Polyester urethane based biocomposites

Bc. Markéta Navrátilová

Master thesis
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Tomas Bata University in Zlín
Faculty of Technology

ZADÁNÍ DIPLOMOVÉ PRÁCE
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Jméno a příjmení: **Bc. Markéta NAVRÁTILOVÁ**
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Forma studia: **prezenční**

Téma práce: **Biokompozity na bázi polyester-uretanových matric**

Zásady pro vypracování:

1. Vypracujte literární rešerši na téma biokompozity na bázi biorozložitelných polyesterů a jejich kopolymerů. Zaměřte se na způsoby jejich přípravy, zpracování a aplikace.
2. Na základě literární studie připravte polyester-uretanovou polymerní matrici na bázi produktů polykondenzace kyseliny mléčné a charakterizujte ji.
3. Do získané matrice termoplasticky inkorporujte přírodní vlákna a získaný biokompozit charakterizujte.
4. Optimalizujte biokompozitní systém z pohledu materiálových vlastností pomocí zvolených aditiv a chemických úprav plniva. Na základě získaných poznatků navrhněte optimální způsob pro zvýšení mezifázové soudržnosti matrice-plnivo.
5. Získané poznatky přehledně zpracujte a diskutujte s dostupnými literárními zdroji.

Rozsah diplomové práce:

Rozsah příloh:

Forma zpracování diplomové práce: tištěná/elektronická

Seznam odborné literatury:

1) PENCZEK, S., SLOMKOWSKI, S. (Eds), (Bio)degradable Polymers from Renewable
Resources, Macromolecular Symposia 272, Weinheim, Wiley-VCH Verlag GmbH & Co.
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Technology, 2004, ISBN1-85957-384-3
4) Časopisecké a knižní zdroje dostupné prostřednictvím Knihovny UTB ve Zlíně

Vedoucí diplomové práce: **doc. Ing. Vladimír Sedlařík, Ph.D.**
                                  Centrum polymerních materiálů

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Ve Zlíně dne 11. února 2013

doc. Ing. Roman Čermák, Ph.D.   doc. Ing. Roman Čermák, Ph.D.
          děkan   L.S.   *ředitel ústavu*

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ABSTRAKT

Předkládaná diplomová práce je věnována polyesteruratanovým biokompozitům. Zvláště pak se zaměřuje na metody kompatibilizace pro zvýšení mezifázové soudržnosti mezi vlákny a polymerní matricí. Pro potřeby práce bylo připraveno sedