’’ submitted the relevant provisions of the Postgraduate Education and Training Regulation and the EÜ Science Institute Education and Training Directive were evaluated by us and found worthy of defense and in the thesis defense examination held on 22.03.2021 in position.

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ABSTRACT

MODIFICATION OF PLA BASED PLASTICS AND NONWOVEN PRODUCTS MADE OF THEM

ÖZKAYA, Melis

MSc in Material Science and Engineering

Supervisor: Assoc. Prof. Lütfiye ALTAY

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Today, the damage caused by the increasing use of plastic is an important issue. Accordingly, a lot of work is being done to reduce the use of plastic. If we learn how to use and properties of polylactic acids, which is a current issue in society, and their behavior in the process, we can use it in more areas. For this reason, nonwoven polylactic acid fabrics were studied.

In this study, the interaction of 3 different PBATs with PLA and the process usability of spunbond technology used in nonwoven production were examined. After PLA and 3 different PBAT were extruded at different rates, the results of morphological, rheological and mechanical tests of the materials were examined. The obtained data were interpreted according to the ease of processing and the rate of development of the material in the PLA. In the results of working; The most suitable PBAT for spunbond processing was determined as PBAT2. According to the tensile strength test results, the networking of nonwovens was examined and the best result was determined as PBAT1 and PBAT2. In general, the maximum PBAT usage rate for forming nonwoven fabric with the spunbond process is determined as 10%; It was observed that the rate showing the best feature was 5%.

Keywords: Spunbond technology, PLA/PBAT, antibacterial, biodegradability, nonwoven, Polylactic acid

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LIST OF SYMBOLS

AA Antibacterial activity

CFU Colony-forming unit

PBS Polybutylene succinate

PCL Polycaprolactone

PE Polyethylene

PET Polyethylene terephthalate

PHA Polyhydroxy-alkanoates

pKa Acid dissociation constant

PS Polystyrene

R Antimicrobial activity (according to ISO 22196)

SEM Scanning electron microscopy

Tc Melt crystallisation temperature

Tcc Cold crystallisation temperature

Tg Glass transition temperature

Tm Melting temperature

Xc Crystallinity

1. INTRODUCTION

Polymers are materials that have many applications and large standing in human living. The world's plastic need is growing step by step, especially in coating industry. Polymer industry, in line with this need; Electricity from transport containers of various compositions and properties, which can be molded as desired produces plastics with a wide range of use in the industry up to the cables (Board 2012; Yoruç et al., 2017).

Plastics obtained from polymers are very preferred today. Because it is low cost, lightweight, recyclable and simple to shape. Plastics are used very often in daily life, also have serious harm to the environment (Yoruç et al., 2017).

Due to the use of petroleum-based materials in the production of plastic raw materials, the increased carbon emission in the atmosphere poses a danger to the ecosystem due to their long-term degradation in nature, their carcinogenic effects and their inclusion in the food chain. Although plastic materials have many disadvantages, their harm to the environment is their biggest disadvantage. As mentioned above, the pulling out of petroleum- grounded polymers from consumed regular resources have taken the lead researchers to concentrate on bio-based polymers originated from renewable sources due to increasingly deadly environmental concerns. With the increasing usage of bio-based polymers, dependency on oil will decrease and pollution will be prevented (Flaris and Singh, 2009; Yoruç et al., 2017).

Today, the use of biodegradable materials has increased to prevent increased environmental pollution. Polylactic acid has attracted great attention while the most advanced substances obtained for a extensive variety of usages. Polylactic acid based plastics can be widely used into fabric uses in order to several motives.

Polyesters used in ready-to-wear; Primarily PET accounts in order to above 40% of globe textile spending (more than 70% of synthetic fibers in the meantime) and their use is increasing day by day. Most of the polyesters used to date are made from non-renewable sources and cannot be biodegradable. On the other hand, PLA fiber is renewable, 100% able to get fertilize, and its lifetime cycle theoretically lowers CO_2 quantity of planet. Since Polylactic acid has features such as low moisture absorption, high resistance to ultraviolet light, mechanical performance and lightness, it can provide a significant advantage for the textile industry and can be extended. In this way, indispensable benefits by using PLA fibers, outdoor furniture, automotive interior fabrics, clothing, shoe linings, medical and hygienic applications or as an environmentally friendly, human-friendly alternative to existing textile fibers and fabrics for the production of many products such as disposable diapers and wipes (Yoruç et al., 2017).

However, Polylactic acid has its own weaknesses: low impact strength (~4 kJ/m^2), low HDT (<60°C) and easy flammability, etc. Therefore, changes in PLA are required to overcome these inadequacies (Lin et al., 2014).

Numerous methods are tried to recover the delicate construction of PLA in the sector. That way, it is pointed to donate to the environment by increasing the usage area of PLA. One of the methods that widely used in the industry is adding polybutylene adipate terephthalate (PBAT) to PLA. Though, the adding of PBAT, exchanges the viscosity and viscosity is an significant standard for the textile manufacturing in fiber fabrication, in the melt spinning process that offers the process (Jiang et al.,2020). So that progress the toughness and workability of PLA, it has actualize work by addition a eco-friendly thermoplastic PBAT to the PLA. Consequently the adding of a minor quantity of decomposable poly ester amide to Polylactic acid augmented ductileness and reduced the melt viscosity of the last combination (Rasal et al., 2010). Melting viscosity and tensile strength of the material in the production process of fiber; Tg and Tc temperatures greatly affect the manufacturability depending on the tensile strength of the material. For this reason, it is useful to find the PBAT that is most suitable for workability and usage rate in the market. (Gupta, 2007).

PLA fibers are commonly consumed in the manufacture of material fabrics for instance cushions, quilts, coverlets, mattress pads, rugs, workplace panel fabrics, and covers. Scientific studies conducted today focus on personal care and household cleaning products. Feminine hygiene products provide benefits in areas such as beauty treatment cleansing, functional and hemorrhoid treatments, diapers. PLA fibers are not "antimicrobial" if not treated. (Blackburn et al., 2005). It will be helpful to review antibacterial PLA fibers for role in hygienic purposes.

PLA was chosen for use in this thesis because of its biodegradability and mechanical properties. These are very promising features in the future. Environmental biodegradable nonwoven fibers can be useful in disposable packaging, disposable tissues, or medicine. In this study, not only the pure polymer was characterized, the elongational viscosity was also characterized as a function of the addition of different kinds of PBAT as a plasticizer to investigate significantly affects spinning or not.

The aim of this work is to relate the elongation properties of PLA/PBAT blend melts with their spunbond ability. Therefore, even before the tough spinning process, know whether it will spin good or not. It is generally known that the materials which has higher elongation strain rate is better for spinning. Therefore, we wanted to find out which material is the most suitable for the spinning process and to obtain nonwoven fabric. In the literature, no study has been found to examine the selection of suitable PBAT type for nonwoven fabric production according to its rheology.

In the first part of the study, together with general information about the fibers used in the textile industry, characterization methods applied for classification of these structures, determination of their production and properties are presented. In the second part of the study, literature information has been researched and presented. It includes the parts that describe the properties of the materials used in the third part of the study, the production method and the characterization methods. In the fourth part of the study, the results of the tests applied to the materials obtained and the interpretation of these results are included. In the last section, the conclusion of the thesis study and recommendations for future research are given.

2.GENERAL INFORMATION

2.1 Biodegradable Polymers

Biodegradation can be defined as a process in polymer chemistry that contains the division of enzymatic or hydrolytic ways (Figure 2.1) or weak connects in the polymer that causes loss of the polymer (Ghanbarzadeh, 2013).

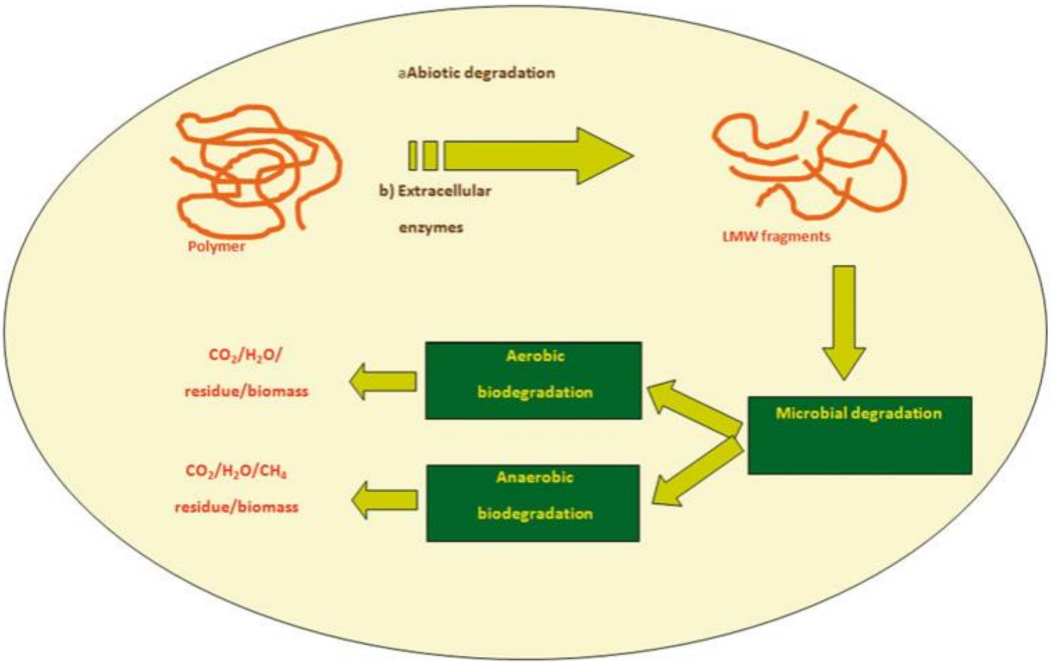


Figure 2. 1 Representation of chemistry on biological degradation (Luckachan, 2011).

Biodegradable polymers can be classified according to many different criteria. (Pollet and Avérous, 2012; Ghanbarzadeh and Almasi, 2013). Eco-friendly polymers are separated in two parts and four subgroups according to their origin. (Figure 2.2). The most important groups are a) natural polymers originated directly from natural bases and b) synthetic polymers that can be produced from monomers or artificial monomers bio-derived from petrochemical produces. Additional subclassifications are performed according to the method by which they are found polymers:

- in a straight line removed from biomass for example agricultural polymers extract from agricultural reserves,
- synthesized from conventional and chemically bio-derived monomers,
- synthesized from remnant funds (Pollet & Avérous, 2012).

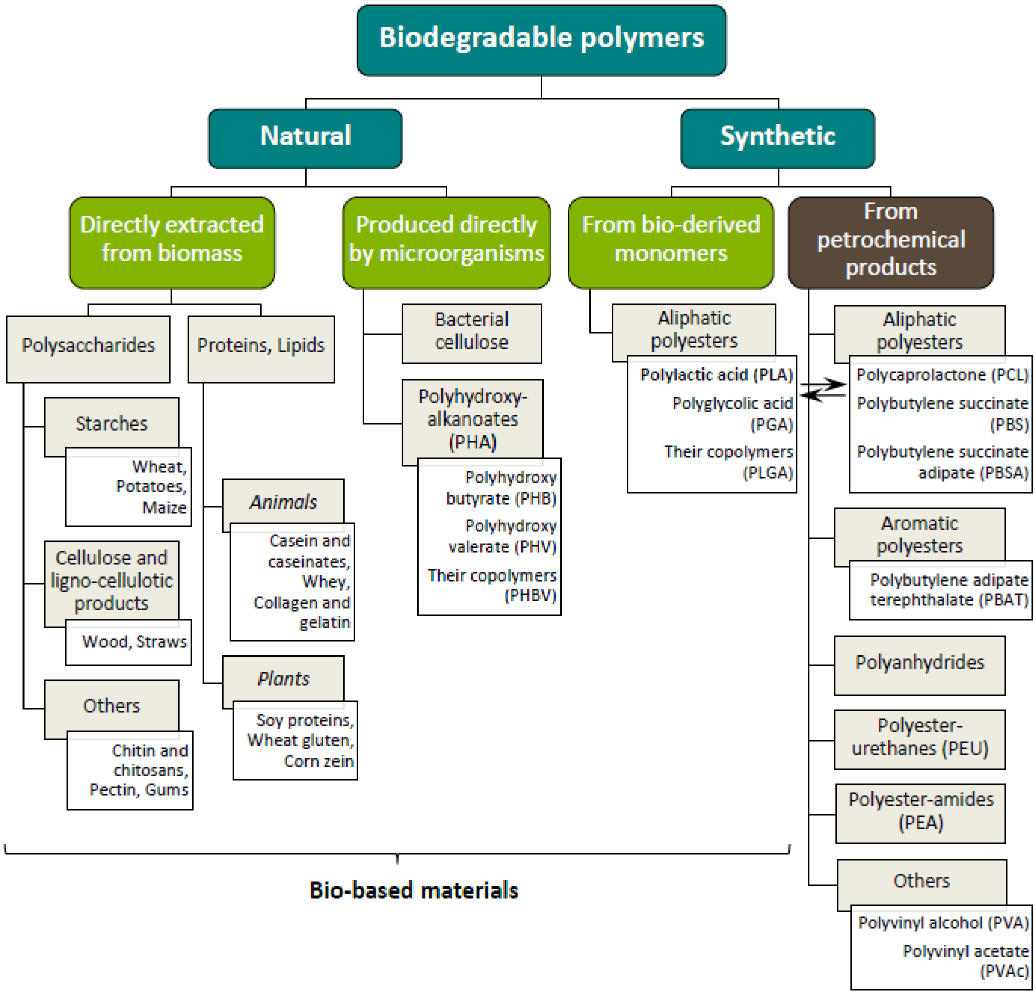


Figure 2. 2 Classification of biodegradable polymers (Holčapková,2018).

Biodegradable polymer materials have a higher applicability rate. They can be found in many market segments from packaging, agriculture and horticulture, customer goods, electronic engineering, automotive to the textile business and several further parts. It is clear that the most application area of biodegradable polymers remains in 2019, with packaging (mostly used in food applications), which accounts for about 60% of the total biodegradable plastics market in Europe. (European Bioplastics, nova-Institute, 2019).

Besides, biodegradable polymers put forward excessive ability in biomedical uses for example drug transportation, tissue engineering, gene healing, recreating, drug, provisional implantable machines, etc. (Luckachan and Pillai, 2011; Doppalapudi et al., 2014).

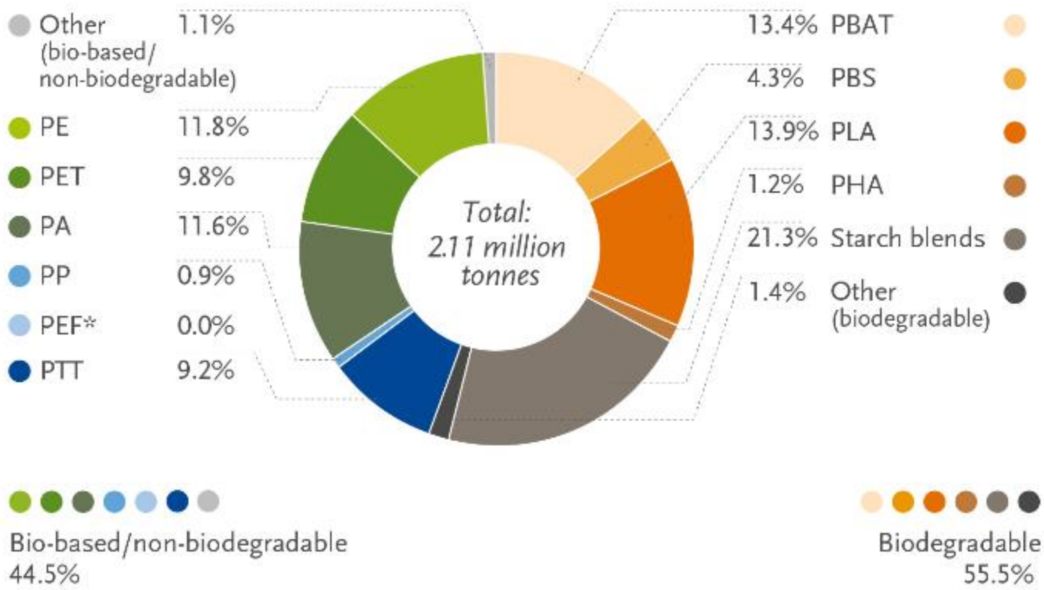


Figure 2. 3 Production volume rates of biodegradable and bio-based / non-biodegradable plastics in 2019 (by market section) (European Bioplastics, nova-Institute, 2019).

The production capacities of biodegradable plastics in the world in 2019 and their estimates for 2024 are given in Figures 2.3 and 2.4. As can be seen the most biodegradable plastics are PBAT, PBS and PHA, starch mixtures, PLA. Moreover, worldwide manufacture volumes of biodegradable plastics are estimated to increase from about 1200 thousand tons in 2019 to about 1.3 million tons by 2024, where PLA and PHA will be the main growth factors in this area (European Bioplastics, nova-Institute, 2019).

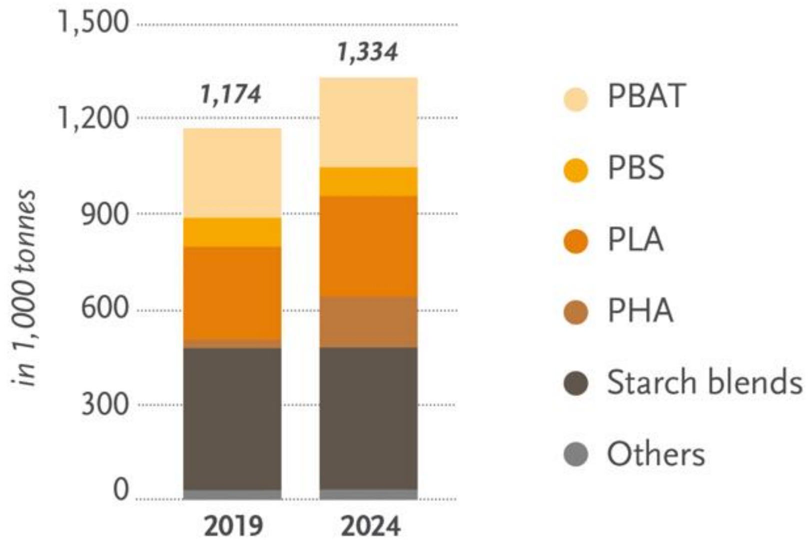


Figure 2. 4 Worldwide stages of creation of biodegradable plastics in 2019 and 2024 (European Bioplastics, nova-Institute, 2019).

2.1.1 Natural biopolymers

Biodegradable polymers in nature are formed during the growing recur of all living things, thus they are moreover called biopolymers or agricultural polymers (Ghanbarzadeh, 2013; Avérous, 2012). Production of natural polymers, commonly occurring through difficult metabolic processes in cells, includes chain- cultivation and enzyme-catalyzed polymerization chemical reaction of active monomers (Ghanbarzadeh, 2013; Olatunji, 2016).

Polysaccharides such as cellulose and starch are the most common natural polymers derived directly from the biological organism, but also find various applications such as proteins, lignin, chitin and chitosan, etc. (Doppalapudi, 2014; Babu et al., 2014).

2.1.2 Synthetic biopolymers

Synthetic biodegradable polymers can be distinguished by the origin of the monomers from which they are synthesized, the monomers of the petrochemical industry, or their combination.

It is typical for synthetic biodegradable polymers that hydrolyzable bonds within the backbone, such as hetero chains containing oxygen and nitrogen, contain amide, anhydride, ester, orthoester or urethane (Ulery, 2011; Pavelková, 2015). Polyesters, polyglycolic acid (PGA), PLA, PBAT, polycaprolactones (PCL), polybutylene succinate (PBS), etc., together with their copolymers are the most common. Polyurethanes and polyamides degrade more difficult than polyesters. For example, it can be aided by the introduction of the hydrolytically sensitive bond to form polyester-urethanes and polyester-amides, respectively (Ulery, 2011).

Additionally, fewer several groups of artificial biodegradable polymers contain polymers with a C–C spine chain. Usual samples of this party are polyvinyl alcohol (PVA) and polyvinyl acetate (PVAc) (Ghanbarzadeh, 2013).

2.1.2.1. Polylactic acid (PLA)

PLA is a aliphatic polyester which is biodegradable obtained from an acid. Lactic acid happens L(+) and D(-) optical stereoisomers. PLA can be obtained from petrochemicals (Karamanlioglu et al. 2017; Domenek and Ducruet, 2016). While PLA is eco-friendly and compostable, also it is able to be produced via fermentation of common polysaccharides as an example corn, potatoes, beet and also sugar cane. (Domenek and Ducruet, 2016; Castro-Aguirre et al., 2016).

Polylactide manufacture keeps through direct condensation ring-opening polymerisation, azeotropic dehydrative condensation polymerization (Fig.2.5) (Karamanlioglu et al.2017; Castro-Aguirre et al., 2016).

Polylactide properties are highly dependent on stereochemistry and molecular weight. Conditional on its thermal history and the structure of the enantiomer, PLA can be solid shape, amorphous or semi-crystalline. Mostly the PLA is semi-crystalline, when the D-isomer is existing at a smaller amount than around 6%. Alternatively, then the polymer can be counted as amorphous, if the D-isomer substance is >6%, (Karamanlioglu et al., 2017; Kolstad et al., 2012). While its melt temperature (Tm) scales starting 130°C to 180°C , the regular Tg varieties from 50°C to 80°C. For case in point, enantiomerically unmixed PLA is a partial-crystalline along with a Tg is 55°C and Tm is 180°C (Avérous, 2008).

The crystallinity of PLA has advantages that consist of better chemical and high temperature resistance, hardness and porousness. In this background, with falling crystallinity (higher D-isomer subctance) Tm and mechanical characteristics are also falling and it has been described that the degeneration is earlier. Hence, for biomedical machines, amorphous PLA is generally preferred, however half-crystalline Polylactic acid is primarily consumed in products wherever greater technical characteristics are preffered (Karamanlioglu et al., 2017).

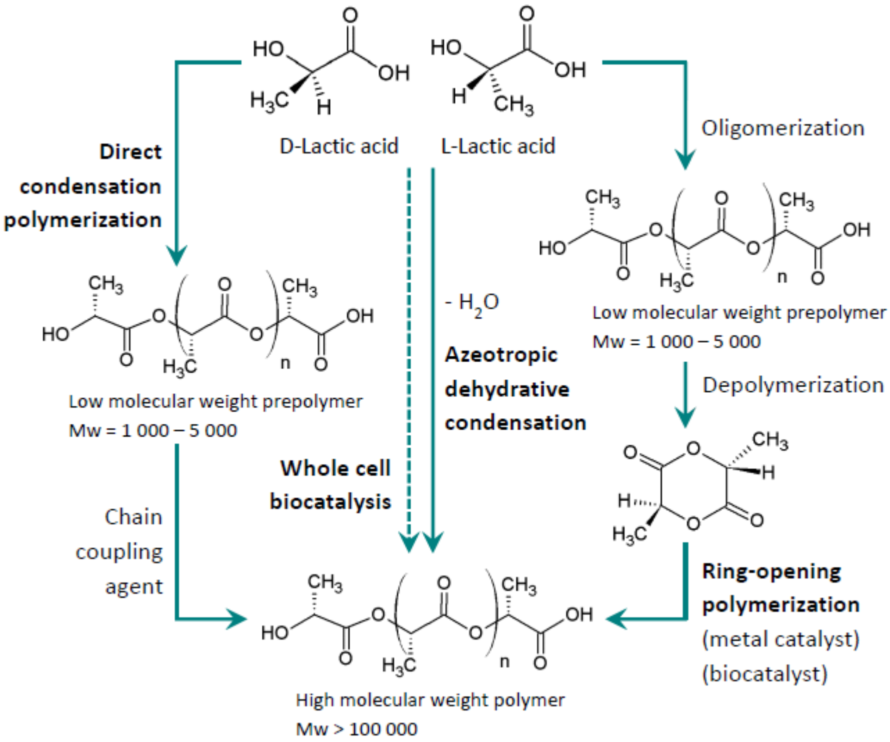


Figure 2. 5 Principal ways for the production of PLA (Domenek, and Ducruet, 2016 ;Holčapková, 2018).

According to mechanical specifications, PLA is commonly described as a rigid polymer showing a high Young´s modulus between ~2–3 GPa and the tensile strength is between 50–70 MPa. These features are class with or even surpass those of non-biodegradable usual plastics (PE, PET, PS, PP, etc.). On the other hand, Polylactic acid is fairly fragile, alongside fewer according as elongation at break (10%) which forms a issue limiting its usage in products requiring plastic distortion underneath extreme stress (Karamanlioglu et al., 2017; Castro-Aguirre et al., 2016).

As a result, significant efforts have been made to progress the characteristics of PLA, with the seek of finding a more elastic material at a lesser price. This can be gotten either by moderating PLA with biodegredable modifiers or by mixing it with another non-biodegradable or biodegradable polymers (Castro-Aguirre et al., 2016; Meaurio et al., 2014).

2.1.2.2. Poly (butylene-adipate-co-terephthalate)(PBAT)

All through evolving biodegradable polyesters and polymers are a mainly motivating categorize of polymers (Jian et al., 2020; Chandra and Rustgi, 1998). Moreover aliphatic polyesters have been presented as simply eco-friendly for the reason that their ester connections, which are sensitive to decompose by water. Unluckily, aliphatic polyesters which are like PHB and polycaprolactone, present low thermal and mechanical properties (Doi, 1990; Mochizuki and Hirami, 1997). Then again, Polyethylene terephthalate (PET) which is aromatic polyesters and polybutylene terephthalate (PBT), show very respectable physical characteristic however effective resistance to hit by microorganisms (Mueller, 2006).

Among the many aliphatic-aromatic co-polyesters, the greatest hopeful and well-liked together with possible improvement forecasts, poly-condensation obtained by PBAT. It has been made to be the greatest suitable blend, observing brilliant properties and beneficial biodegradability. As trading presented PBAT is listed in Table 1 (Ferreira et al., 2019).

Polyesters usually are produced by polycondensation from mixtures of dicarboxylic acids and diols (Okada, 2002). PBAT, exactly, be capable of created by polycondensation substance of AA, PAT, and BDO effective typical polyester technology and also tools, as drawn in Figure 2.6 Organometallic compounds grounded on Zn, titanium and tin able to used as polycondensation catalytic agent. The production of Polybutylene adipate terephthalate can be divided up in before addition, before polymerization and last polymerization process. Arrangement of Polybutylene adipate terephthalate needs extensive chemical reaction period, elevated temperature and vacuum, normally greater according to 190°C. The situations which are mentioned are essential to help condensation chemical reactions and also remove the fewer weight molecules as a result (Sousa et al., 2015; Diaz et al., 2014).

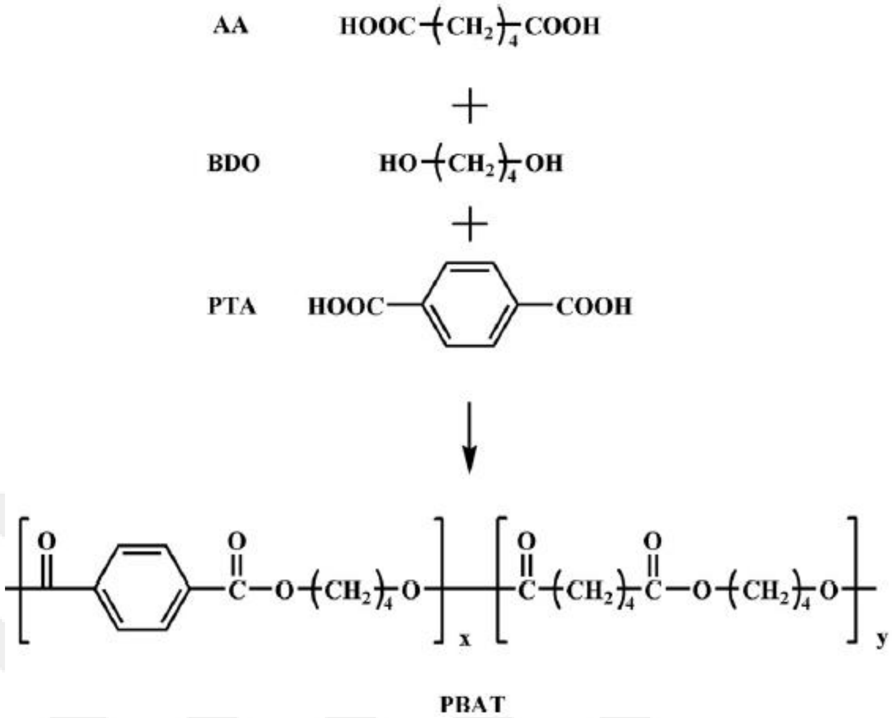


Figure 2. 6 Main techniques for the mechanism of PBAT (Jian et al., 2020)

Witt et al. researched once more the records which represent that the bio compostable rate of Polybutylene adipate terephthalate be contingent on the PTA's substance into the polymer (Figure 2.7) (Jian et al., 2020; Witt et al., 1996).

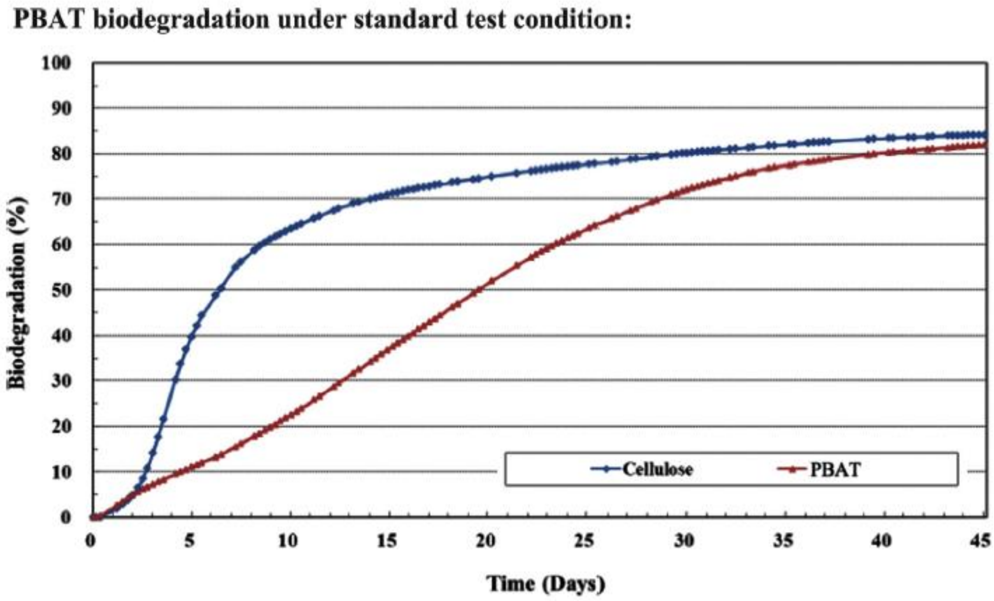


Figure 2. 7 Graph of PBAT and cellulose (Jian et al., 2020)

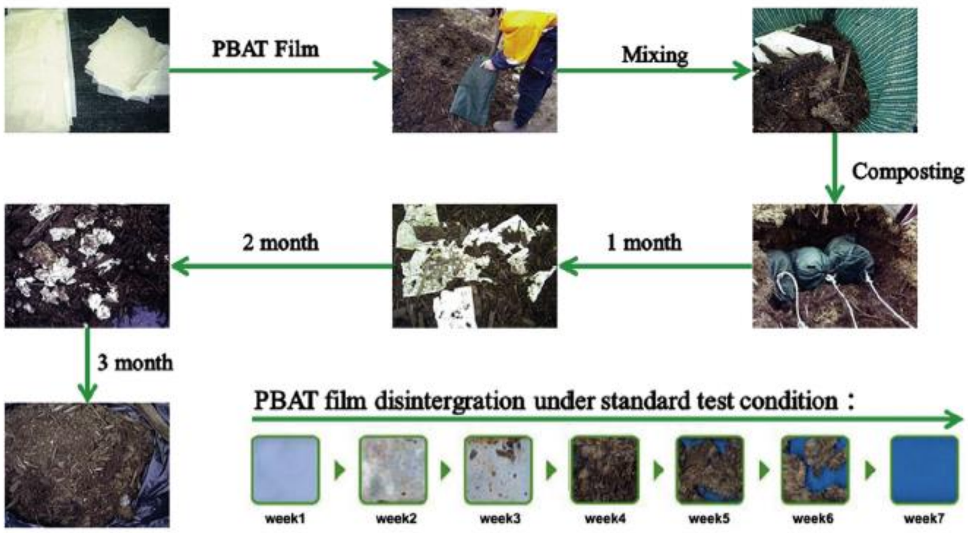


Figure 2. 8 Selected fertilizer testing consequences of PBAT. (Jian et al., 2020)

Several obtainable experiment consequences are presented in Figure 2.8. as a typical outcome it able to specified that material Polybutylene adipate terephthalate does greatest the estimation conditions for substance possessions, disintegration, compost property and also biodegradation which are summarized in these standards. Poly butylene adipate terephthalate can consequently be concluded to be totally compostable (Jian et al., 2020).

PBAT presents not only suitable biodegradability in line for the aliphatic element in the fragment sequence, nevertheless moreover excellent mechanical characteristic, because of the aromatic component into the particle sequence. Likened to the greatest biodegradable polyesters for instance PLA and PBS, the mechanical characteristic of PBAT present extra flexible, and are alike to those of LDPE (Bordes et al., 2009; Nagarajan et al., 2013). These are mechanical features make PBAT an extremely hopeful recyclable material for a broad range of probable purposes (Jian et al., 2020).

Liquefy and crystallization of PBAT considered DSC in conditions which is cooling and heating rate (10°C/min) and the thermal constancy of PBAT was as well examined by thermogravimetric analysis (TGA)with the condition which is through heating rate (20°C/min) under N2. The TGA data are additionally shown in Table 2.1 (Jian et al., 2020).

Table 2. 1 The mechanical and thermological feature of PBAT. (Jian et al., 2020)

Properties	Test method	Test Condition	Units	PBAT
Mechanical Properties				
Tensile Strength	ASTM D638	50 mm/min	MPa	21
Elongation at break	ASTM D638	50 mm/min	%	670
Flexural Strength	ASTM D790	2 mm/min	MPa	7.5
Flexural Modulus	ASTM D790	2 mm/min	MPa	126
Thermal Properties				
Melt point	DSC	10 °C/min	°C	115–125
Crystallization point	DSC	10 °C/min	°C	60
5% weight loss temperature	TG	20 °C/min	°C	350
Heat Distortion Temp.	ASTM D648	1.82 MPa,6.4 mm	°C	55
Other Properties				
Melt Flow Index	ASTM D1238	190 °C, 2.16 Kg	g/10min	4.0
Specific Gravity	ASTM D792	23 °C	g/cm^3	1.22

PBAT able to be simply produce consuming usual polyester process machinery, which create it can be imaginable to get enough volume for PBAT in a snatchy term. From the time when PBAT presents not only good biodegradability but additionally admirable possessions, PBAT can be useful in many areas, specially in package and protection film uses. So PBAT is consider as one of the greatest favorable environmental polyesters (Jian et al., 2020).

2.2 Antibacterial Modifications

The bacterial antibiotic durability has quickly boosted mainly in line for the abuse of antibiotics all through the ended 20 years, especially in hospital ecosystems, thus the cure of nosocomial contagions has become harder. Between hospital-acquired contagions, medical device connected infections (MDIs) have been known as one of the fast growing and important problems, principally for the insertion of indwelling machines, which approach into close contact with the inner of the human form (Bazant, 2013). The usage of antimicrobial polymers and blends promises improved efficacy of tolerable existing antimicrobial instruments and minimize environmental harms accompanied with the usage of usual antimicrobial agents by the decrease of residual poisonousness of agents, rise of their effectiveness and selectivity, and continuation of the lifecycle of the antimicrobial proxies (Bazant, 2014).

In the role of polymers are the greatest used materials in medicinal machines, antimicrobial polymer additions (APA) can participate an essential role (Gabriel et al., 2007). Even though many antimicrobial additions are referred to in place of biocides, there are in fact two different results: biocidal (destroying the organism) and biostatic (avoiding the reproduction). Inorganic additions bring together with biocidal and biostatic possessions, so, the usage of inorganic APAs blended into the polymer substance, the named antimicrobial polymer systems (APS), can create a great antibacterial result for medical usage (Simmons, 2000). Lately, attention has been motivated on several metal oxides, metals and metal salts which have confirmed their antibacterial performşng, especially if consumed in the appearance of nanoparticles (Chaloupka et al., 2010; Marambio-Jones and Hoek, 2010).

Special methods are utilized for the arrangement of such hybrid technique with certain functional characteristics tailored to the desired usage, e.g., sol–gel, photoreduction process, laser heating method, photolysis system, ultrasonic spray pyrolysis, microwave (MW) method, and so on (Catauro et al., 2004; Bhattacharyya and Gedanken, 2008).

Necessities on antimicrobial polymer systems;

•Simply and inexpensively manufactured

•Constant in long-term application and storage at the heat of its intended implementation,

•Not solvable in water for a water sterilization usage,

•Does not decay to and/or release poisonous products,

•Should not be poisonous or irritant to those who are controlling it,

•Can be renewed upon damage of activity,

•Biocidal to a wide spectrum of infective microorganisms in short times of contact (Kenawy et al., 2007).

The antibacterial deed of ceramic powders have took attention as a latest way that can substitute for usual methods consuming organic agents. Ceramic powders of calcium oxide (CaO), zinc oxide (ZnO) and materimagnesium oxide (MgO) were found to presentation obvious antibacterial achievement (Yamamoto et al., 1998,2000; Yamamoto, 2001). The usage of these ceramics has the following benefits: they include mineral elements fundamental to humans and reveal strong antibacterial action in minor amounts with no the existence of light. It was created that ZnO shows antibacterial action at pH values in the vary between from 7 to 8

(Yamamoto et al., 1998), and these significances are fit for usage in water used for cleaning and drinking (Bazant, 2014).

Antimicrobial attributes of silver salts, blends and the metal shape of silver itself have been identified for a extended time and have created a type of usages for example biomedical usage, water and air cleansing, food creation, cosmetics, textile, and many household produces (Marambio-Jones and Hoek, 2010, Mahendra et al., 2008). The large rise in the number and event of antibiotic-tolerant bacterial straining has stimulated a repeated interest in the usage of silver by way of an antimicrobial factor for the period of last two decades (Stobie et al., 2008).

The study on ZnO in place of an antimicrobial substantive substance had by now started as primary as 1950s (Bartels, 1947). Later then, more academics have paid notice to the basic reports on the antimicrobial behavior of metal oxides. ZnO shows remarkable antimicrobial behavior in opposition to Gram-positive bacteria (Enterococcus, Streptococcus, Staphylococcus) (Sawai et al., 1995).

While ZnO presents better antimicrobial performance against from gram-positive to gram-negative bacteria, silver presents impressive antimicrobial efficiency in contrast from gram-negative to gram-positive bacteria, (Yamamoto et al., 2001; Zeng et al., 2007; Shrivastava, et al., 2007; Bazant, 2014),. Jafari et al. assessed antimicrobial actions of silver, ZnO and Ag/ZnO. Their research paper presented that Ag/ZnO has synergistic result in contrast to both, gram positive and negative bacteria. Needed quantity of Ag/ZnO nanoparticles is various times lesser than that of basic silver or basic ZnO particles to get the equal stage of antibacterial action. Table 2.2 shows difference of antibacterial actions of numerous bacterial strains (Jafari et al., 2011). Other writers confirmed synergetic effect of Ag/ZnO, too (Lu et al., 2008; Ghosh et al., 2012; Yang et al., 2006; Zhang, 2011).

Table 2. 2 Difference of antibacterial activities of several bacterial strains (Jafari et al.,2011).

Bacteria	Nano particles	Disc diffusion test (mm)	Agar dilution test (mm)	MIC (µg/ml)	MBC (µg/ml)
P. aeruginosa	ZnO	10	8	256	4096>
	Ag	12	10	>4096	>4096
	Ag/ZnO	12	10	64	1024
B. subtilis	ZnO	15	20	512	4096
	Ag	10	Negative	>4096	4096
	Ag/ZnO	10	Negative	128	2048
S. galinarium	ZnO	10	15	128	512
	Ag	10	10	>4096	>4096
	Ag/ZnO	12	10	32	2048
E. coli	ZnO	12	15	64	512
	Ag	8	10	2048	>4096
	Ag/ZnO	10	10	32	512
S. aureus	ZnO	12	15	256	2048
	Ag	8	10	1024	4096
	Ag/ZnO	12	10	128	2048

2.2.1 Metal oxides

One of the most suitable and broadly active nanomaterials are metal oxides, either as effective catalyst or as supportive material. Some groups of metals, principally transition metals, have concerned much notice for the reason that their outer electron shape. As a result of the structural organization of metals in blended metal oxide arrangements, blended oxides have been operate in numerous effective conversion activities (Zhang et al., 2011). The arrangement of the atmosphere of the positive ion to the biomolecule is signified as the benefit of a blended metal oxide orderliness. The appear-initiated metal nanoparticles are created by making a effective contact among organic and also inorganic molecules (Abu-Reziq et al., 2002; Lai et al., 2011).

Metal Oxides (MOs) participate very serious role in lots of areas of scholarship development for example physics, chemistry, engineering and also medication.

Metal elements are able to create chemical connections with oxygen to occur oxidic blends. These oxidic blends can continue considerable number of shape geometries with an electronic composition that can show metallic, semiconductor, or insulator uniqueness. These days, Mos have been consumed extensively in the production area of sensors, solar cells, fuel cells, in piezo-electric devices and catalysis process

2.2.1.1.ZnO

The investigate on ZnO like an antimicrobial matter had started as matutinal as 1950s (Bartels, 1947). Thenceforth, even more academics have paid notice to the essential studies on the antimicrobial behaviors of the metal oxides. The ZnO shows remarkable antimicrobial activity against Gram-positive bacteria (Enterococcus ,Staphylococcus, Streptococcus) (Sawai et al., 1995). Besides, ZnO has more than a few special advantages: presenting a strong antimicrobial activation in inactive region which pH value shows 7 and existence a mineral element fundamental to homo sapiens. Hence, lots of reports devoted to the antimicrobic efficiency of ZnO (Yiamsawas Et Al., 2008; Sawai et Al., 1995; Yamamoto, 200; Bazant, 2014). Issues connected to the antimicrobial activities have been considered, for instance the dilution of the metal oxide elements (Sawai et al., 1995; Yamamoto, 2001; Ohira et al., 2008), the element dimenson of the metal oxide grind (Zhang et al., 2007; Sawai, 1996) and the exact appear area of the grind.

The processed of the antimicrobial interest of Zinc oxide elements are not good knew yet, even though Sawai et al. (1996, 1997, 1998) suggested the generation of hydrogen peroxide as the major thing of the antimicrobial interest, while Stoimenov et al. (2002) showed that the linking of the spalls on the bacteria exterior in line for the electrostatic powers could be replacing in mechanism (Zhang et al., 2008).

ZnO is explained as a useful, strategic, have potential, and flexible inorganic material with a wide range of applications. It is known as II–VI semiconducting material (Gertrude, 2007), from the time when Zn and O are categorized in groups in the periodic table, respectively. ZnO shows a irreplaceable optical, chemical detection, semiconducting and electric conduction properties. The broad band hole of ZnO has important effect on its goods, for example the electrical conduction and optical inhalation. The excitonic release can continue upper at room temperature (Janotti and Van de Walle, 2009) and the conductivity rises when ZnO fixed with other metals (Wang, 2004). Although ZnO presents light covalent property, it has great powerful ionic connection in the Zn and O atoms. Its prolonged stability, higher choosiness, and heat stregth are headed than carbon-based and non carbon-based materials (Padmavathy and Vijayaraghavan, 2008). The production of nano-sized ZnO has headed to the study of its usage as latest antibacterial instrument.

Contradictory consequences have been described of the affect of particle dimension on the antimicrobial efficiency of ZnO. Determined that minor ZnO particles were greater poisonous than larger particles, however this dimension connected result was not discovered in different research by Li et al. (2008).

3. FIBERS

3.1. General Information about PLA Fibers

PLA fiber has numerous characteristics that are related to several other thermoplastic fibers, for example; regulated crimp, soft surface and modest moisture regain. One exceptional things in comparison is that it is the just melt-operationable fiber from once a year renewable natural resources. The physical goods and construction have been published by various researchers (Blackburn et al., 2005; Drumright, 2000), and these researchs corroborated that this polymer has important commercial capacity as a textile fiber. Its mechanical properties are well-thought-out to be broadly same to those of usual polyethylene terephthalate (Lunt and Bone, 2001) and possibly as a result of it has decrease melting and become softer temperatures, similarities to polypropylene are also appropriate (Palade et al., 2001). About PLA fibers;

Form: Fibers are commonly rotary in cross- segment and possess a soft surface.

Density: The certain gravity is 1.25 g cm^{-3} less than natural fibers and PET.

Refractive index: The refractive table of 1.35–1.45 is less than PET (1.54). Trilobal and other forms can be created and give enhanced anti-soiling properties.

Thermal characteristics: PLA is a rigid polymer at room heat. The glass transition temperature is generally around 55–65°C. The melt down temperature of PLA including either the L- or D-isomeric shape alone, is in the middle of 160–170°C. The DSC images for PET and PLA are presented in Figure 3.1. It can be understood that PLA shows an endothermal peak melting point at around 166°C (Farrington et al., 2005).

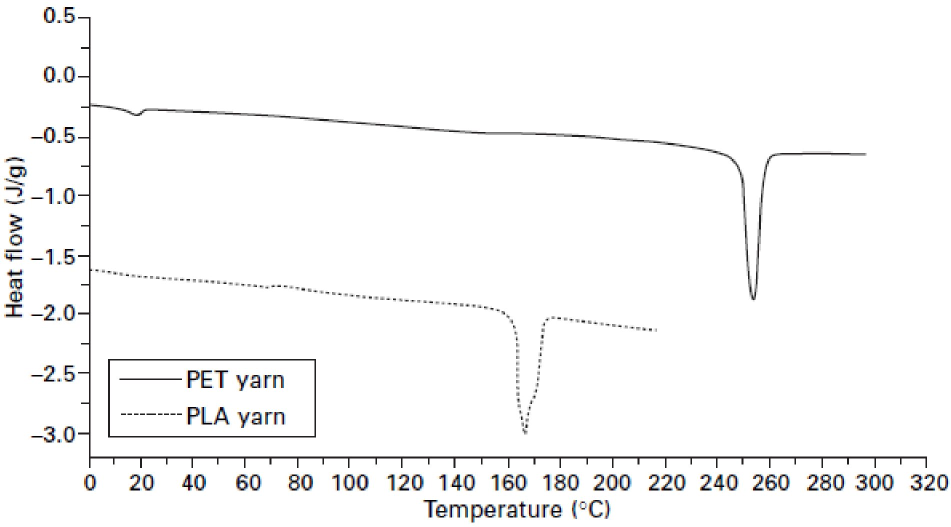


Figure 3. 1 DSC images of PLA and PET (Farrington et al., 2005).

Tensile characteristics: The tensile features of PLA fiber as charity in staple shape for textile manufacturing are shown in Fig. 3.2 Obviously they are so different from those of great persistence polyester and greater similar to fabric with a elevated fiber addition when stressed and quite low final insistence. The starting modulus which shows 2% extension in the graph has very similarity to lots of other textile fibers(Farrington et al., 2005).

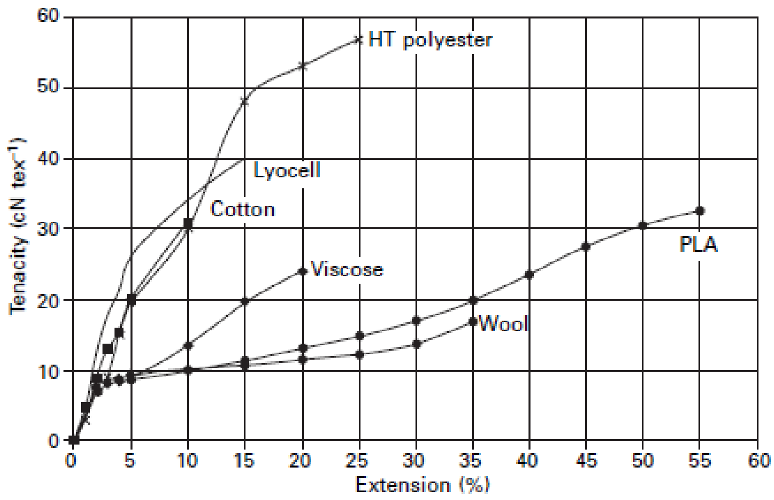


Figure 3. 2 Tenacity and extension graph has shown which conditions is 20°C with 65% RH for PLA and also other commonly used textile fibers (Farrington et al., 2005)

UV resistance: Different according to other synthetic fibers, PLA does not internalize light in the observable area of the spectrum; this drive out to very less strength damage according to petroleum-based fibers when visible to ultraviolet light(Farrington et al., 2005).

Great water vapor radiation speed of PLA oftenly precludes its usage in appliances where humidity barrier is important. But, this things can be leveraged for constructing fibers consumed in garments to enhance their “inhalability”. Whereas Polylactic acid filaments are not as absorbing humidity as cotton, they exhibit much higher water vapor diffusion than nylon or else polyester filaments (Lim et al.,2008). Extrusion of the polymer in single filament and multifilament may be completed by spinning production methods (Gupta et al., 2007; Lim et al.,2008). General PLA fibers are commonly produced via the melt spinning technique (Lim et al.,2008; Fambri et al., 1997; Cicero et al., 2002; Eling et al., 1982).

Its translation to fiber by melt spinning generally has benefits over wet spinning; i.e. it is a resolvent -free progression and offers a more economical and environmental route. Manufacture rates are generally more than in solution spinning (Gupta et al., 2007). At some situations, melt spinning is not imaginable, either for the reason that the polymer decomposes while melting is thermally unbalanced. In dehydrated spinning, resolvents are eliminated by thermal vaporization during which in wet spinning the clotting of the polymer is achieve in different liquid that is well-matched with the spinning resolvent but is not itself a resolvent for the polymer (Gupta et al., 1997,2007).

3.2. Applications of PLA Fibers

PLA fibers have several application in many fields;

Homeware: Standard products included in this segment variety from pillows, duvets, office panel fabrics, mattress pads, blankets, carpet tiles, curtain to attached fiber products for instance mattresses. The strength to UV and small flammability, little smoke production and low poisonous gas on burning are appealing things for this market segment, which tell apart PLA fabrics formed from conventional petrochemical-based artificial (Farrington et al., 2005).

Apparel: The apparel fiber commercial in 2002 was projected at around 30 million tonnes (Table 3.1) and forecasts for 2015 indicate that it will develop to 42 million tonnes. The sector is controlled by fibers which is ground as cotton and PET, and as the total necessity increases, it is PET that is expected to become the majority material. Apparel is by some way the greatest part in the worldwide fiber business, and is a extremely technical, quickly changing, and challenging industry in drawing, style, color, aesthetic, and presentation (Farrington et al., 2005; Lunt and Shafer, 2000; Gross, 2002). Main usages are in fibres of PLA is active, sport, fashion wear and underwear (Avinc, 2009).

Table 3. 1 Apparel spending by filament class in 2002 (Farrington et al.,2005)

Fiber type	Million tonnes	%
Cotton	13.0	43
Wool	1.3	4
Polyester	10.2	34
Acrylic	2.0	7
Cellulosic	1.8	6
Nylon	1.2	4
Others	0.5	2
Total	30.0	100

Nonwovens: Nonwoven produces are a main application section offering huge potential for the exceptional properties of PLA fibers. Outdoor of the fiberfill produces the main bazaars are in trade and home wipes, spunbond and also hygiene (Farrington et al.,2005).

Medical applications: Fibers for textile industry can be consumed to grow different homo sapiens organs. The procedure involves culturing in living groups, taken from homo sapiens organs, on a textile scaffolding, to the needed 2 dimensional and/or 3 dimensional forms. (Farrington et al.,2005).

3.2.1. Melt spinning process of PLA

Melt spinning is one of the greatest well-liked methods for industrial polymeric filaments. PLLA with a viscosity be an average of molecular mass (Mv) around 0.5–3.5x10^5 is consumed for melt spinning (Ashwini et al., 2003). While there are various methods available for filament manufacture, melt spinning is the maximum economical method as a consequence of the presence of resolvents and the plainness of the process (Rawal and Mukhopadhyay, 2014).

In melt spinning, the polymer granules are served into an extruder containing of a screw for melting by process of heat, and later the polymer melt is pushed through with a spinneret in force. The extruded polymer is later quenched with chilly air and the liquefied quantity is solidified into filaments (Kiron, 2020; Lim et al.,2008).

A common melt spinning process necessitates a stable mass flow speed of liquefied polymer, which is supported by a metering or a spinning push commonly positioned in the spinning top, as shown in Figure 3.3 (Rawal and Mukhopadhyay, 2014; Lim et al.,2008).

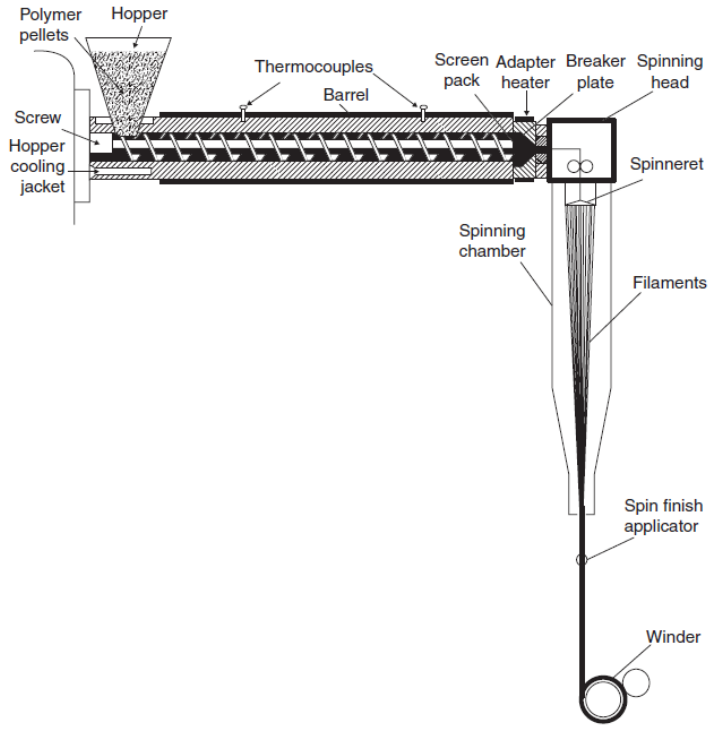


Figure 3. 3 A usual melt spinning method (Rawal and Mukhopadhyay, 2014; Kiron, 2020).

The liquefied polymer is guided into a number of unusual capillary holes of described froms and dimensions appear in the spinneret. For each orifice is in charge for individual filaments. Then, the long unbroken filaments extruded throughout the spinneret mouth are chilled-off frozen, and saved on a winder (Rawal and Mukhopadhyay, 2014; Beyreuther and Brunig, 2007).

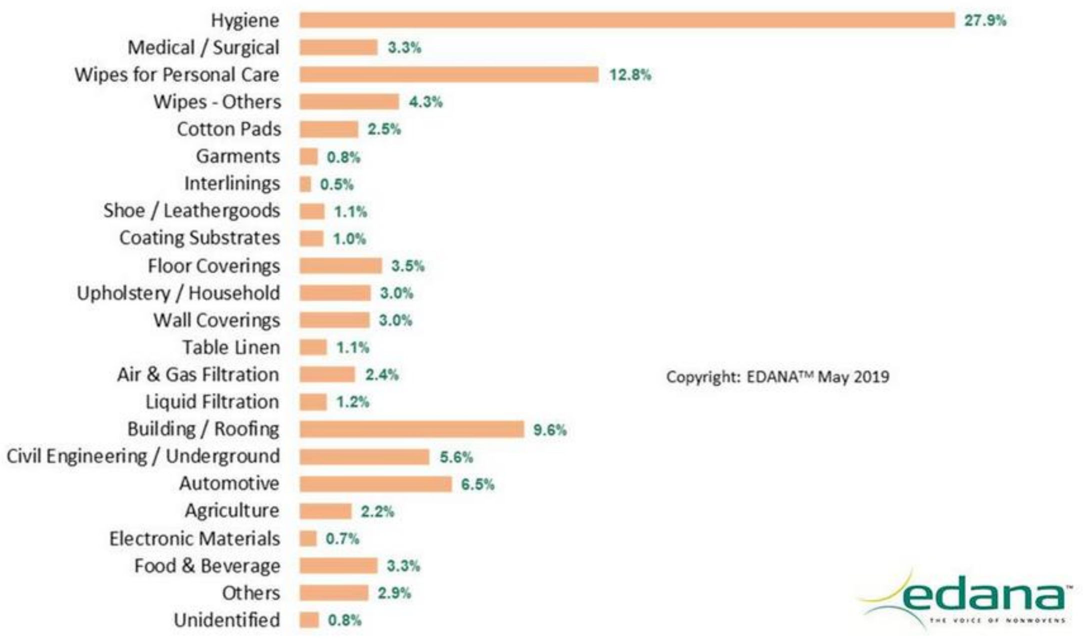
In one of the reports, the molecular mass was decreased from 330,000 to around 120,000 and 105,000 for in the same way as spun and drawn fibers individually (Fambri et al., 1997). Degradation ratio is higher when upper shear speeds are put on, as in the situation of upper molecular mass PLA. Molecular mass humiliation is recognized to the ester categorize cleavage as a result of the hydrolytic process at the elevated process heat conditions of melt spinning process in the attendance of residual water in the polymer (Ashwini et al., 2003).

3.2.2. Non-woven fabrics

The expression ‘nonwovens’ originate from as a minimum part a century ago, at what time the materials were oftenly observed as low-price replacements for conventional textiles and mostly prepared from carded, staple filaments on transformed textile processing equipment (Wilson, 2010). Nonwoven fabrics are in line, spongy sheets or web shapes that are made directly from split fibers or from liquefied plastics. Nonwovens can be formed from natural or synthetic fibers or else directly from polymers by a variety of methods that involve web construction and paste (Bhat and Rong, 2005; Niaounakis, 2014).

Nonwoven fabrics have turn out to be an greatly significant section of the textile manufacturing in past years. The appliance of nonwoven fabrics can be categorized as one-use and resistant. (Tom, 1989; Turbak, 1998; Bhat and Rong, 2005). For example the data which is shown in Table 3.2 presents the ratio for respectively end use in relative to the entire weight of nonwoven transports as stated by investigation by organizations in Europe and USA like INDA and EDANA that publicized statistical data be combined in 2018. Cleanliness is the biggest of these classifications, calling for above 27.9% of nonwoven manufacture, stayed on by wipes for individual care with 12.8%. The high development in latest years of the usage of wipes (EDANA, 2020).

Table 3. 2 Data on transports of nonwovens in apiece purpose (EDANA, 2020)



Appeal for nonwovens in the US is imagined to rise by 3.9% for each year to around $5 billion in 2007. Growth trend in the globe and the progress tendency for American nonwovens bazaar are presented in Figures 3.4 and 3.5 (Bhat and Rong, 2005).

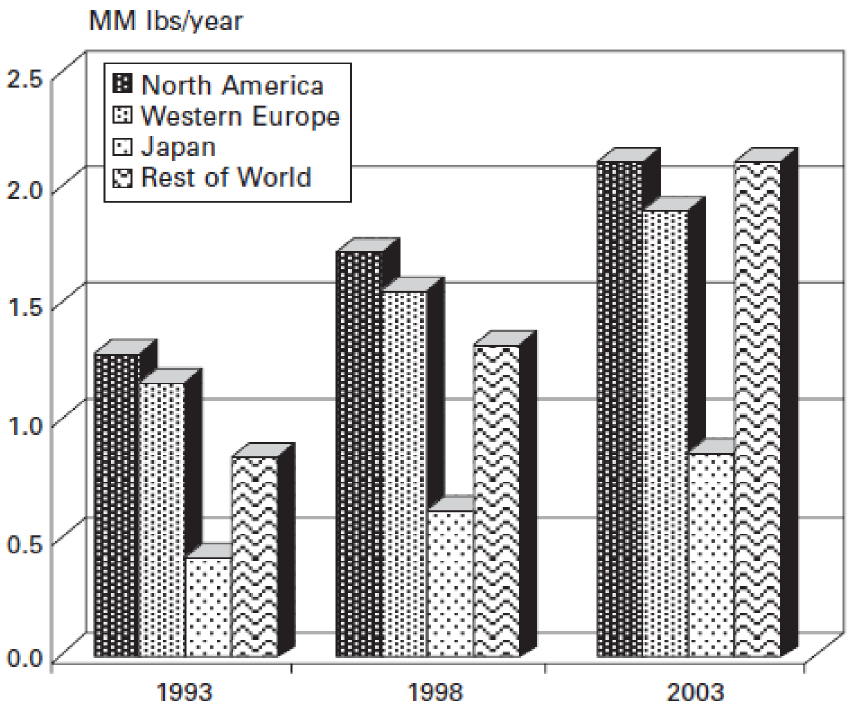


Figure 3. 4 Tendency in globe nonwovens fabrication (Nonwovens Handbook, 2004).

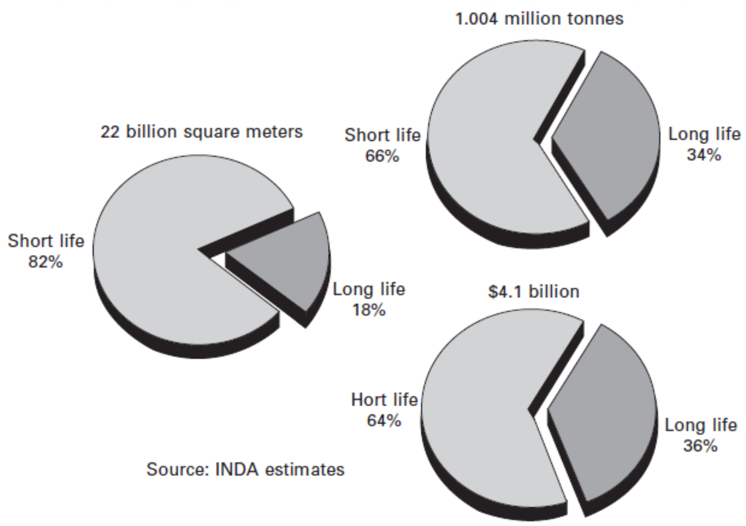


Figure 3. 5 Capacity and purchases in North American nonwovens (Nonwovens Handbook, 2004).

According to the statistics that is obtainable, continual development in nonwovens is additional in the recyclable region and the single use nonwovens is aimed at stay considerably large. Seeing the detail that great share of these considerable and developing resources are throwaway products, it is valuable that issues connected with their elimination be gently addressed (Bhat and Rong, 2005).

These throwaway products are commonly produced from conventional thermoplastics like polypropylene, polyethylene, polyethylene terephthalate, polyamide and polycarbonate, which are not eco-friendly. Although, according to rising ecological realization and requests of governmental experts, the production, usage and elimination of products made of like standard polymers are reflected more significantly (Bhat and Rong, 2005; Lunt, and Shafer, 2000; Lunt, 2000).

PLA nonwoven products have many great characteristics in contrast with PET: the melting point and T_g of PLA are minimal; it is completely reproduce from a renewable reserve, presently from maize; and it is able to be biodegraded following usage. Spunbonded nonwovens are self- connected with not at all chemical binders, accordingly all these specifications mean that Polylactic acid can make spunbonded nonwovens cloths which are completely ecological friendly (Bo, 2009).

Though, PLA nonwoven webs usually have a nominal bond elasticity and high roughness because of the high Tg and slow crystallization ratio of PLA. This dissertation, added some plasticizers to resolve this issue. Modifiers have been consumed in an venture to decrease Tg and develop paste and softness. But the extra of modifiers causes other issues, for example humiliation in melt spinning, decrease in melt power, able to draw, and also an augmented trend to stage distinct and immigrate out of the fiber construction during aging, so decreasing modifiers effectiveness over time.(Mceneany et al., 2012).

Consequently it can be encouragingly specified that PLA is suitable for spunbonded technology (Bo, 2009).

3.2.2.1.Nonwoven production methods

The eco-friendly thermoplastic filaments can be bring into being by using a variety of old-style techniques reputed in the art, with the presence of spunbonding technology and melt spinning technology shown in figure 3.6.(Niaounakis, 2014; Bhat and Rong, 2014; Pourmohammadi, 2013).

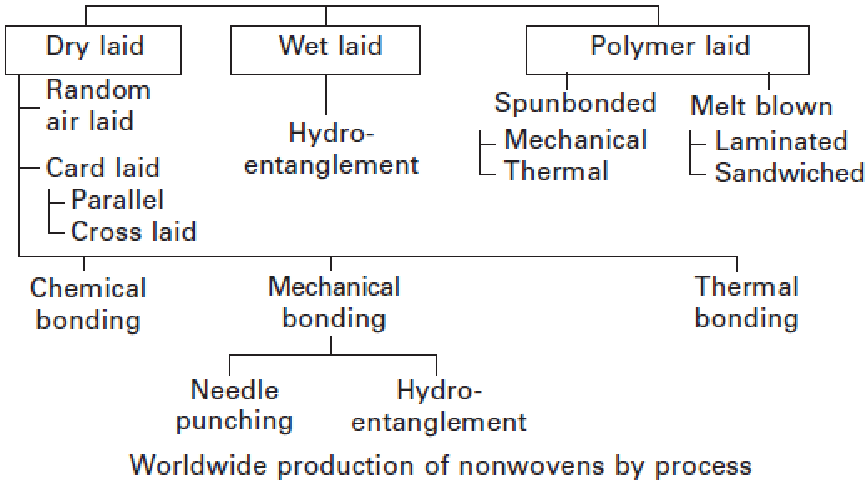


Figure 3. 6 Worldwide production of nonwovens by process (Turbak,1998; Bhat and Rong, 2005).

In melt spinning, a liquify manufactured decomposable thermoplastic polymer is made warm greater than its Tm and the melted polymer is compulsory during a spinneret. A usual melt rotating process is shown in Figure 3.7 (Niaounakis, 2014).

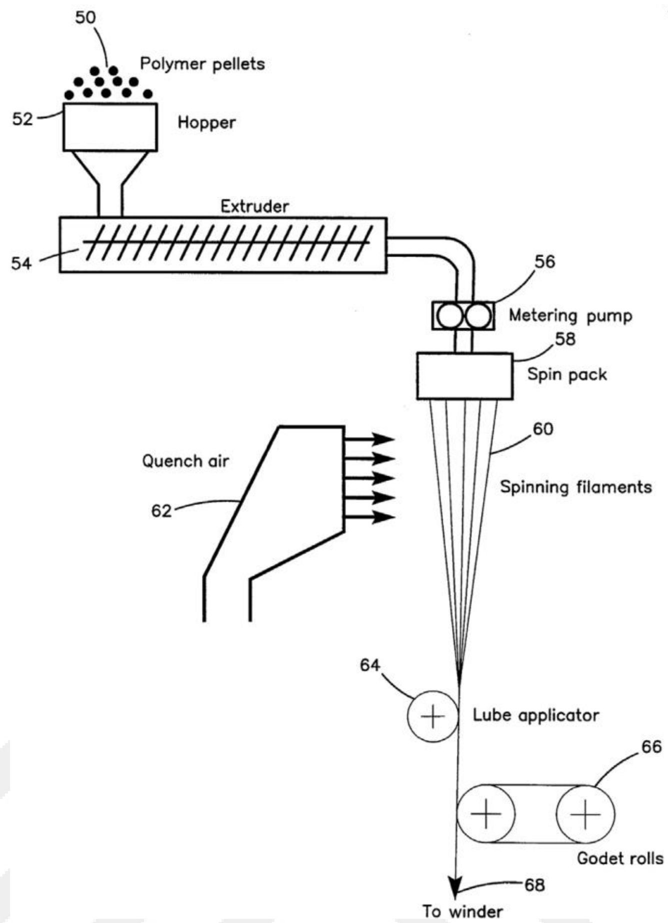


Figure 3. 7 Melt spinning procedure (Michael et al., 1998; Niaounakis, 2014).

The spunbonding process is frequently aforethought a kind of melt spinning. A important dissimilarity is that spunbonding includes air entrainment to tie the fibers slightly than godet cylinder classically seen in the melt spinning procedures. A typical spunbonding procedure is described in Figure 3.8 (Niaounakis, 2014; Bhat and Rong, 2005; Lunenschloss and Albrecht, 1985).

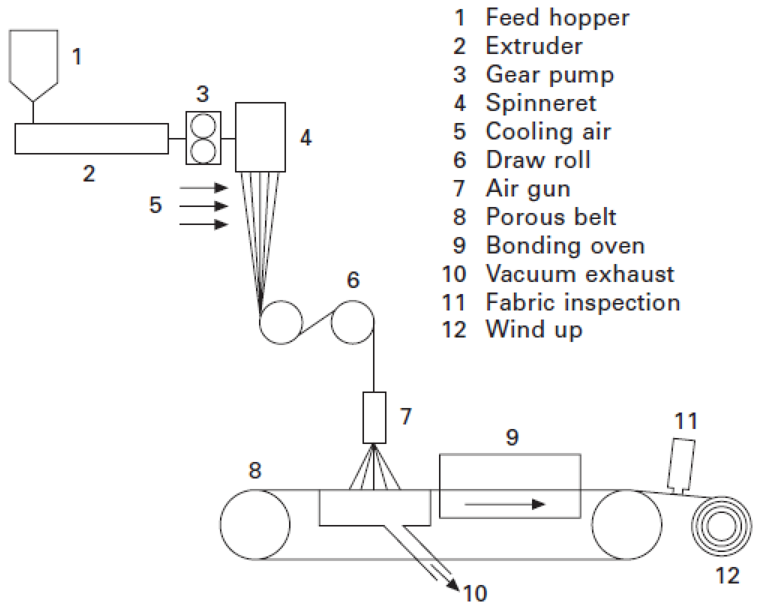


Figure 3. 8 Scheme of a spunbonding technology process method (Lunenschloss and Albrecht, 1985; Bhat and Rong, 2005).

A great - rate air coup the molten decomposable thermoplastic polymer from an extruder die tip onto a conveyor to technique great fibers in melt blowing process. Fibers made by melt blowing, in dissimilarity, are usually greater in diameter but fewer purposeful. A typical melt blowing procedure is show in Figure 3.9 (Hansen, 1993; Bhat and Rong, 2005).

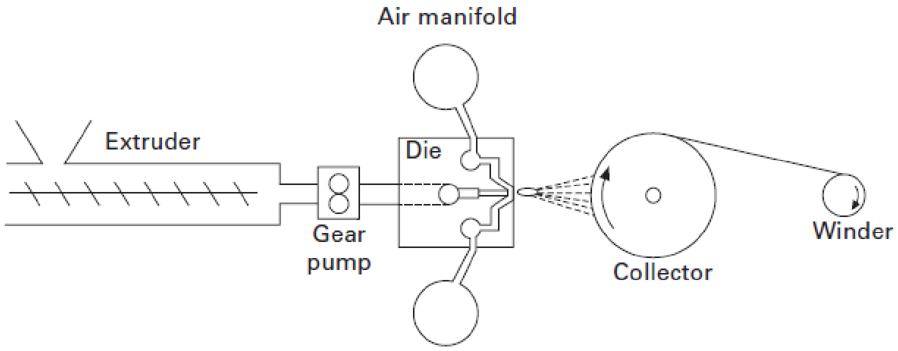


Figure 3. 9 Scheme of a melt blowing method (Bhat and Rong, 2005).

Thermoplastic decomposable polymer is solved in a resolvent and also the polymer resolution is extruded underneath force owing to in a spinneret dried spinning. The jet of polymer solution is passed across a warming zone where the diluter evaporate and thread harden (Niaounakis, 2014).

An environmental thermoplastic is at the same time resolved and the solution is put on through a spinneret that is underwater in a coagulation bath in wet spinning,. As the polymer mixture appears from the spinneret orifices inside the coagulation bath, the eco-friendly polymer is either fell or chemically renewed. Generally, all these procedures necessary more drawing for valuable possessions to be found (e.g., to serve as textile fibers) (Hansen, 1993; Bhat and Malkan, 2002; Bhat and Rong, 2005).

The worldwide purchases of nonwoven materials spin well in 2008 were show up to get to to $17.3 billion (Table 3.3), the polymer- grounded nonwovens manufacture, involving online combinations in Europe, has decreased as unexpected from 46% in the year of 2007 to 44% in 2008. The part of another fabrication processes is shown in Figure 3.10 (Pourmohammadi, 2013). As can see from the table, spunlaid process is the most used method.

Table 3. 3 Nonwovens manufacture in Europe by webforming procedure

Process	2006		2007		2008	
	1,000 tonnes	Growth (%)	1,000 tonnes	Growth (%)	1,000 tonnes	Growth (%)
Spun-laid	710.6	9.4	776.5	9.3	758.7	−2.3
Dry-laid	623.8	5.8	659.6	5.7	685.7	4.0
Wet-laid	106.8	8.8	107.8	0.9	115.7	7.4
Air-laid	140.2	5.7	154.8	10.4	162.3	4.8
Total	1,581.4	7.6	1,698.7	7.4	1,722.4	1.4

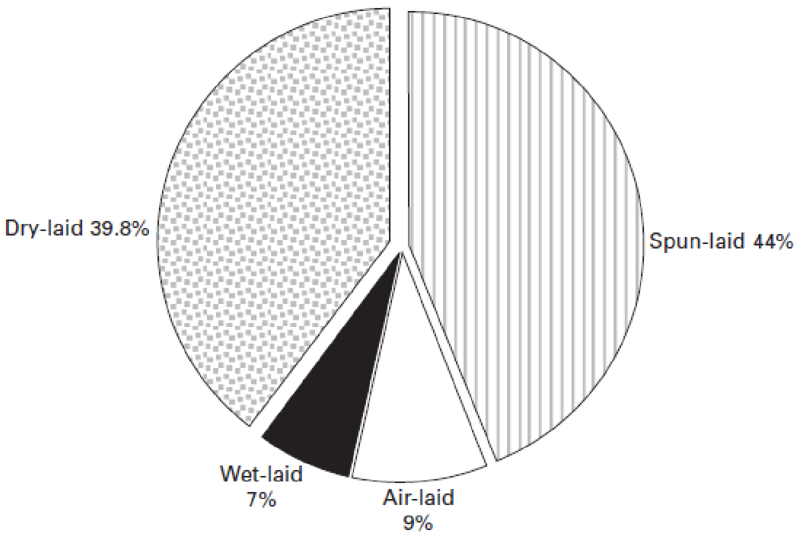


Figure 3. 10 Nonwovens manufacture in Europe by procedure in 2008 (Pourmohammadi, 2018).

3.2.2.2.Spunbonded technology process

The spunbond progression, one of greatest consumed nonwoven production technology, shares basic rules of fiber melt spinning process. It contains direct change of a polymer into nonwovens containing of unsystematically laid constant filaments. Hence the spunbond process is one of the greatest economical technology to transform polymers to fabrics. Shown in figure 3.11 that usage ratio of spunbond manufacturing process by years. Spunbond nonwovens are generally consumed in diversity of another applications containing carpet backings, medicinal, and clarification applications (Batra and Pourdeyhimi, 2012). Great percentage of spunbond nonwoven produces are one-use applications for example wipes and diapers. PLA, with its biodegradability, is an gorgeous material in the spunbond process (Gruber et al., 2000).

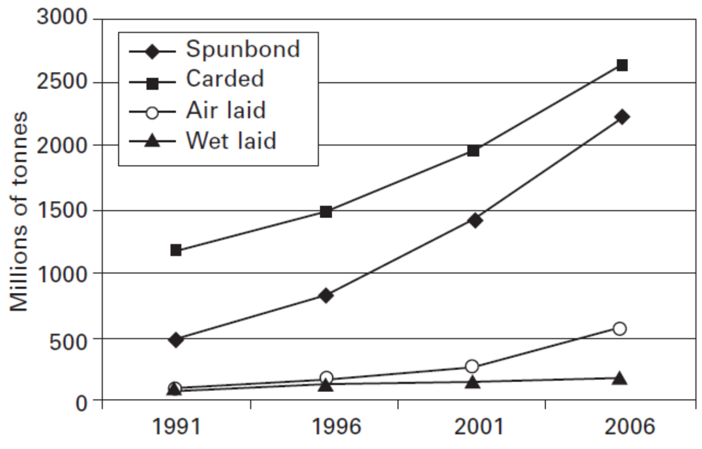


Figure 3. 11 Universal nonwoven manufacture by progression (Watzl, 2004; Bhat and Rong, 2005).

Initially in spunbond progression is fiber creation where polymers are molten, extruded, hardened, and represented. It is developed starting filament melt spinning process, input equal principles of fiber materialization and the stage where microstructure and fiber features are defined (Persson et al., 2013; Bruckmoser and Resch, 2015; Shim et al., 2016).

Spunbonded is presented as small technological method and great efficiency. PLA pieces are straight put in the screw extruder to make nonwovens within 20 min, which keeps time and energy. It is a hopeful method of Polylactic acid nonwovens (Zhao, 2006; Feng and Jiao, 2011).

In difference, old-style textile molten filament spinning method which creates filament fibers are two-step method includes of melt extrusion and drawing. Molten polymers are extruded through with spinnerets, removed, and gathered by the winder. The spinning rate of fibers created will be controlled by the winder rotating speed. So greater detailed control of the spinning rate can be gotten in the melt spinning (Persson et al., 2013; Bruckmoser and Resch, 2015; Shim et al., 2016).

It is critical to select appropriate technological factor to manufacture nonwoven through suitable intensity. Process condition should be about 200°C. Draft rate better between 2000-3500 m/min. The greatest temperature of pressure roller is 145 ° C (Bhat et al., 2008; Feng and Jiao, 2011). PLA nonwovens are highlighted as fine climate durability and tension retention. It is appropriate for the products of health materials and wipes (Blechschmidt et al, 2008).

4.EXPERIMENTAL PART

The experimental steps made within the scope of the thesis consist of four stages; First of all, in order to shed light on future studies, ZnO production and optimum utilization rate to be used as an antibacterial additive to the PLA / PBAT mixture; It consists of determining the best processable ratio for different types of PBAT additives modified with PLA and finally producing it by spunbond yarn production method to examine the processability of PLA / PBAT nonwoven fabric.

4.1. Preparation and Characterization of ZnO Particles

Materials and Chemicals

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and ammonium carbonate ($(NH_4)_2CO_3$), which are used as basic raw materials during ZnO production, were brought from Penta Chemicals in Czech Republic. The required quantities were weighed using the milligram range sensitive (0.0001g) by Sartorius GP603-S balance. Compounds in solid form were used by dissolving with distilled water to form a solution. Acetone which is used in the purification of ZnO formed at the end of the synthesis has technical purity. The Climate chamber Memmert VO400 (Figure 4.1) was used as the drying-oven to dry the product; device features, Climate chamber with adjustable pressure in the range of 10 - 1000 mbar for defined sample conditioning and the maximum operating temperature is 200 °C.

Figure 4. 1 Universal nonwoven manufacture by progression (Watzl, 2004; Bhat and Rong, 2005).

Annealing process, one of the purification steps of the generated ZnO, was done in LAC-LMH muffle furnace (Figure 4.2).

Figure 4. 2 LAC-LMH muffle furnace for purification of ZnO complex

Figure 4. 3 MiniFlex™ 600 X-ray diffractometer

X-ray diffraction peaks of ZnO were gotten using MiniFlex™ 600 X-ray diffractometer (Rigaku,Japan) with CoKβ as source (λ = 1.79 Å). Functioning voltage and current were maintained at 40 kV and 15 mA, separately for the measurement. XRD for the sample was took from 2θ range 5°–90° with 10°/s as stage time and 0.02° as a stage size.

Preparation of Samples

$(NH_4)_2CO_3$ (Figure 4.4) and $Zn(NO_3)_2.6H_2O$ supplied by Penta Chemicals were weighed in a precision balance to 1 M and dissolved in distilled water at room conditions.

Figure 4. 4 (NH4) 2CO3 in solid form in the beaker.

Ammonium carbonate; During the synthesis, it was continuously mixed in the beaker at 500 rpm with the help of a magnetic stirrer. Zinc nitrate hexahydrate was added dropwise to the ammonium carbonate solution at room temperature during this time. Depending on the amount added, after this process, which lasted about 2 hours, the ZnO complex to be purified was created (Figure 4.5).

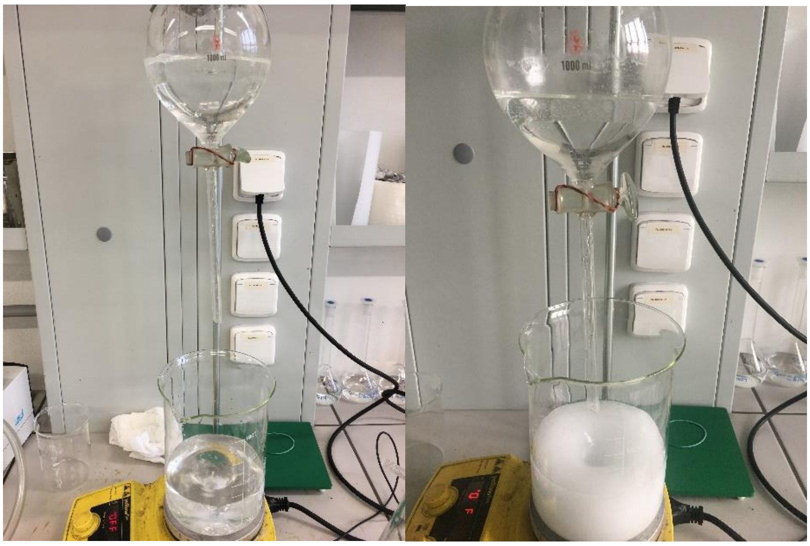


Figure 4. 5 a) Zinc nitrate hexahydrate, which has just begun to drip. b) The solution with the ZnO

The resulting ZnO complex semi product was filtered with a vacuum filter. After filtration, it was cleaned with distilled water and alcohol for purification. The obtained ZnO complex was taken into the container and dried at 90 ° C temperature, under 50% fan and 100% Flap conditions for 24 hours in the oven. Finally, it was kept in an muffle furnace at 500 ° C for about 2 hours to obtain the crude product.

After weighed 100 grams of ZnO complex and annealing process, 64 grams of ZnO was formed. In other words, 64% of the complex formed as a result of the reaction is ZnO.

Test Methods of Samples

Table SEM (Figure 4.6) (Desktop scanning electron microscope Phenom Pro) was used to see wheter the ZnO complex was formed or not. Table SEM has a growth range between 5 and 10kV; the light optic offers zoom from 20 to 135x and the electron optics from 20 to 130000x. It is good at imaging non-conductive materials such as paper, organic materials, glass and ceramics. The sample size should not exceed 32 mm (Ø) and 30 mm (h). Thanks to the ProSuite feature, it can match the 3D image sharply and automatically.

Figure 4. 6 Desktop scanning electron microscope Phenom Pro.

ZnO complex was imaged by SEM under the conditions are shown in Figure 4.7.

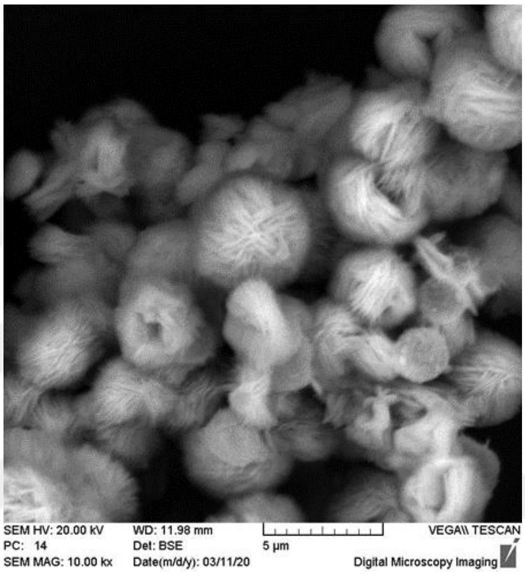


Figure 4. 7 ZnO complex which is produced.

At the same time, the formation of ZnO was supported by XRD. ZnO formation is observed as seen in Figure 4.8. All diffraction peaks were certainly assigned by the suitable structure and reflection plane indices, and no other crystalline phases were found (Figure 4.8).

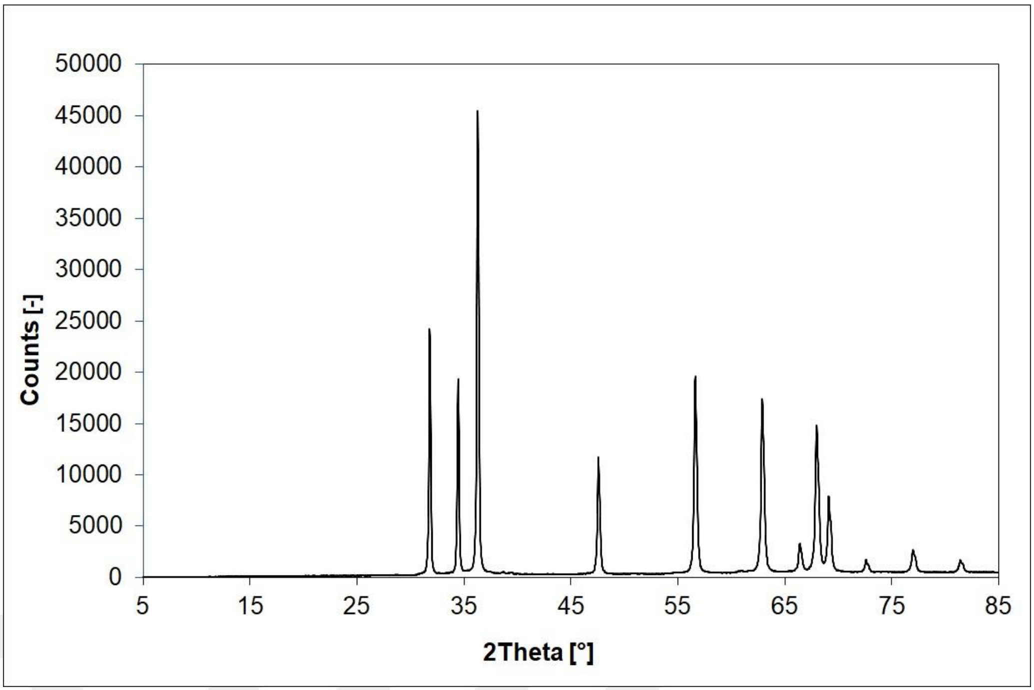


Figure 4. 8 XRD graph of ZnO

4.2. Preparation and Characterization of PLA/PBAT

Materials and Chemicals

PLA (Ingeo ™ Biopolymer 6100D) used as matrix material was supplied from NatureWorks; material properties are shown in Table 4.1.

Table 4. 1 Technical features of PLA (Ingeo™ Biopolymer 6100D Technical Data Sheet).

Physical Properties	**Ingeo 6100D**	**ASTM Method**
Specific Gravity (g/cm^3)	1.24	D792
Relative Viscosity[(2)]	3.1	D5225
Melt Index (g/10 min at 210°C)	24	D1238
Melt Density (g/cm^3 at 230°C)	1.08	
Glass Transition Temperature (°C)	55-60	D3417
Crystalline Melt Temperature (°C)	165-180	D3418
Typical Fiber Properties		
Denier per Filament (g/9000m)	≥0.5 dpf	
Tenacity (g/d)	3.0-6.0	D2256/D3822
Elongation (%)	10-70	D2256/D3822
Modulus (g/d)	55-65	D2256/D3822
Boiling Water Shrinkage (%)	3-10	D2102
Hot Air Shrinkage (% at 130°C,10 min)	3-10	D2102

3 different PBATs (biodegradable polyester compounds) which are used to eliminate the brittleness of PLA and find the one that meets the optimum conditions in process, have been supplied from the companies; technical specifications are shown in table 4.2. PBAT1 is biodegradable, statistical, aliphatic-aromatic copolyester based on the monomers 1.4-butanediol, adipic acid and terephthalic acid in the polymer chain, PBAT2 and PBAT3 are biodegradable polyester compounds. The density and mechanical properties of the 3 different PBATs different from each other and also ordinary PBAT. Because these 3 different PBATs are blend compounds. Therefore, as can be seen from Table 4.2, their colors are different from each other. For this reason, we wanted to examine the effects of these differences on rheology and process.

Table 4. 2 Technical features of 3 different supplied PBAT

Material	Standard	Unit	PBAT1	PBAT2	PBAT3
Density	ISO 1183	g/cm^3	1.26	1.41	1.35
Melt Volume Rate 190°C/2.16 kg	ISO 1133	$cm^3/10min$	2.5-4.5	2-5	2-5
Tensile Strength	ISO 527-3	Mpa	35	30	27

As seen in Table 4.3; 3 different PBATs were used; The apperiance and naming of the granules are given below. $cm^3/10min$

Table 4. 3 Apperiance of 3 different PBAT granules.

	**PBAT 1**
	**PBAT 2**
	**PBAT 3**

The drying process of PLA before participate in the process was carried out by the continuous drying system (Figure 4.9).

Figure 4. 9 Continuous drying system for hydroscopic materials

Climate chamber Memmert VO400 drying-oven was used in the drying process of PBAT.

Scientific brand double screw laboratory type extruder was used in the mixing process of PLA and PBAT (Figure 4.10). Laboratory twin screw extruder with modular co-rotating screws of 26 mm in diameter and length 48D. Device is corrosion and abrasion resistant and is capable of 120 rpm with capacity up to 60 kg/hour. Device is equipped with two positions for top feeding of powders or pellets, two side positions for feeding of powders or pellets and one side position for feeding of liquids.

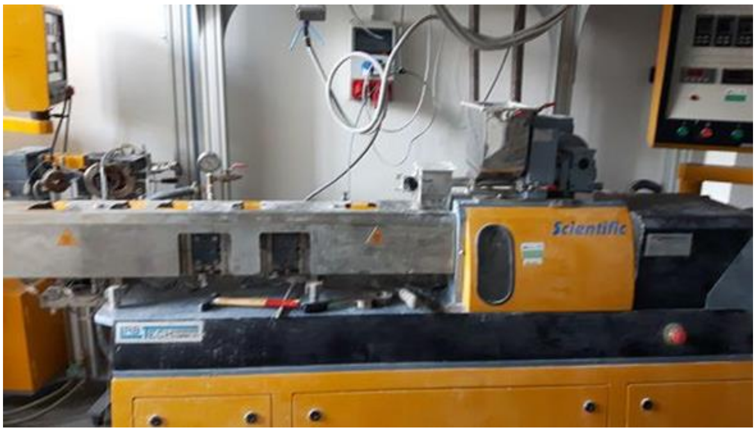


Figure 4. 10 Scientific Twin Screw Extruder

Preparation of Samples

PLA dried in the dryer at 60°C for 3 hours and PBAT dried in the drying-oven at 60°C for 3 hours was made ready for the twin screw extruder process. PBAT1, PBAT2 and PBAT3 were produced in the process settings shown in table 4.4 in a twin-screw extruder with PLA, which is the matrix separately, in the ratios shown in table 4.5. First, after the PLA was passed through the extruder alone, PBAT1 / PLA, PBAT2 / PLA, PBAT3 / PLA were mixed in different proportions and a total of 13 productions were made.

Table 4. 4 Process of PBAT1 / PLA, PBAT2 / PLA, PBAT3 / PLA blends in twin screw extruder

Zone PLA/PBAT1											
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
80	180	185	190	192	195	197	200	202	205	208	210
Torque						Rpm					
50						100					

Zone PLA/PBAT2											
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
80	180	185	190	192	195	197	200	202	205	208	210
Tork						Rpm					
53						90					

Zone PLA/PBAT3											
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
80	180	185	190	192	195	197	200	202	205	208	210
Tork						Rpm					
50						100					

Table 4. 5 Ratio of PBAT1/PLA, PBAT2/ PLA, PBAT3/ PLA mixtures

PBAT1	0%	3%	5%	10%	20%
PLA	100%	97%	95%	90%	80%
PBAT2	0%	3%	5%	10%	20%
PLA	100%	97%	95%	90%	80%
PBAT3	0%	3%	5%	10%	20%
PLA	100%	97%	95%	90%	80%

The image of the productions is given in Figure 4.11.

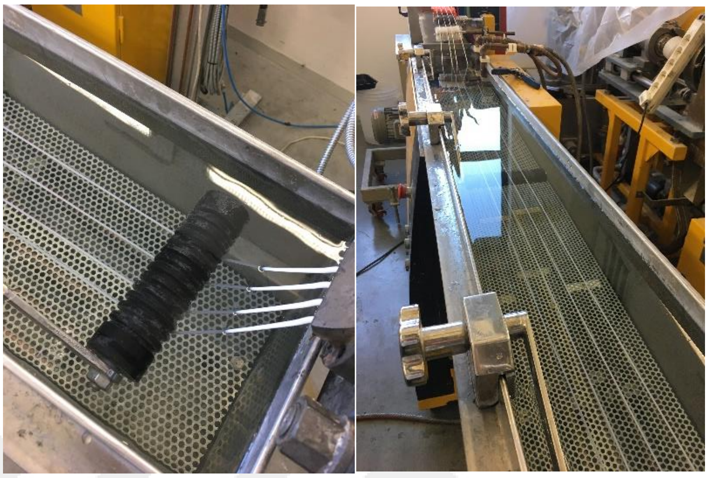


Figure 4. 11 View of the productions made in twin screw extruder

Test Methods of Samples

High pressure capillary rheometer RG 25-50 (Göttfert) was used to measure the elongation viscosity at elongation strain rates of the 13 productions (Figure 4.12).

Figure 4. 12 Göttfert capillary rheometer

Rheological performance is different for shear and elongation loads. Velocity gradient is in the direction of flow at extension stress. The reotens method shown in the Figure 4.13 is used by rotatable wheels, which is part of the balance under the capillaries, to determine the elongation viscosity due to the resistance to extension of the polymer melt from the reservoir through the capillary. Piston speed increases over time and applies force to the balance. The applied melt force is recorded and the elongation viscosity is determined according to the resistance force development during the melt elongation acceleration (Malkin et al., 2012).

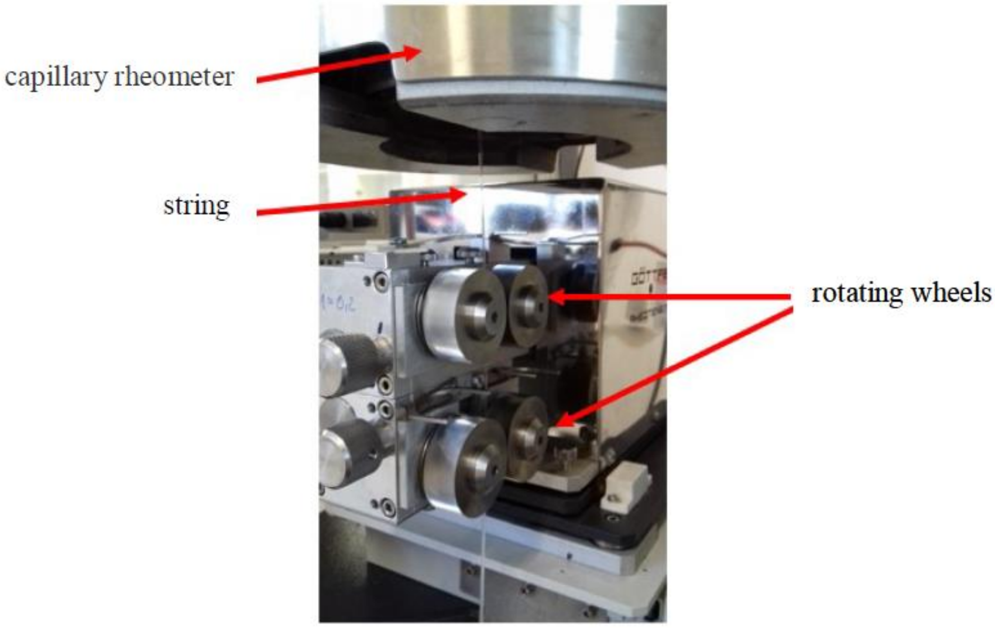


Figure 4. 13 Capillary rheometer Göttfert with Rheotens device (Vilem, 2019).

Measured at temperature 180°C. capillary diameter 2 mm and length 20 mm. Constant piston speed 0.25 mm/s (not 0,32 as was written). Starting speed of rotating wheels (strand speed at start of run) is 0,15 mm/s.

DSC test was performed in order to understand the crystal structure of the produced PLA / PBAT blend materials and raw materials to analyze them. For this reason, Mettler Toledo DSC 1/700 in Tomas Bata University was used (Figure 4.14).

The DSC method is based on the comparison of the encapsulated sample and the blank reference in the heated crucible. The sample is heat up in the furnace with applying the same heating movement. Therefore, when the thermal evolution region of the material are achieved, for instance, the endothermic, the temperature interval in the crucible with trial occur comparing to the reference pan from the time when the endothermic transition expends more energy. Thus, the principle of the DSC technique is to calculate the difference in temperatures relating the sample and the reference crucible. Most often are measured by DSC is the melting temperature, the glass transition temperature, the recrystallization temperature, and also the heat capacity.

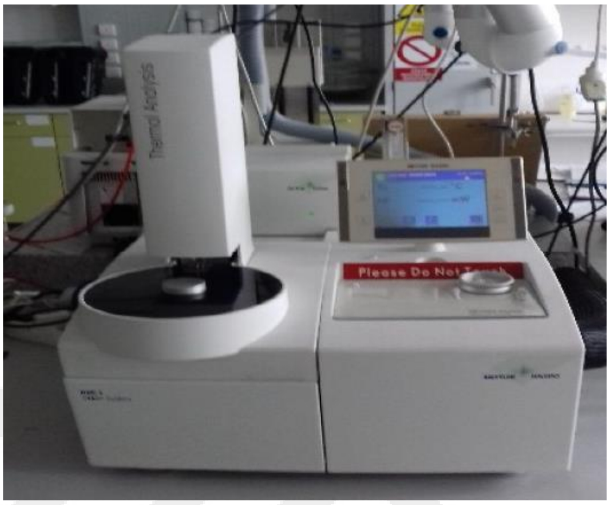


Figure 4. 14 Mettler Toledo DSC 1/700

DSC analysis of 8 samples was made. Raw materials (PLA, PBAT1, PBAT2 and PBAT3) and the produced PLA granules with 5% PBAT additive (extruded PLA, PBAT1 / PLA 5%, PBAT2 / PLA 5%, PBAT3 / PLA 5%) were tested under appropriate conditions.

Utilized temperature profile was following:

1. The first heating from 20 ºC to 230 ºC; heating rate 10 ºC/min

2. Cooling from 230 ºC to 20 ºC; cooling rate 10 ºC/min

3. The second heating from 20 ºC to 230 ºC; heating rate 10 ºC/min

The analysis was carried out under inert atmosphere of nitrogen flow of 40 ml/min and the curves are marked as: !$]2[1st heating ; !$]4[cooling ; !$]6[2nd heating.

4.3. Preparation and Characterization of PBAT/ZnO

Materials and Chemicals

For PBAT / ZnO antibacterial tests, PBA used as one type of PBAT to see antibacterial behaviour of ZnO on PBAT and to determine ratio of ZnO. Mini extruder was used for the mixture.

ZnO particles synthesized at Tomas Bata University were ground in a mortar supplied from Tomas Bata University and pulverized in smaller sizes. PBAT1 / ZnO mixture was made in Microhunter Xplore MC15 mini extruder (Figure 4.15). Device features; Two-screw microhunter for the preparation of mixtures of materials with a basic volume of 15mL, which can also work in volumes of 3,7 or 15 mL,The device allows you to adjust both conical and counter rotating conical screws, Maximum temperature 400 ° C, maximum torque 12 N.m

Figure 4. 15 Microhunter Xplore MC15 Mini extruder

The granules which are obtained in the mini extruder were prepared in 2 x 2 cm pieces by hot-cold press (Manual cooling press and manual hot press by Tomas Bata University, Czech Republic) (Figure 4.16) to prepare samples for antibacterial testing. Manual cooling press device features; Device features for cooling the polymer test specimen forming the compression mold at high pressure; It is 300x 300mm and its height is 200mm. Plates are opened and closed manually.

Figure 4. 16 a) Manual hot press, b) Manual cooling press

Bacteria used for PBAT1 / ZnO antibacterial test; G+: Staphylococcus aureus (CCM 4516), Enterococcus faecalis (CCM 3956), G–:Escherichia coli (CCM 4517) taken from the Czech Collection of Microorganisms, Czech Republic. Culture media and solutions which is used in antibacterial tests; suspension medium = 1/500 nutrient broth (1/500 NB) solution (NB – HiMedia, India), physiological saline solution (0,9%NaCl) (NaCl – IPL, Czech Republic)- plate count agar (PCA) (PCA – HiMedia, India),70% ethanol (Tomas Bata University, Czech Republic).

Preparation of Samples

PBAT1, which was dried at 60°C for 2 hours in the drying-oven, and ZnO, which was pounded in a mortar and turned into a small powder, were made ready to be processed in a mini extruder.

It was weighed with PBAT1 on precision scales to include 0%, 3%, 5%, 7% and 10% ZnO. The weighed raw materials were mixed by being melted in the mini extruder in the appropriate process (220°C temperature,100rpm) after mixing (Table 4.6). Since this mixture will be used to prepare antibacterial test plates and these plates will be 2x2 in size, therefore small production was made.

Table 4. 6 Mini extruder PBAT1 / ZnO process conditions

	Unit	Zone1	Zone2	Zone3
Front	C°	219	220	219
Rear	C°	217	220	219
Melt	C°	205	-	-
Force	N	178	-	-
Speed	rpm	102	-	-

The melt mixture formed in the mini extruder was poured linearly onto the aluminum foil and was allowed to cool and harden. Since there is no cooler and cutter in the mini extruder, these operations were done manually. The cooled polymer was cut into granules and in equal sizes with the help of scissors.

The obtained granules, in order to prepare antibacterial test samples; It was made into 2x2 plastic plates (ISO 22196) with the help of hot-cold press (Figure 4.17).

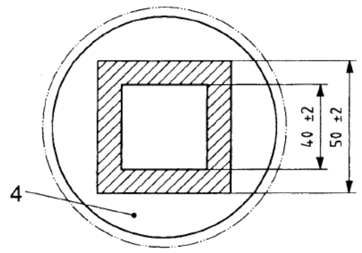


Figure 4. 17 Appearance of 2x2 plastic plates (International Standard, 2007).

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. The sample was prepared regularly in order to distribute the granules that melt in the hot press evenly and to create the appropriate thickness. Thus, when the material melted in the press, an equal thickness was created. Five plates of each material were prepared. Wide and equal thickness plates obtained in hot and cold press were cut with scissors in 2x2 dimensions for antibacterial tests.

Test Methods of Samples

Sterile microbiological equipment: inoculating loops, automatic pipettes, pipette tips, screw-capped test tubes, Petri dishes, tweezers, balance, autoclave, hot-water bath, laminar flow box, laboratory gas burner, vortex mixer, incubator (Tomas Bata University, Centrium of Polymer System, Czech Republic)(Figure 4.18).

Figure 4. 18 Sterile area where samples was prepared.

2x2 cm samples (2,5 x 2,5 cm PP cover films), sterilized in 70% ethanol. Then 1/8 inoculating loop of the test bacteria was transfer into 10 ml of 1/500 NB and dispersed well using vortex mixer, approximate concentration (106 CFU/ml) was verified using Bürker chamber, determination of the exact concentration of bacterial suspension was carried out by agar dilution technique (Figure 4.19) prepared Petri dishes (Figure 4.20) with PCA and bacteria were incubated at 35 °C for 24 hours.

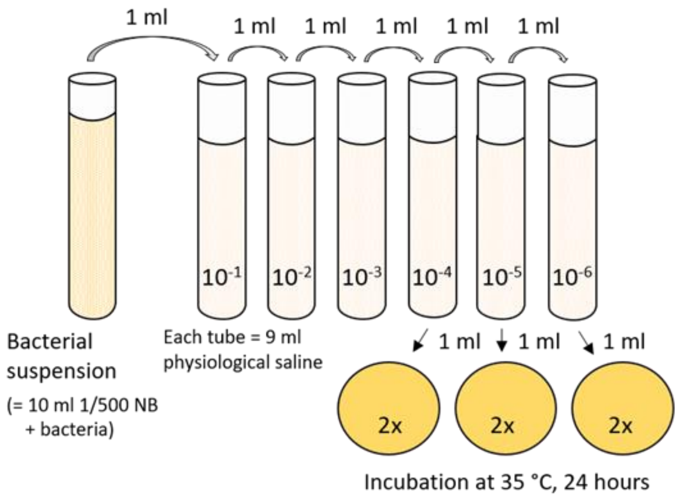


Figure 4. 19 Determination of exact concentration of bacterial suspension

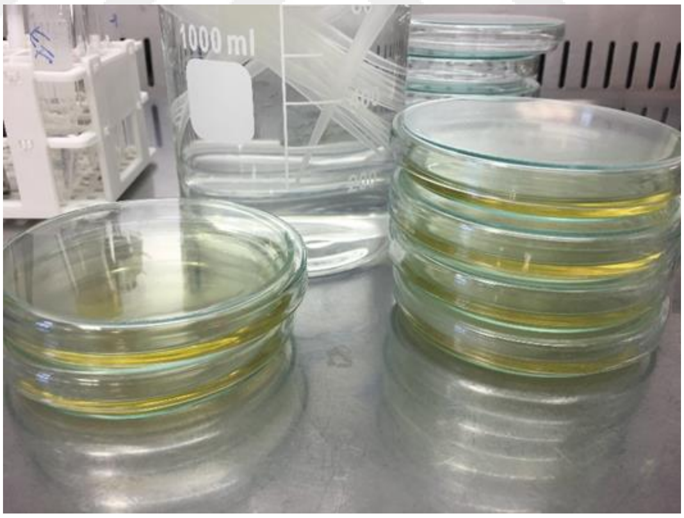


Figure 4. 20 Petri dishes with agar

After incubation colonies in the Petri dishes were calculated, consequences were stated as group making elements per ml (CFU/ml):

$$N = \frac{\sum C}{(n_1 + 0{,}1 \cdot n_2) \cdot d}$$

N – number of colony creating units each 1 mL of bacterial suspension (CFU/ml)

C – sum of all colonies counted on selected dishes (containing 30–300 CFU)

n1 – number of dishes used for the calculation from the 1st countable dilution

n2 – number of dishes used for the calculation from the 2nd countable dilution

d – dilution factor (for the 1st countable dilution)

Sterile PP film was placed into Petri dish and inoculated with 50 µl of bacterial suspension, inoculum was covered with prepared sterile sample, inoculated test samples in Petri plates were keep warm at 35 °C for 24 hours, min %95 humidity, testing was presented twice for apiece taster and also bacteria.

Afterward incubation, the cover foil was removed with sterile tweezer and the test specimen was imprinted 3x on a sterile agar plate with the side on which the bacterial suspension was applied, the order of the prints was previously marked on the bottom of the Petri dish, the agar plates were incubated at 35 °C for 24 hours, determination was completed twice for every sample and bacteria.

4.4.Preparation and Characterization of Nonwoven

Materials and Chemicals

Spunbond technology is used in nonwoven fabric production. Name of device polymer melt filament laboratory line, model LBS-300 (Hills) (Figure 4.21). Laboratory line for continuous preparation of nonwoven textiles (spunbond, meltblown technology) from polymer melt filaments (e.g. PP, PLA, PA, PET) with high degree of process control. Line consists of 2 single screw extruders, gear pumps and pressure indicators. System is corrosion resistant in order to allow processing of fluoropolymers including inserts for filaments rounded and unequal cross-section in configuration: homo-filament and bi-component filament (alongside, sheath/core, islands in the sea). Single screw extruders have hopper containing vent for nitrogen purging of hydroscopic polymers, the throat of extruder is water cooled to prevent bridging, screw D=19 mm, L/D 30 with mixing element (Maddox). Max operating temperature is 450°C and extruder barrels are corrosion resistant in order to allow processing of fluoropolymers. Spunbond accessories: Die 100 mm wide having 25 holes/1 inch (25.4 mm), corrosion resistant in order to allow processing of fluoropolymers. Haul-off conveyor with rpm regulation 100-1000 m/min.

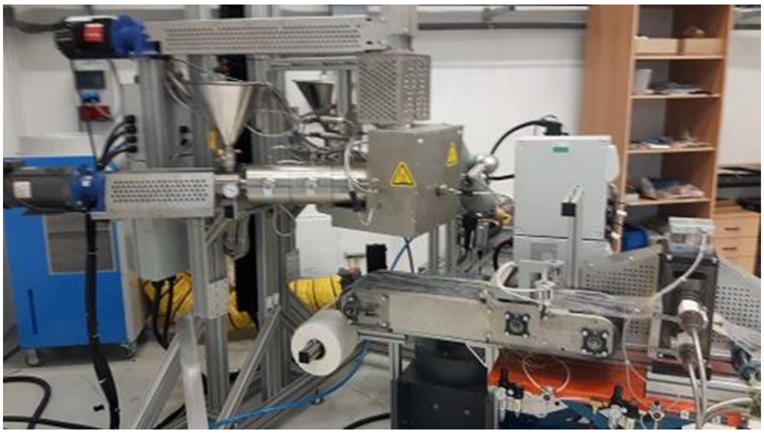


Figure 4. 21 Polymer melt filament laboratory line, model LBS-300

The PLA / PBAT produced by the twin screw extruder in the 2nd step used as raw material.

Preparation of Samples

PLA / PBAT granules with PBAT additives of 0%, 3%, 5%, 10% and 20% were kept in the oven at 60 °C approximately 2 hours and also made ready for the process (Table 4.7).

Table 4.7.

Table 4. 7 The nonwoven fabric produced with spunbond technology; raw material ratios

PBAT1	0%	3%	5%	10%	20%
PLA	100%	97%	95%	90%	80%
PBAT2	0%	3%	5%	10%	20%
PLA	100%	97%	95%	90%	80%
PBAT3	0%	3%	5%	10%	20%
PLA	100%	97%	95%	90%	80%

Process parameters of the production are shown in the Table 4.8.

Table 4. 8 Spunbond technology production process parameters

Extruder			Spinning Die		
Zone 1 hopper	Zone 2	Zone 3	Melt pump	Spinhead	Packwell
°C	°C	°C	°C	°C	°C
210	210	230	230	230	230

Extrusion			Winding			Aspirator
Extruder pressure	Melt Pump	Output (72 cap.)	Belt Speed	Calender Speed	Bonding Temp. Upper/Lower	Air Intensity Inside Aspirator
bar	rpm	g/min kg/h	value m/min	value m/min	°C	kPa
25	5	9	2.3	1.68	85-87	80

In PBAT1 and PBAT 2, there was no problem in the processability of the production up to 10%, but there was a problem in processing after 3% in PBAT3. The problem was that the polymer melt fibers start to come in batch and therefore cannot spin properly. Although the process was changed accordingly, the problem could not be solved. This situation was previously predicted in the elongational viscosity test made on the materials before the process and the process parameters were determined accordingly. Despite this, the expected results were seen. The results seen in elongation viscosity have been validated in this process.

Nonwoven fabric production is shown in Figure 4.22.

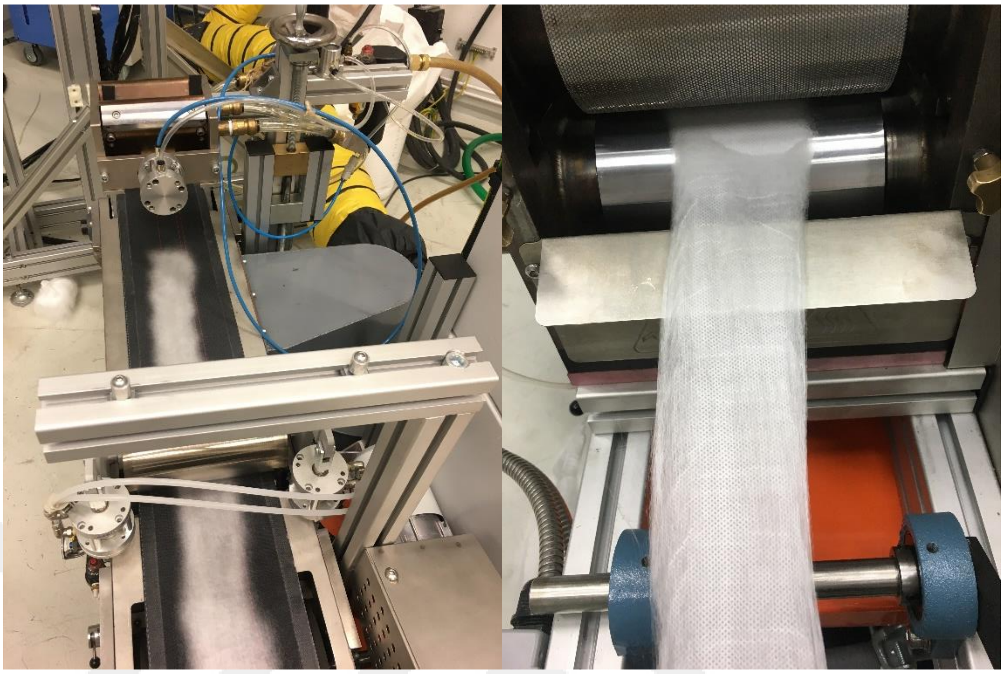


Figure 4. 22 Nonwoven fabric production

Test Methods of Samples

The tensile strength test on nonwovens was done with the Testometric MT350-5CT Universal Testing Machine (Figure 4.23). Test Speed : 100,000 mm/min, Pretension : 0,500 N,Sample Length : 30,000 mm.

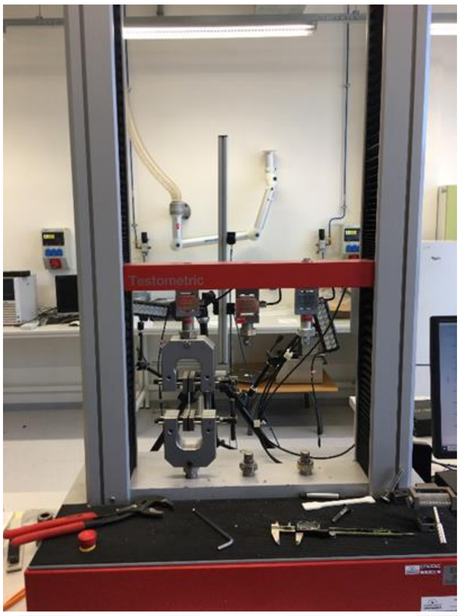


Figure 4. 23 Testometric MT350-5CT universal testing machine for testing mechanical behavior

The nonwoven fabrics that obtained were cut into 2.5x5 cm pieces for tensile strength test sample preparation. While preparing the sample, samples were taken from the middle part of the fabric, which was determined as the smoothest and strongest part of the nonwoven fabric.10 repetitions of each production were made (Figure 4.24). Test was made under following conditions: Test speed: 100,000 mm/min, Pretension : 0,500 N, Width : 25,000 mm, Thickness : 0,160 mm, Sample Length : 30,000 mm.

The prepared samples were carefully placed in the holders and the test was started. The material was separated in the machine direction.

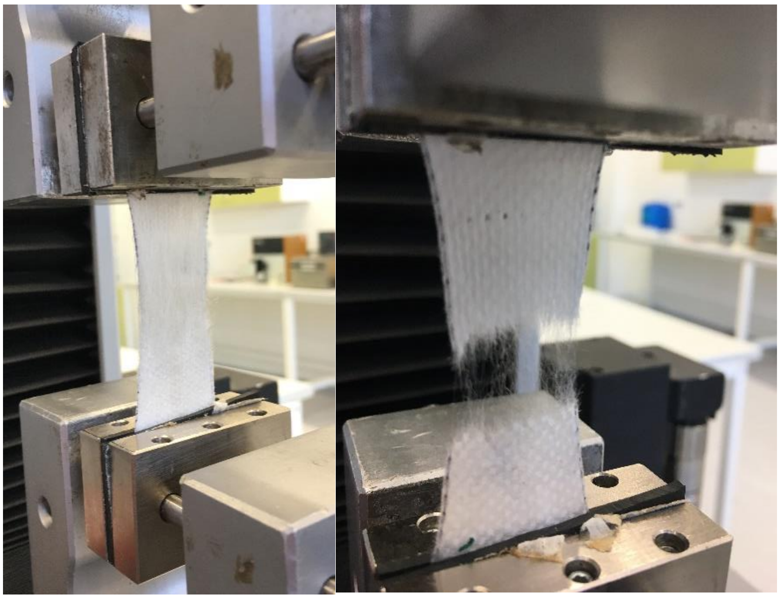


Figure 4. 24 Tensile strength test of nonwoven products.

In this way, the texture of the material during nonwoven production can be interpreted from the tensile strength test. In addition, to support the theory; Samples separated from each other were placed in the SEM device and their surfaces were examined. The measurements made were made at 5kV.

5.RESULTS AND DISCUSSION

5.1. Rheometer Test Results

The molten granules which are made with PLA / PBAT1-2-3 at different ratios (3%, 5%, 10%, 20%) were pressed out from capillary rheometer Göttfert RG25-50 with the constant piston speed of 0.25 mm.s-1. The extruded string was pulled by the four wheels of the Rheotens machine. After beginning of the measurement, the liftoff speed was gradually increased up to the speed when the string was wrecked. Several curves were determined and they are overlapped in the following graphs (Figure 5.1).

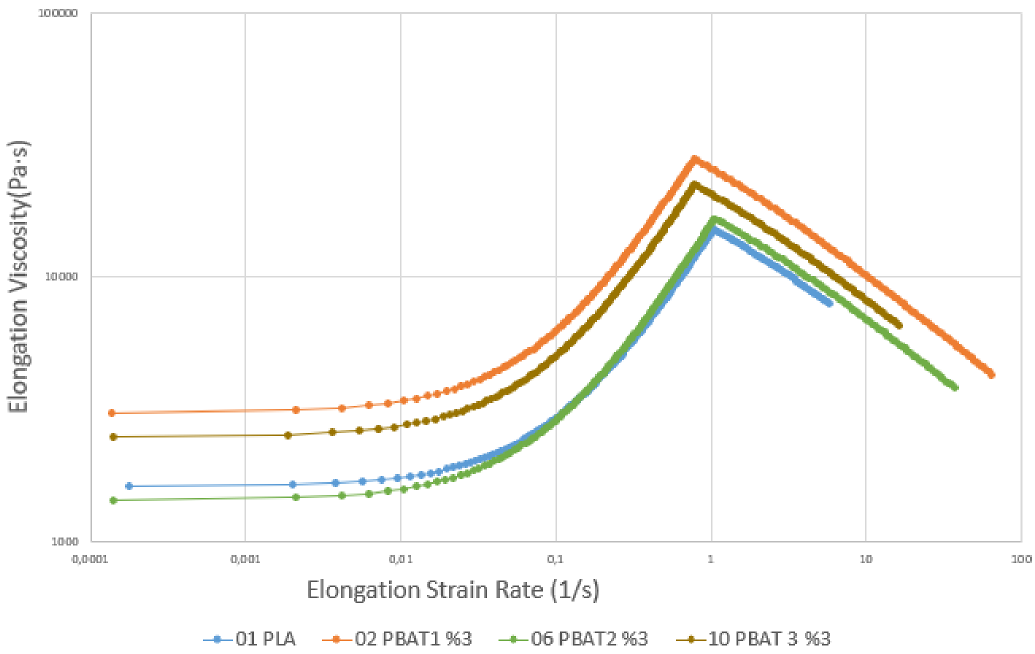


Figure 5.1 13% elongation viscosity rheometer chart of PBAT1, PBAT2 and PBAT3

Strain hardening is detected as a strengthening of a material through big strain deformation. It is made happened by large scale orientation of chain molecules and lamellar crystals. This experience is quite often observed when plastic materials are stretched beyond their yield point. Polymers that show better strain hardening are frequently tougher and undertake ductile rather than easily broken failure (Miehe et al., 2009; Polymerdatabase, 2021). Strain hardening is cause increase in melt strength. So, when elongation strain rate (1/s) increased, also elongational viscosity increase, but only to some certain value which is to maximum value of strain hardening. Than the strength of the polymer melt is getting lower and elongational viscosity is decrease.

It can be seen in the Figure 5.2 that PLA and PBAT 2 have a lower values of elongation viscosity comparing to PBAT 1 and PBAT 3. However, the peaks of strain hardening of PLA and PBAT 2 were observed at the higher values of elongation strain rate. But as seen in the graph, PBAT2 has better strain hardening according to PLA. So, %3 rate of PBAT1 and PBAT3 do not affect to melt strength of the material. In connection to the results of nonwoven textile manufacturing when PBAT2 proved to be better for spinning in %3 ratio, seems to be the strain hardening the crucial property defining ability of polymeric material for fiber production. It is also worth pointing out that this measurement process is closest to practical spinning.

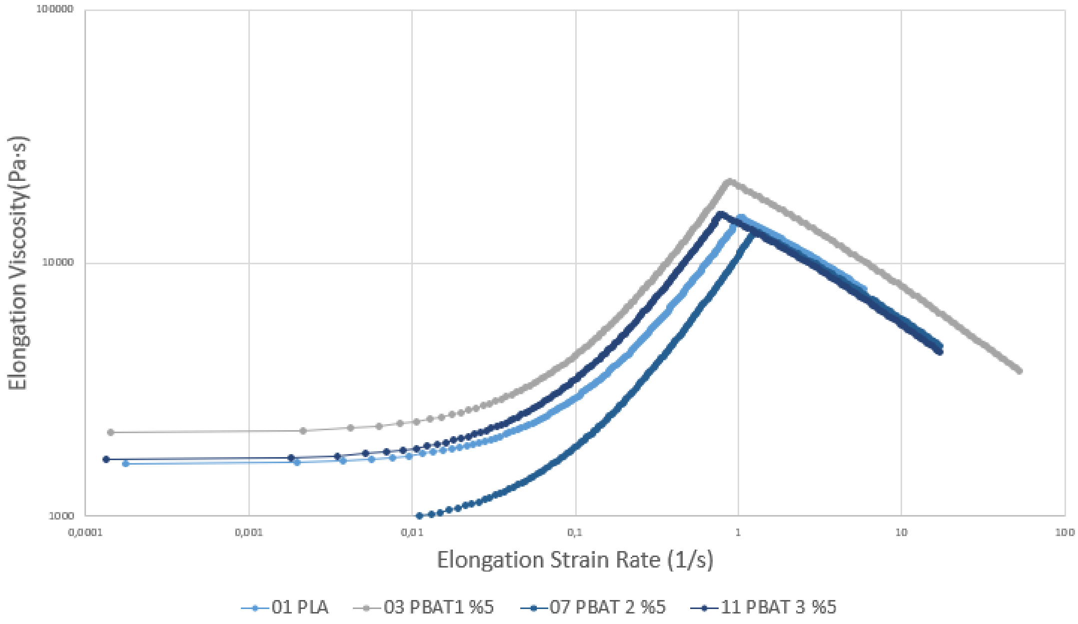


Figure 5. 2 5% elongation viscosity rheometer chart of PBAT1, PBAT2 and PBAT3

With the addition of 5% PBAT with different kinds can be seen in the Figure 5.2 that PBAT 2 has the lowest value of elongation viscosity. PBAT2 has the best strain hardening according to other kind of PBATs.

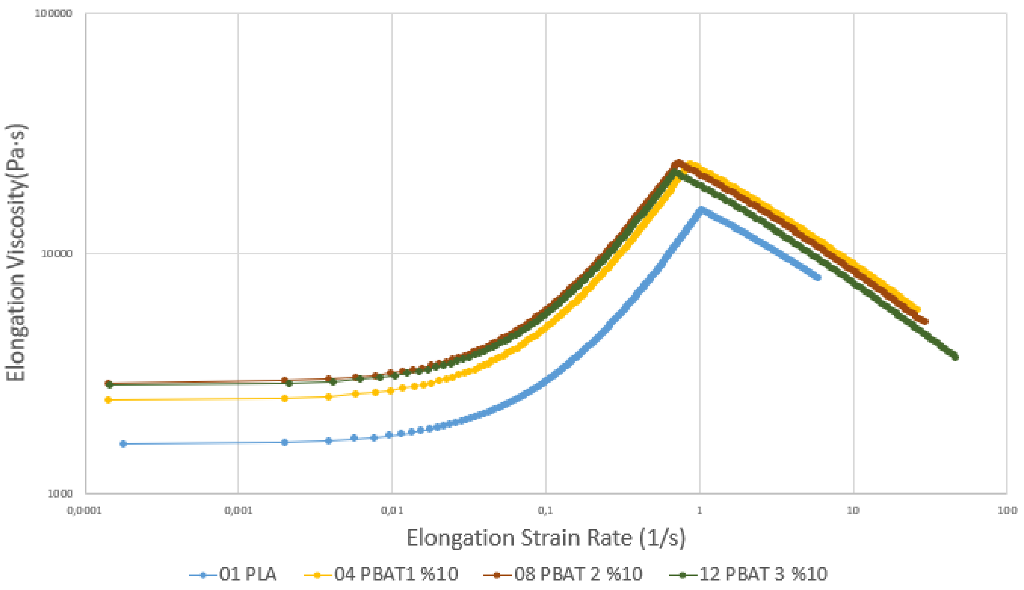


Figure 5. 3 10% elongation viscosity rheometer chart of PBAT1, PBAT2 and PBAT3

With the addition of 10% PBAT with different kinds can be seen in the Figure 5.3 that PLA has the lowest value of elongation viscosity and PBAT1-2-3 have same elongation viscosity value. PLA has the best strain hardening according to PBAT types.

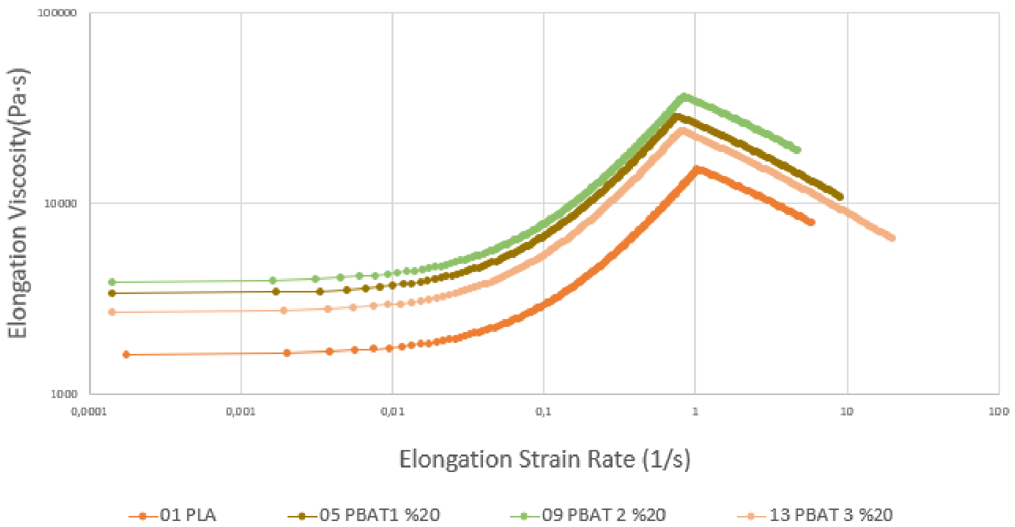


Figure 5. 4 20% elongation viscosity rheometer chart of PBAT1, PBAT2 and PBAT3

With the addition of 20% PBAT with different kinds can be seen in the Figure 5.4 that PLA has the lowest value of elongation viscosity. At the same time PLA has the best strain hardening according to PBAT types.

As a result, PBAT2 is the most suitable for processability of spunbond production technology according to elongation rheometer. In addition, when the behavior of all 3 materials depending on the ratio was examined while the rheometer test was performed, problems were encountered in the production of thinning and rupture of the material, both in rheology test and during production with spunbond for PBAT3.

5.2. Antibacterial Test Results

Antibacterial test results of 5 productions made with PBAT1 / ZnO at different rates (3%, 5%, 7%, 10%) were examined; 2 tests were done for 3 different bacteria, a total of 30 samples were examined (Figure 5.5). Close-up view of one of the examples is given in Figure 5.6.

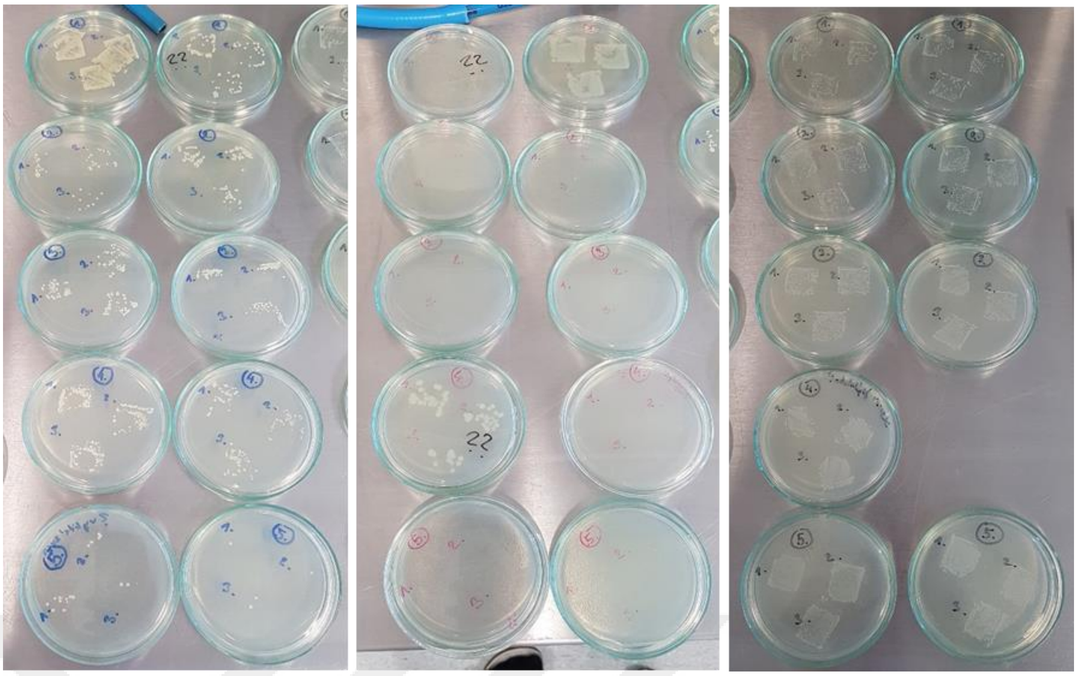


Figure 5. 5 Results of antibacterial testing (S. aureus – blue; E. coli – red, E. faecalis – black)

Figure 5. 6 Close-up view of one of the test samples.

After the incubation, the bacteria concentration in the environment can be seen clearly (Table 5.1).   .

Table 5. 1 Exact concentration of bacterial suspensions

S. aureus	$1{,}3 \,.\, 10^{6}$ CFU/ml
E. coli	$2{,}6 \,.\, 10^{6}$ CFU/ml
E. faecalis	$1{,}1 \,.\, 10^{6}$ CFU/ml

After incubation, antibacterial properties of the samples were evaluated according to the given scale (Table 5.2).

Table 5. 2 Evaluation of antibacterial properties

	Sample	Evaluation					
		S. aureus		*E. coli*		*E. faecalis*	
1	PBAT1 (Ecoflex)	5	2??	0??	5	4-5	5
2	PBAT1 + 3% ZnO	1-2	2	0	0	4-5	4-5
3	PBAT1 + 5% ZnO	2-3	2	0	0	5	5
4	PBAT1 + 7% ZnO	3-4	2-3	3??	0	5	-
5	PBAT1 + 10% ZnO	1	1	0	0	5	5

?? = strange result

- = undefined result

- 0 – no colony forming units
- 1 – countable quantity (individual colonies)
- 2 – countable quantity (joined colonies)
- 3 – 2nd print recognizable colonies, 3rd print countable
- 4 – 3rd print recognizable colonies
- 5 – overgrown (continuous growth)

effective ineffective

All tested ZnO-containing samples were effective against Escherichia coli and ineffective against Enterococcus faecalis. In the case of Staphylococcus aureus, ZnO-containing samples were partially effective, however the best result was observed for sample PBAT1 + 10% ZnO.

5.3. SEM Results

Table SEM was used to examine the surface of PLA / PBAT / ZnO blended nonwoven fabric products produced with spunbond technology. In the method, surface smoothness of 13 samples of PBAT / PLA nonwoven fabric was examined. Results are given in 500x size, 5kV. Depending on the participation rate of the same type of PBAT, in order to examine the effect on the smoothness of the surface, the effect of the addition ratio of PBAT1, PBAT2 and PBAT3 to 0%, 3%, 5%, 10% and 20% PLA will be examined respectively.

SEM images of PBAT's participation rates in 0%, 3%, 5%, 10% and 20% PLA on nonwoven fabric are given in Figure 5.7.

Looking at the SEM results; For PBAT1, it is observed that as the ratio increases, the fibers do not melt and the integrity of the nonwovens is preserved.

It is observed that as the ratio of PBAT2 increases, the fibers melt and the integrity of the nonwoven fabrics is disrupted.

For PBAT3, after 10%, it is seen that the fibers melt and the integrity of the nonwoven fabric is disrupted.

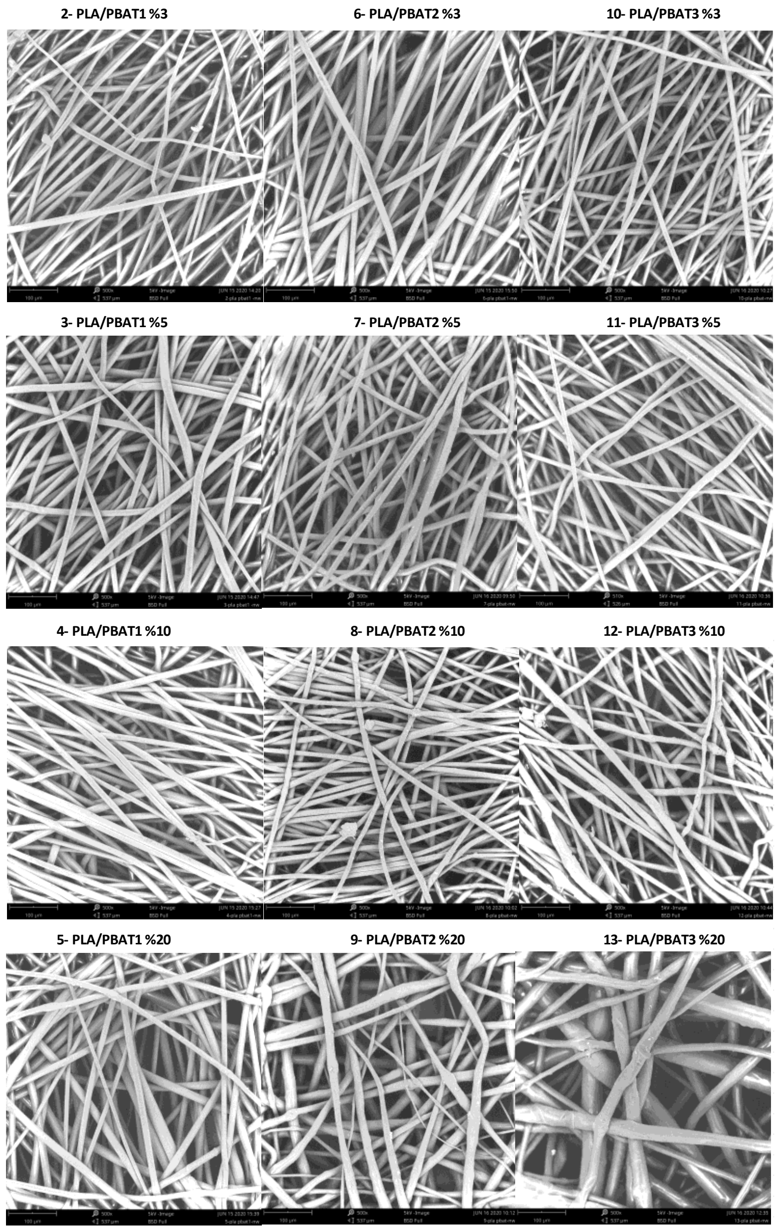


Figure 5. 7 Surface image change in nonwoven fabric by adding different PBAT to PLA at the same rates

5.4. Strength Test Results

Tensile strength test and tensile strength at break, obtained as a result of the tensile strength test, were examined.

Accordingly, in Figure 5.8, the tensile strength is examined according to the increasing PBAT ratio and type.

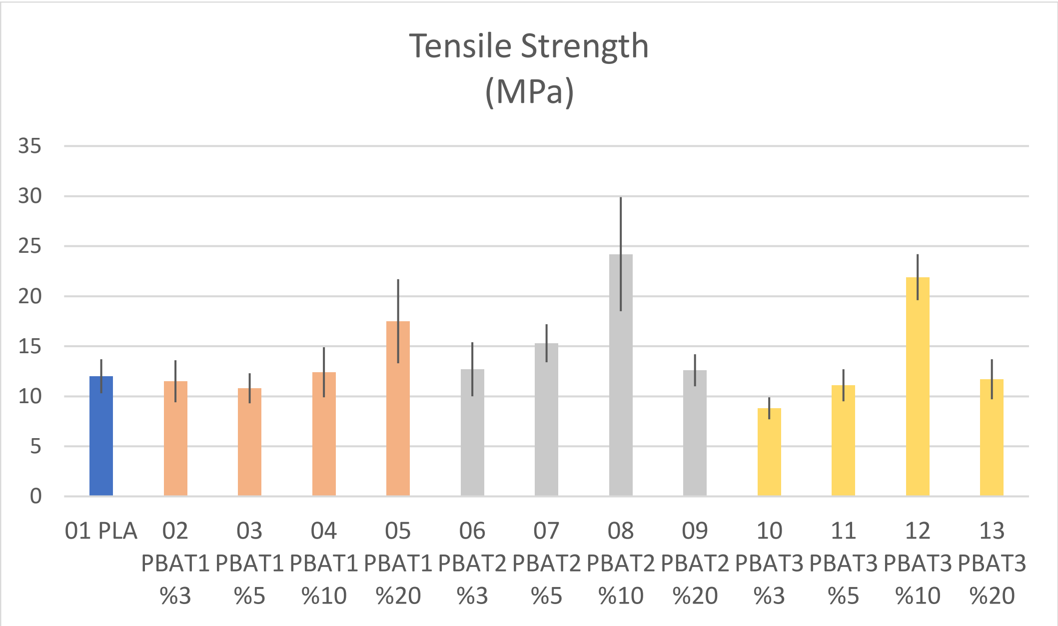


Figure 5. 8 Tensile strength graph of nonwoven productions

The appropriate PBAT added should not adversely affect PLA. The high tensile strength indicates that the material melts too much during calendaring. This situation makes the material harden. Suitable material, nonwoven fabric webs need to be formed properly. As PBAT1 is added in the graphic, not much change was observed in the tensile strength of the material. It is observed that the fibers melt and harden slightly as a result only 20% PBAT1 contribution. This shows that the material is generally more resistant to heat and easy to process. Considerable increase was observed when PBAT2 and PBAT3 were added by 10%. It is seen that the materials are not suitable for the use of 10%, and the nonwoven fabric melts and hardens during the process. Besides, for other ratios, it is seen that PBAT2 has a slightly higher tensile strength than PLA, but still its processability is suitable. For the other added ratios of PBAT3, the tensile strength is slightly lower. This shows that nonwoven fabric webs are softer.

In Figure 5.9, strain at break is analyzed according to increasing PBAT rate and type.

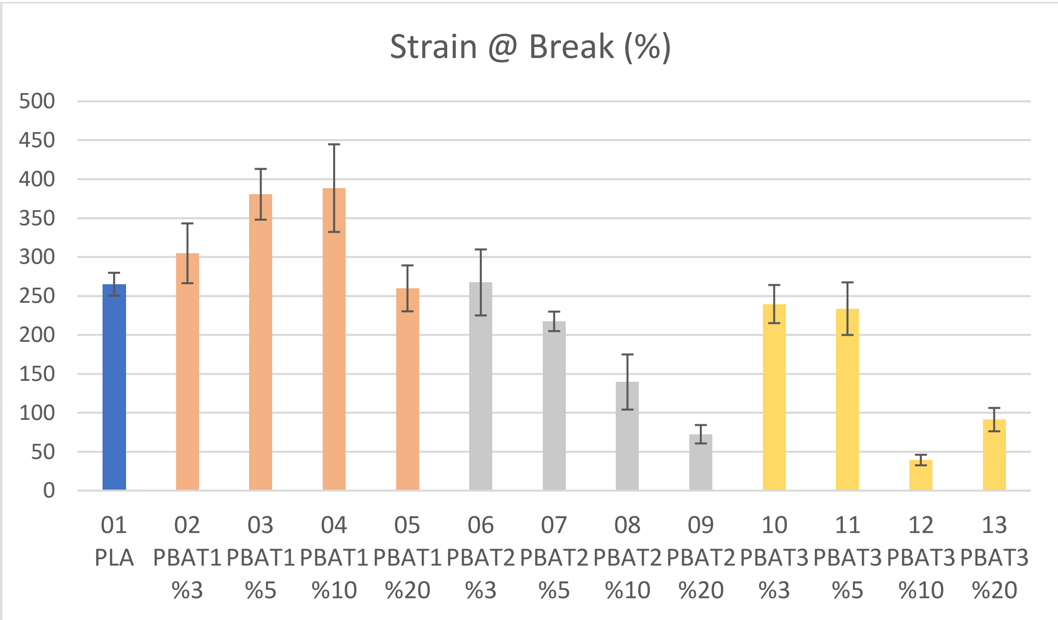


Figure 5. 9 Strain at break graph of nonwoven productions

The webs of suitable nonwoven fabrics are smooth and whole. Low strain at break indicates that the integrity of the material is reduced, nonwoven ties are broken and it is not suitable. Likewise, its increase indicates that the integrity of the nonwoven fabric webs is good. According to the graphic, it is observed that the material integrity of PBAT1 increases and PBAT2 decreases as the addition rate increases. For PBAT3, it is seen that the material integrity does not change with the addition rate up to 10%, but then the material integrity decreases.

5.5. DSC Analysis Results

Samples for DSC were prepared from granules produced and raw materials. DSC analysis of the raw materials with the ratio of 5% of the PLA / PBAT mixtures has been made and there are 8 in total. The purpose of DSC analysis was to determine the melting temperature, glass transition and crystallization points of raw materials and blends. Melting temperature was important for setting up the machines in downstream production processes and experimental steps. While the thermal behavior of pure PLA and PBAT grades is shown in Figure 5.10-5.14, PLA compounds containing 5% PBAT by weight and extruded pure PLA are shown in Figure 5.14-5.16, respectively.

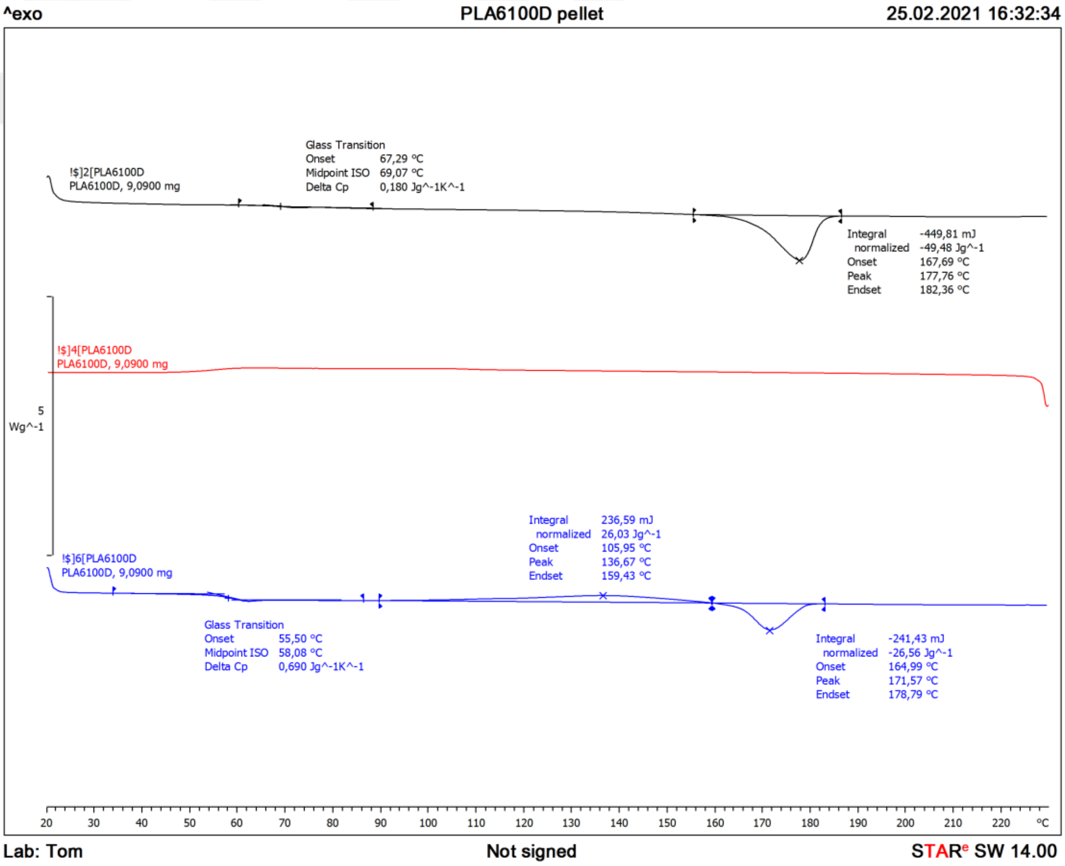


Figure 5. 10 DSC analysis of pure PLA

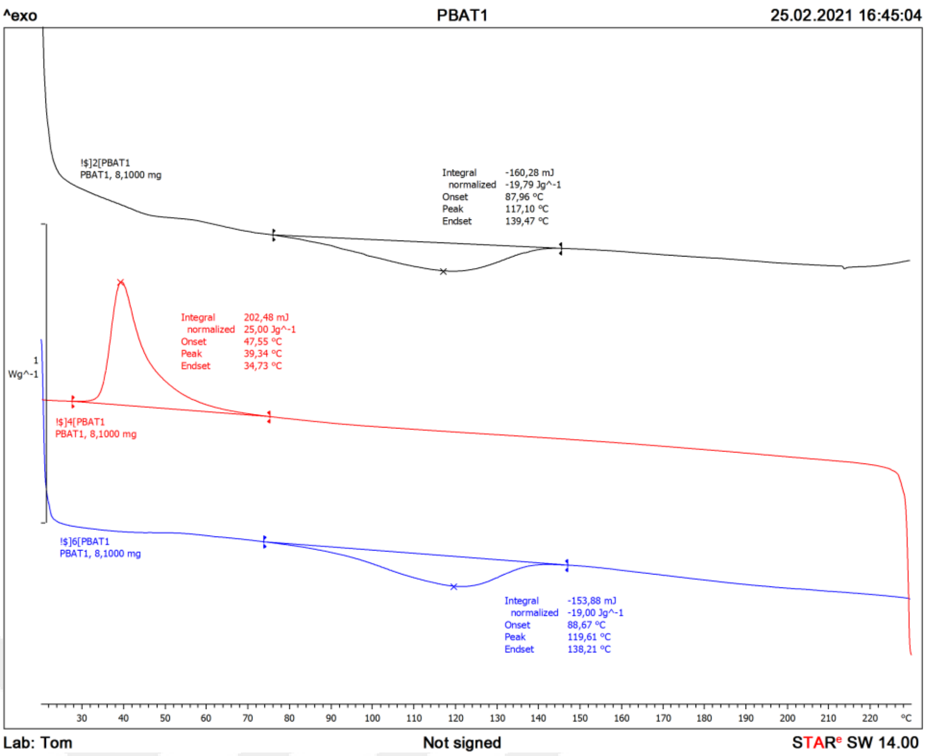


Figure 5. 11 DSC analysis of PBAT1

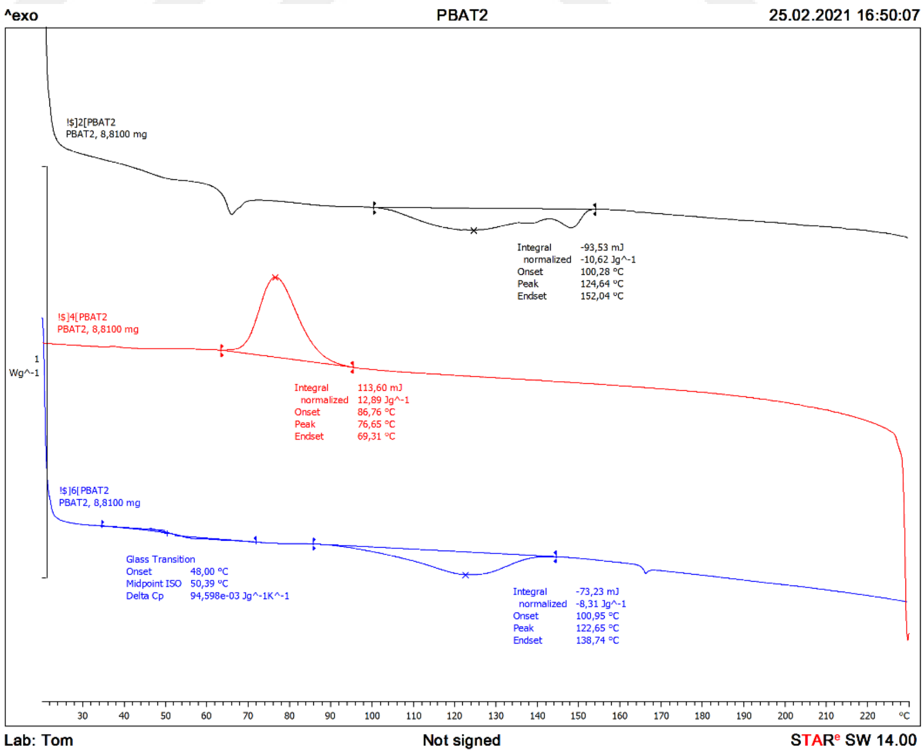


Figure 5. 12 DSC analysis of PBAT2

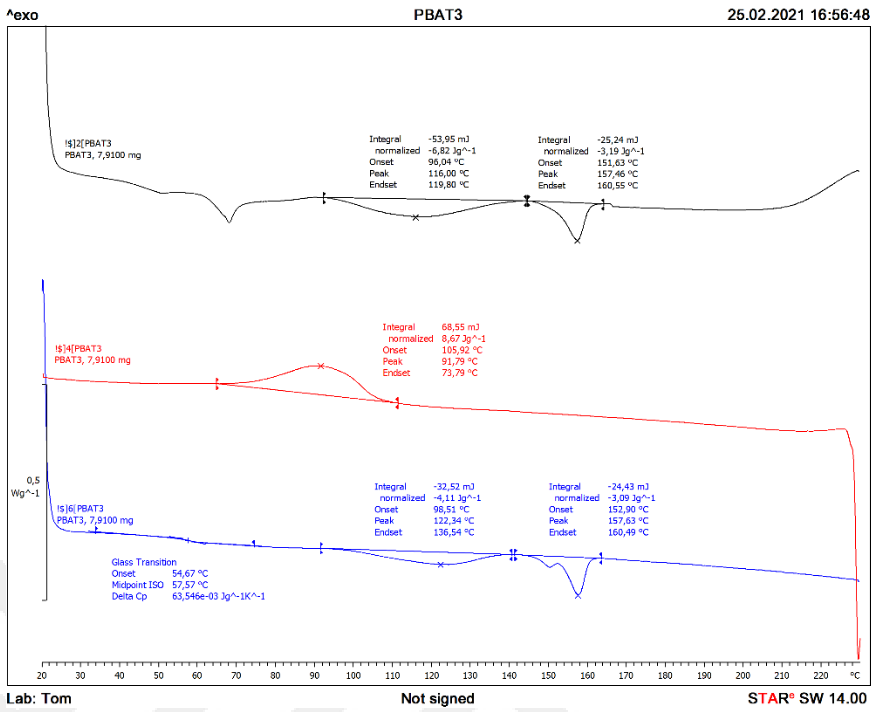


Figure 5. 13 DSC analysis of PBAT3

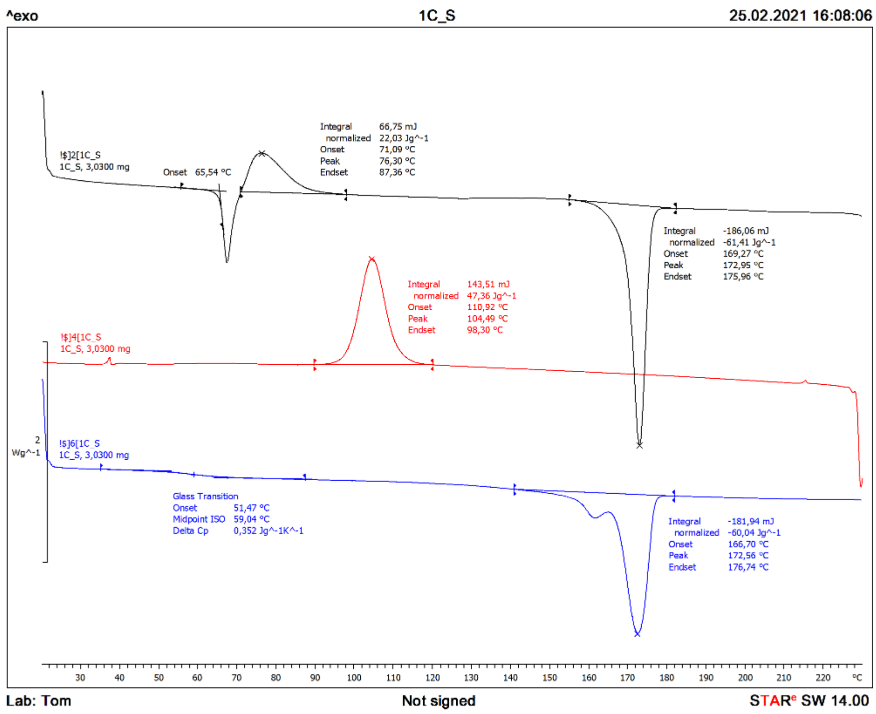


Figure 5. 14 DSC analysis of extruded PLA

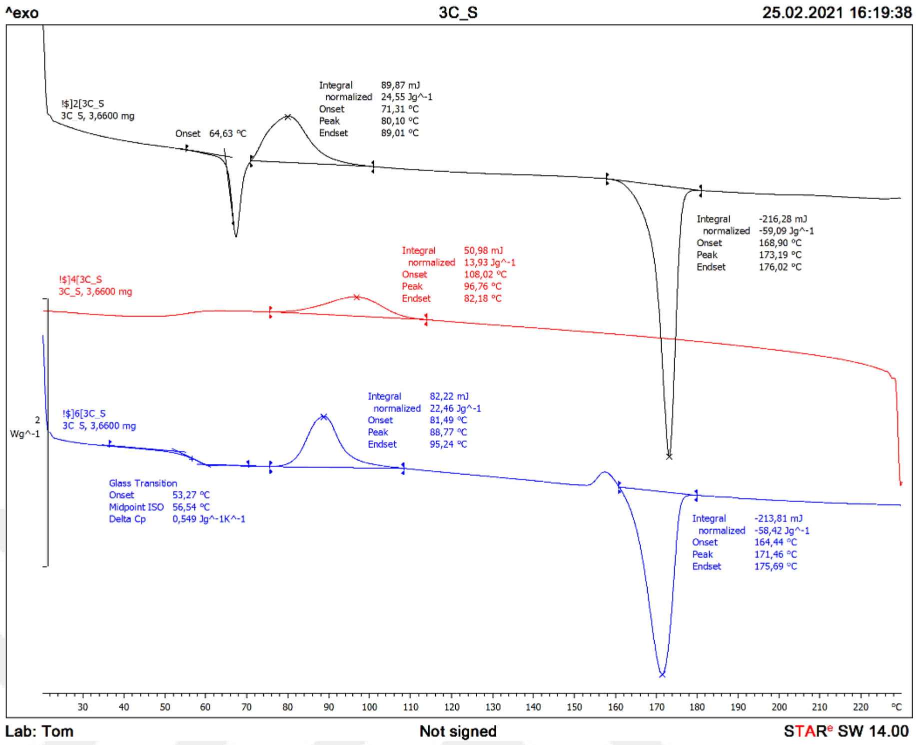


Figure 5. 15 DSC analysis of PLA/5%PBAT1

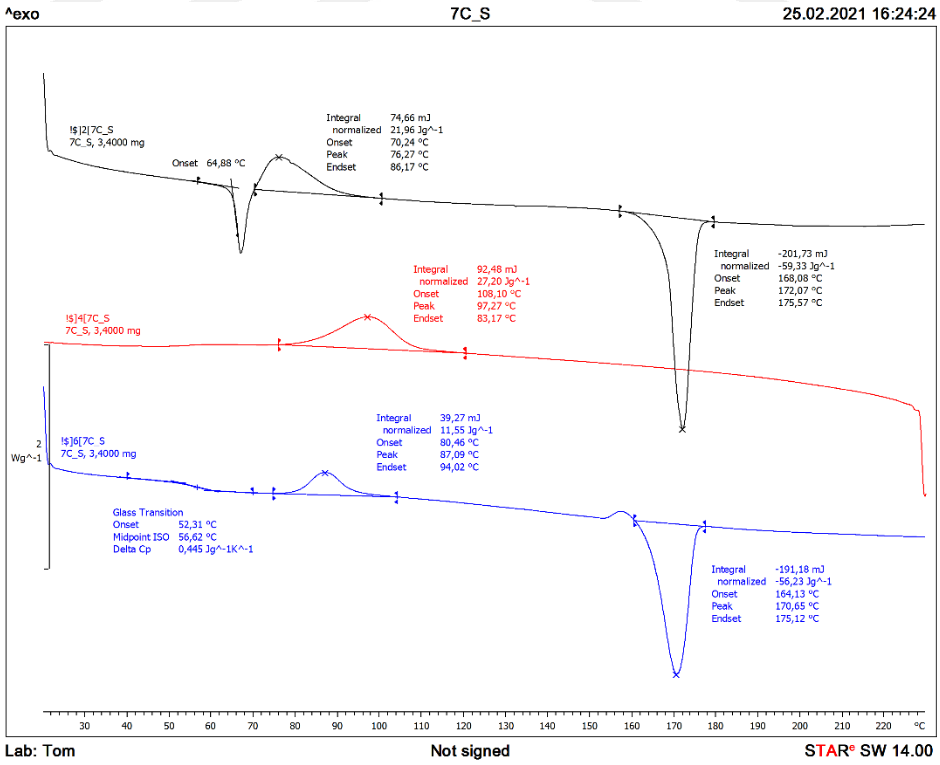


Figure 5. 16 DSC analysis of PLA/5%PBAT2

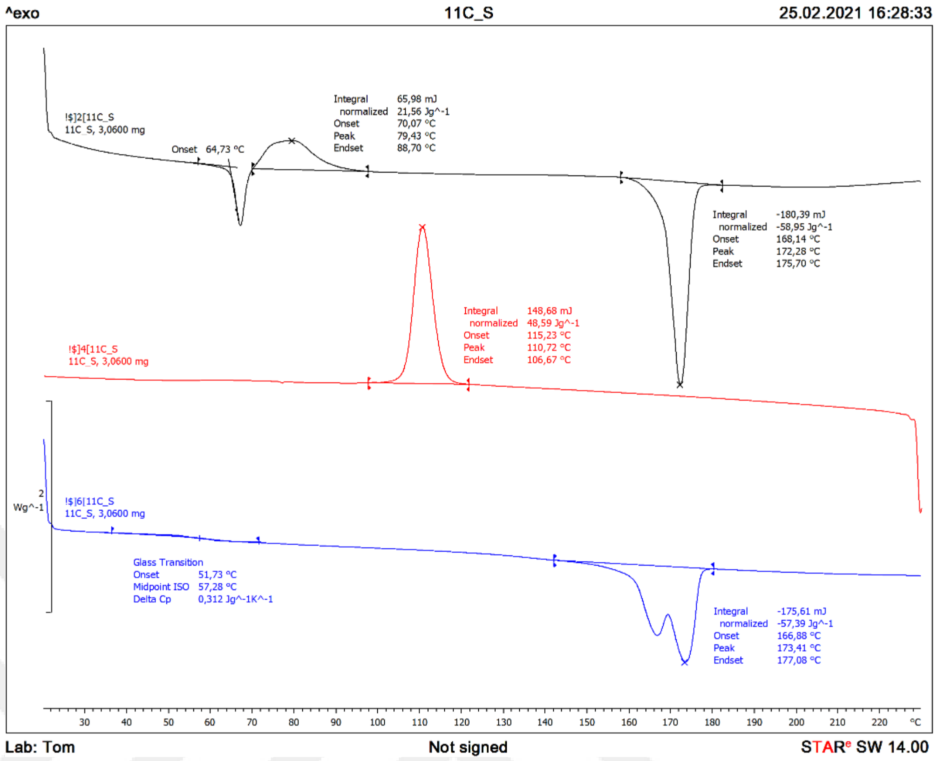


Figure 5. 17 DSC analysis of PLA/5%PBAT3

Table 5.3 shows the characteristic temperatures of the materials. The melting point for pure PLA is 172 ° C and for compound PLA 173 ° C; It is 120 ° C for PBAT1, 123 ° C for PBAT2 and 158 ° C for PBAT3. Accordingly, predictions can be made for the temperature adjustment required for rheology testing as well as for other processes. For example, a temperature of 180 ° C was set to characterize the rheological properties.

The glass transition temperature (T_g), melting temperature (T_m) and cold-crystallization temperature (T_{cc}) were defined. The percentage of crystanility (X_c) of the materials was estimated with using the equation.

$$X_c = \frac{\Delta H_m}{\Delta H_f \times W_{PLA}} \times 100\%$$

Where X_c is percentage of crystallinity; ΔH_m is the heat of fusion of the sample; ΔH_f relates to the heat of fusion of 100% crystalline material, and also W_{PLA} is the net weight fraction of the PLA. ΔH_f shows that the heat of fusion of 100% crystalline PLA and PBAT and PLA is approximately 93 J/g and PBAT is approximateley 114 J/g.

Table 5. 3 Tg,Tm,Tc,%X values of the materials

Material	Glass transition temperature [°C]	Cold crystallization temperature [°C]	Melting temperature [°C]	ΔH_m [J/g]	Crystallinity [%]
Pure PLA	58	172	172	26.56	28
PBAT1	50	120	120	19	16.6
PBAT2	50	123	123	8.31	7.3
PBAT3	58	158	158	4.11	3.6
Extruded PLA	59	173	173	60.04	64.5
PLA/ 5%PBAT1	57	172	171	58.42	63.5
PLA/ 5%PBAT2	57	171	171	56.23	61.1
PLA/ 5%PBAT3	57	173	173	57.39	62.3

6.CONCLUSIONS

Knowing the elongational viscosity, it is thought that the spunbond spinning process will provide prediction and the nonwoven formation networks of the good process will be healthy; By looking at elongational viscosity, it is understood that the spunbond process can be predicted. The results are consistent with each other; however, it has been found that it does not give an exact result about the nonwoven formation network.

The estimation of spunbond process by looking at elongational viscosity has been proven; It has been observed that high strain hardening provides good spinning. Accordingly, PBAT2 gave the best strain hardening result in elongational viscosity. Best results have been up to the addition of 10% PBAT. Higher rates are not favorable. This result has also been confirmed during the production phase; Also, unlike the result of elongation viscosity, PBAT1 was found to be suitable up to 10% like PBAT2 in the spunbond process. Considering the tensile strength test, unlike elongation viscosity results, PBAT1 gave the best result. All materials had trouble forming the nonwoven web properly after the addition of 10% PBAT. It is thought that the reason why PBAT1 gives the best result is related with the high resistance of the material.

The use of nonwoven nonwoven fabrics is increasing day by day, and it has been thought that antibacterial properties can be gained in order to be competitive in hygienic wipes and medical fields.In the production of PBAT / ZnO antibacterial material, which has been made to shed light on future studies, it has been determined that the most suitable ZnO usage rate is 10% and the best result is given on E.coli.

7.REFERENCES

Ashwini K., Bhalla, A., Bhalla, R., 2003, Advances in the Production of Poly(Lactic Acid) Fibers, A Review, Journal of Macromolecular Science, 479-503p.

Avérous, L., 2008, Polylactic Acid: Synthesis, Properties and Applications. In Monomers, Polymers and Composites from Renewable Resources, Amsterdam, 433–450 p.

Avérous, L., Pollet, E., 2012, Biodegradable Polymers in Environmental Silicate Nano-Biocomposites, Green Energy and Technology, London.

Avinc, O., 2009, Overview of Poly(lactic acid) (PLA) Fibre: Part I: Production, Properties, Performance, Environmental Impact, and End-use Applications of Poly(lactic acid) Fibres, Fibre Chemistry, 41(6):391-401p.

Bao, Z., 2009, Experimental Study and Numerical Analysis for Prediction Of The Fibre Diameter Of Polylactic Acid (PLA) Spunbonded Nonwovens, Fibres and Textiles In Eastern Europe, 17(5): 82-86 p.

Bartels, H. A., 1947, The Effect of Eugenol And Oil of Cloves On The Growth of Micro Overddot Organisms, American Journal of Orthodontics and Oral Surgery, 33:458-465p.

Batra, S., Pourdeyhimi, B., Introduction to Nonwoven Technology; Destech Publications,337p.

Bazant, P., 2014, Preparation and Properties of Composite Materials For Potential Medical And Sanitary Application, Doctoral Thesis, Tomas Bata University, 156p (unpublished).

Bazant, P., Kuritka, I., Hudecek, O., Machovsky, M., Mrlik, M., Sedlacek, T., 2013, Microwave-Assisted Synthesis of Ag/ZnO Hybrid Filler, Preparation, and Characterization of Antibacterial Poly(vinyl chloride) Composites Made From the Same, Polymer Composites, 26p.

Beyreuther, R. and Brunig, H., 2007, Dynamics of Fiber Formation and Processing, Modelling and Application in Fibre and Textile Industry, 276 p.

Bhat, G. and Rong, H., 2005, Biodegradable and Sustainable Fibres, Woodhead Publishing Series in Textiles, 310-342p.

Bhat, G.S. and Malkan, S.R., 2002 Extruded Continuous Filament Nonwovens: Advances in Scientific Aspects, Journal of Applied Polymer Science-., 83:572–585p.

Bhat, G.S., Gulgunje, P., Desai, K., 2008, Express Polymer Letters, p. 49-56

Bhattacharyya, S. and Gedanken, A., 2008, The Journal of Physical Chemistry C, 112:659p.

Blackburn, R., Davies, S., Lunt, J., Farrington, D., 2005, Poly(lactic acid) Fibers, Biodegradable And Sustainable Fibres, England, 441p.

Blechschmidt D., 2008, Melliand China in Chinese,12:51-56 p.

Board, NIIR. 2012. Polymers and Plastics Technology Handbook. In.: ISBN 81-78-33076-8. http://www. niir. org/books/book/polymersplasticstechnology-handbook-niir-board/isbn-8178330768/zb,, 54, a, 0, 0, a/index. html (Acc.10.10.2020).

Bogaert, J. C., Coszach, P., 2000, NonwovensWorld, 9:83-91 p.

Bordes, P., Pollet, E., Averous, L., 2009, Nano-Biocomposites: Biodegradable Polyester/Nanoclay Systems, Progress in Polymer Science, 34(2):125-155p.

Bruckmoser, K., Resch, K., 2015, Journal of Applied Polymer Science,132p.

C. Miehe, S. Goektepe and J. Mendez Diez, 2009, Int. J. Of Solids and Structures, Vol. 46, 1, 181-202p.

Castro-Aguirre, E., Iñiguez-Franco, F., Samsudin, H., Fang, X., Auras, R., 2016, Poly(lactic acid) Mass Production, Processing, Industrial Applications, and End of Life, Advanced Drug Delivery Reviews, 107:333–366 p.

Catauro, M.G. Raucci, F. De Gaetano, and A. Marotta,J., 2004, Journal of Materials Science: Materials in Medicine, 15:831p.

Chandra, R., Rustgi, R., 1998, Biodegradable Polymers, Progress in Polymer Science, 23 (7):1273-1335p.

Chun, S.W., Kim, S.H., Kim, Y.H., Kang, H.J., 2000, The Effect of Thermal History Induced by Melt Spinning On The Mechanical Properties of Polylactic Acid Fibers, Polymer Korea, 24 (5):656–663 p.

Cicero, J.A., Dorgan, J.R., 2002, Physical Properties and Fiber Morphology of Poly(Lactic Acid) Obtained From continuous Two-Stepmelt Spinning. Journal of Polymers and Environment,10 p.

Cicero, J.A., Dorgan, J.R., Garrett, J., Runt, J., Lin, J.S., 2002, Effects of Molecular Architecture on Two-Step, Melt-Spun Poly(Lactic Acid) Fibers, Journal of Applied Polymer Science,;86(2839): 46p.

Cicero, J.A., Dorgan, J.R., Janzen, J., Garrett, J., Runt, J., Lin, J.S., 2002, Supramolecular Morphology of Two-Step, Melt-Spun Poly(Lactic Acid) Fibers. Journal of Applied Polymer Science, 86(2828), 38 p.

Diaz, A., Katsarava, R., Puiggali, J., 2014, Synthesis, Properties and Applications of Biodegradable Polymers Derived From Diols And Dicarboxylic Acids: From Polyesters To Poly(ester amide)S, *International Journal of Molecular Sciences*,15 (5):7064-7123 p.

Doi, Y., 1990, Microbial Polyester, VCH, New York.

Domenek, S., Ducruet, V., 2016, Characteristics and Applications of PLA in Biodegradable and Biobased Polymers for Environmental and Biomedical Applications, John Wiley & Sons,171–224 p.

Doppalapudi, S., Jain, A., Khan, W., Domb, A. J., 2014, Biodegradable Polymers An Overview, Polymers for Advanced Technologies, 25, 427–435 p.

Drumright, R.E., Gruber, P.R. and Henton, D.E., 2000, Advanced Materials, 12 (23), 1841p.

E. Gross, 2002,Text. World, 150(2), 76p.

EDANA, 2018, Nonwovens Markets, Facts And Figures, https://www.edana.org/nw-related-industry/nonwovens-markets, 2020 (Acc.10.10.2020).

Eling, B., Gogolewski, S., Pennings, AJ., 1982, Biodegradable Materials of Poly(L-Lactic Acid), 1. Melt-Spun and Solution-Spun Fibres, Polymer, 23:1587–1593 p.

EN 13432:2000. Requirements For Packaging Recoverable Through Composting And Biodegradation - Test Scheme and Evaluation Criteria For The Final Acceptance of Packaging.

EN 14995:2006, Plastics - Evaluation Of Compostability - Test Scheme and Specifications.

European Bioplastics, Nova-Institute, 2017 Available online: http://www.european-bioplastics.org/bioplastics/materials/ (Accessed on May 14, 2020).

European Bioplastics, Nova-Institute, 2019 Available online: https://www.european-bioplastics.org/bioplastics/materials/biodegradable/ (accessed on May 14, 2020).

Fambri L, Pegoretti A, Fenner R, Incardona SD, Migliaresi C., 1997, Biodegradable Fibres of Poly(L-Lactic Acid) Produced by Melt Spinning, Polymer, 38:79–85p.

Feng, S., Jiao, X., 2011, The Application of PLA Resin on Nonwovens Production, Advanced Materials Research, 332-334 p.

Ferreira, F.V., Cividanes, L.S., Gouveial, R.F., Lona, M.F., 2019, An Overview on Properties And Applications of Poly(Butylene Adipate-Co-Terephthalate) Based composites, Polymer Engineering and Science, 59p.

Gabriel, G.J., Som, A., Madkour, A.E., Eren, T. and Tew, G.N., 2007, Material Science and Engineering, 28 p.

Ghanbarzadeh, B., Almasi, H., 2013, Biodegradable Polymers in Biodegradation, Life of Science; InTech: Rijeka, ISBN 978-953-51-1154-2.

Ghosh, S., Goudar, V.S., Padmalekha, K.G., Bhat, S.V., Indi, S.S., Vasan, H.N., 2012, Zno/Ag Nanohybrid: Synthesis, Characterization, Synergistic Antibacterial Activity and Its Mechanism, Rsc Advances., 2(3):930-940 p.

Gruber, P. R., Kolstad, J. J., Ryan, C. M., Conn, R. S. E., Hall, E. S., 2000, United State Patent 6111060.

Gupta, B., Revagade, N., Hilborn, J., 2007, Poly(lactic acid) Fiber: An Overview, Progress in Polymer Science, 32:455–482 p.

Hansen, S.M., 1993, Nonwoven Engineering Principles, Nonwovens – Theory, Process, Performance and Testing', edited by Turbak, A.F., TAPPI Press, Atlanta, GA.

Holčapková,P., 2018, Utilisation Of Whey Fermentation Products For Antimicrobial Modification Of Biodegradable Polymers, Tomas Bata University in Zlin, Doctoral Thesis, Tomas Bata University, 121p (unpublished).

Hyon, S.H., Jamshidi, K., Ikada, Y., 1984, Melt Spinning of Poly-L-Lactide And Hydrolysis of The Fiber In Vitro, In Polymers as Biomaterial, Plenum Press, New York, 1984; 51–65p.

International Standard, 2007, ISO 22196, Plastics-Measurement of Antibacterial Activity on Plastic Surfaces.

J. Simmons, 2000, Plastic Additive Compound, 2(20).

Jafari, A., Ghane, M., Arastoo, S., 2011, Synergistic Antibacterial Effects of Nano Zinc Oxide Combined With Silver Nanocrystales, African Journal of Microbiology Research,5(30):5465-5473p.

Janotti, A., Van de Walle, C.G., 2009, Fundamentals Of Zinc Oxide As A Semiconductor, Reports on Progress in Physics, 72(12):29 p.

Jian, J., Xiangbin, Z., Xianbo, H., 2020, An Overview On Synthesis, Properties And Applications Of Poly(Butylene-Adipate-Co-Terephthalate)e PBAT, Advanced Industrial and Engineering Polymer Research, 19-26 p.

K. Chaloupka, Y. Malam, and A.M. Seifalian, 2010, Nanosilver as a New Generation of Nanoproduct in Biomedical Applications, Trends Biotechnol, 28(11):580-8 p.

Karamanlioglu, M., Preziosi, R., Robson, G. D., 2017, Abiotic and Biotic Environmental Degradation of The Bioplastic Polymer Poly(Lactic Acid): A Review, Polymer Degradation and Stability, 137: 122–130 p.

Kenawy, E. R., Worley, S.D., Broughton, R., 2007, The Chemistry and Applications of Antimicrobial Polymers: A State-of-the-art Review, Biomacromolecules.,8(5):1359-1384p.

Kiron, M.I., Textile Learner, Melt Spinning Process | Feature of Melt Spinning Advantages and Disadvantage of Melt Spinning, https://textilelearner.blogspot.com/2013/10/melt-spinning-process-feature-of-melt.html, (Access date: 03.06.2020).

Kolstad, J. J., Vink, E. T. H., Wilde, B., Debeer, L., 2012, Assessment of **Anaerobic** Degradation of Ingeotm Polylactides Under Accelerated Landfill Conditions, Polymer Degradation and Stability, 97:1131–1141 p.

Li, Q., Mahendra, S., Lyon, D. Y., Brunet, L., Liga, M. V., Li, D., Alvarez, P.J.J., 2008, Antimicrobial Nanomaterials for Water Disinfection and Microbial Control: Potential Applications and Implications, Water Research, 42(18):4591-4602 p.

Lima, L.T., Aurasb, R., Rubinob, M., 2008, Processing Technologies For Poly(Lactic Acid), Progress in Polymer Science, 33: 820–852 p.

Lin, L., Deng,C.,Lin, G., Wang, Y., 2014, Mechanical Properties, Heat Resistance and Flame Retardancy of Glass Fiber-Reinforced PLA-PC Alloys Based on Aluminum Hypophosphite, Polymer-Plastics Technology and Engineering, 53(6): 613-625p.

Lu, W.W., Liu, G.S., Gao, S.Y., Xing, S.T., Wang, J.J., 2008, Tyrosine-Assisted Preparation of Ag/Zno Nanocomposites With Enhanced Photocatalytic Performance and Synergistic Antibacterial Activities, Nanotechnology, 19(44).

Luckachan, G. E., Pillai, C.K.S., 2011, Biodegradable Polymers:A Review on Recent Trends and Emerging Perspectives, Journal of Polymers and the Environment, 19:637–676 p.

Lunenschloss, J. and Albrecht, W., 1985, Nonwoven Bonded Fabrics, Ellis Horwood Limited, 317p.

Lunt, J. and Bone, J., 2001, AATCC Rev.,1(9):20p.

Lunt, J., 2000, Int. Fibre J., 15(3):48-52 p.

Lunt, J., 2000, Technical Textiles Int., 9(10):11-13p.

Lunt, J., Shafer, A., 2000, Journal of Industrial Textiles, 29:191-205 p.

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

Mamiko, M., Atsushi, M., Koichi, N., 2003, Biodegradable Filament Nonwoven Fabric And Method Of Producing The Same, Tomoegawa Paper Co Ltd;Unitika Ltd.

Marambio-Jones, C., Hoek, E.MV., 2010, A Review of the Antibacterial Effects of Silver Nanomaterials and Potential Implications for Human Health and the Environment, (Report). Journal of Nanoparticle Research, 12(5):1531–1551 p.

Matsui, M., Kondo, Y., 1996, Chemical Fibres International, 46:318p.

Mceneany, R.J., Topolkaraev, V., Aimin, H., 2012, Polylactic Acid Fibers, Kimberly Clark Co.

Meaurio, E., Hernandez M., N., Zuza, E., Sarasua, J.R., 2014, Miscible Blends Based on Biodegradable Polymers in Characterization of Polymer Blends: Miscibility, Morphology and Interfaces, 7–92p.

Michael, R.C., Uzela, N.B., Louis, G.S., Lee, B.A., 1998, Degradable Polymer, Fibers, Biopolymers: Processing And Products.

Mochizuki, M., Hirami, M., 1997, Structural Effects on The Biodegradation of Aliphatic Polyesters, Polymer Advanced Technology, 8 (4):203-209p.

Mueller, R.J., 2006, Biological Degradation of Synthetic Polyesters Enzymes As Potential Catalysts for Polyester Recycling, Process Biochemistry, 41(10):2124-2128p.

Muller, R.J., Kleeberg, I., Deckwer, W.D., 2001, Biodegradation Of Polyesters Containing Aromatic Constituents, Journals of Biotechnology, 86 (2):87-95p.

Nagarajan, V., Misra, M., Mohanty, A.K., 2013, New Engineered Biocomposites from Poly(3-Hydroxybutyrate-Co-3-Hydroxyvalerate) (PHBV)/Poly(Butylene Adipate-Co-Terephthalate) (PBAT) Blends and Switchgrass: Fabrication and Performance Evaluation, Industrial Crops and Products, 461-468p.

Neumark, Y.G., Kuskovsky, I., 2007, Springer Handbook of Electronic and Photonic Materials: Doping Aspects of Zn-Based Wide-Band-Gap Semiconductors, Springer,843–854p.

Niaounakis, M., 2014, Manufacture of Fibers and Fabrics, Biopolymers: Processing and Products, 387-410p.

Nonwovens Handbook, 2004, INDA Publications, Cary, NC,.

Ohira, T., Y.O., Iida, Y., Nakagawa Z., 2008, Antibacterial Activity of ZnO Powder with Crystallographic Orientation, Journal Of Materials Science: Materials In Medicine, 19:1407-1412p.

Okada, M., 2002, Chemical Syntheses of Biodegradable Polymers, Progress in Polymer Science, 27(1):87-133p.

Olatunji, O., Ed., 2016, Natural Polymers: Industry Techniques and Applications; Springer International Publishing, 367p.

Padmavathy, N., Vijayaraghavan, R., 2008, Enhanced Bioactivity of ZnO Nanoparticles:An Antimicrobial Study, Science and Technology of Advanced Materials, 9(3):7p.

Palade, L.I., Lehermeier, H.J. and Dorgan, J.R., 2001, Macromolecules,34 (5):1384p.

Pavelková, A., 2015, Biodegradable Polyesters And Polyanhydrides for Advanced Applications, Doctoral thesis, Tomas Bata University.

Persson, M., Cho, S.W., Skrifvars, M. J., 2013, Material Science, 48:3055p.

Polymer Properties Database, Strain Hardening of Amorphous and Semi-crystalline Polymers, https://polymerdatabase.com/polymer%20physics/Strain%20Hardening.html, (Access date: 20.01.2021).

Pourmohammadi, A., 2013, Woodhead Publishing Series in Textiles, Joining Textiles, 565-581p.

Rasal, R., Janorkar, A., Hirt, D., 2010, Poly(lactic acid) Modifications, Progress in Polymer Science, 35:338–356p.

Rawal, A., Mukhopadhyay S., 2004, Melt Spinning of Synthetic Polymeric Filaments, Advances in Filament Yarn Spinning of Textiles and Polymers, 75-99p.

Sawai, J., Igarashi, H., Hashimoto, A., Kokugan, T., Shimizu, M., 1996, Effect of Particle Size and Heating Temperature of Ceramic Powders on

Antibacterial Activity of Their Slurries, Journal of Chemical Engineering of Japan, 29(2), 251-256p.

Sawai, J., Kawada, E., Kanou, F., Igarashi, H., Hashimoto, A., Kokugan, T., Shimizu, M., 1996, Detection of Active Oxygen Generated from Ceramic Powders Having Antibacterial Activity, Journal of Chemical Engineering of Japan, 29(4):627-633p.

Sawai, J., Kojima, H., Igarashi, H., Hashimoto, A., Shoji, S. and Shimizu, M., 1995, Evaluation of Rowth Inhibitory Effect of Ceramics Powder Slurry on Bacteria by Conductance Method, Journal Of Chemical Engineering Of Japan, 28: 288-293p.

Sawai, J., Kojima, H., Igarashi, H., Hashimoto, A., Shoji, S., Takehara, A., Sawaki, T., Kokugan, T., Shimizu, M., 1997, Escherichia Coli Damage by Ceramic Powder Slurries, Journal of Chemical Engineering of Japan,30(6):1034-1039p.

Sawai, J., Saito, I., Kanou, F., Igarashi, H., Hashimoto, A., Kokugan, T., Shimizu, M., 1995, Mutagenicity Test of Ceramic Powder Which Have Growth Inhibitory Effect On Bacteria., Journal of Chemical Engineering of Japan, 28:352-354p.

Sawai, J., Shoji, S., Igarashi, H., Hashimoto, A., Kokugan, T., Shimizu, M., Kojima, H., 1998, Hydrogen Peroxide as an Antibacterial Factor in Zinc

Sawai, J., Yoshikawa, T., 2004, Quantitative Evaluation of Antifungal Activity of Metallic Oxide Powders (MgO, CaO and ZnO) by An Indirect Conductimetric Assay, Journal Of Applied Microbiology, 96(4):803-809p.

Shim, E., Pourdeyhimi, S., Shiffler, D., 2016, Process Structure Property Relationship of Melt Spun Poly(Lactic Acid) Fibers Produced In The Spunbond Process, Journal of Applied Polymer Science, 133p.

Shrivastava, S., Bera, T., Roy, A., Singh, G., Ramachandrarao, P., Dash, D., 2007, Characterization of Enhanced Antibacterial Effects of Novel Silver Nanoparticles, Nanotechnology,18(22).

Sousa, A.F., Vilela, C., Fonseca, A.C., Matos, M., Freire, C.S.R., Gruter, G.J.M., CoelhoA, J.F.J., Silvestre, J.D., 2015, Biobased Polyesters And Other Polymers from 2,5 Furandicarboxylic Acid: A Tribute To Furan Excellency, Polymer Chemistry, 6 (33):5961p.

Stobie, N., Duffy, B., Mccormack, D. E., Colreavy, J., Hidalgo, M., Mchale, P., Hinder, S. J., 2008, Prevention of Staphylococcus Epidermidis Biofilm Formation Using A Low-Temperature Processed Silver-Doped Phenyltriethoxysilane Sol-Gel Coating, Biomaterials, 29(8):963-969p.

Stoimenov, P. K., Klinger, R. L., Marchin, G. L., Klabunde, K. J., 2002, Metal Oxide Nanoparticles as Bactericidal Agents, Langmuir, 18(17):6679-6686p.

Tom, H., 1989, What are Nonwovens – Again?, Nonwoven Industry.

Turbak, A.F., 1998, Introduction to Nonwovens, TAPPI Press, Atlanta, GA.

Ulery, B. D., Nair, L. S., Laurencin, C. T., 2011, Biomedical Applications of Biodegradable Polymers, Journal of Polymer Science Part B: Polymer Physics,49:832–864 p.

Vilém, R., 2019, Nonwoven Textiles Based on Polylactide, Tomas Bata University in Zlin, Bachelor’s Thesis, Tomas Bata University, 63p (unpublished).

Wang, Z.L., 2004, Zinc Oxide Nanostructures: Growth, Properties and Applications, Journal of Physics: Condens. Matter 16(25):829–R858p.

Watzl, A., 2004, Growth and Prospects for Hydroentangled Nonwovens, Nonwovens World, 13(5):55–58p.

Wells, A.F., 1987, Structural Inorganic Chemistry, 6th Edition Oxford University Press, NewYork, 414p.

Wilson, A., 2010, Woodhead Publishing Series in Textiles, Applications of Nonwovens in Technical Textiles, 3-17p.

Witt, U.,Muller, R.J., Deckwer, W.D., 1996, Evaluation of The Biodegradability of Copolyesters Containing Aromatic Compounds by Investigations of Model Oligomers, Journal of Environmental Polymer Degradation, 4 (1):9p.

Yamamoto, O., 2001, Influence of Particle Size on The Antibacterial Activity of Zinc Oxide, International Journal of Inorganic Materials,3(7):643-646p.

Yamamoto, O., Hotta, M., Sawai, J., Sasamoto, T., Kojima, H. J., 1998, Ceram Soc Jpn, 106:1007p.

Yamamoto, O., Hotta, M., Sawai, J., Sasamoto, T., Kojima, H., 1998, Influence of Powder Characteristic of ZnO on Antibacterial Activity Effect of Specific Surface Area, Journal of The Ceramic Society Of Japan, 106(10), 1007-1011p.

Yamamoto, O., Nakakoshi, K., Sasamoto, T., Nakagawa, H., Miura,K. , 2001, Adsorption and Growth Inhibition of Bacteria on Carbon Materials Containing Zinc Oxide, Carbon, 39(11):1643-1651p.

Yamamoto, O., Sawai, J., Hotta, M., Kojima, H., Sasamoto, T., 1998, Growth Inhibition of Bacteria by MgO-ZnO Solid Solution Powders Influence of Doping Amount of ZnO, Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi/Journal Of The Ceramic Society Of Japan,106(12):1252-1254p.

Yang, L., Mao, J., Zhang, X., Xue, T., Hou, T., Wang, L., Tu, M., 2006, Preparation and Characteristics of Ag/Nano-ZnO Composite Antimicrobial Agent, Nanoscience, 11:44–48p.

Yiamsawas, D., Boonpavanitchakul, K., Kangwansupamonkon, W., 2008, Synthesis and Characterization of ZnO Nanostructures with Antimicrobial Properties, In 2008 International Conference On Nanoscience And Nanotechnology. Ieee: New York,133-136p.

Yoruç, A., 2017, Yeşil Polimerler ve Uygulamaları, Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi, 318-337p.

Zeng, F., Hou, Ch., Wu, S., Liu, X., Tong, Z., Yu, S., 2007, Silver Nanoparticles Directly Formed on Natural Macroporous Matrix and Their Anti-microbial Activities, Nanotechnology, 18(5).

Zhang, J., 2011, Silver-Coated Zinc Oxide Nanoantibacterial Synthesis and Antibacterial Activity Characterization, International Coriference On Electronics And Optoelectronics (ICEOE).

Zhang, L., D.Y., Povey, M., York, D., 2008, ZnO Nanofluids – A Potential Antibacterial Agent, Progress In Natural Science, 18:939–944p.

Zhang, L., Jiang, Y., Ding, Y., Povey, M., York, D., 2007, Investigation Into The Antibacterial Behaviour of Suspensions of Zno Nanoparticles (ZnO nanofluids). Journal of Nanoparticle Research, 9(3):479-489p.

Zhao, Y., 2006, Nonwovens, IN Chinese, 14:8-11p.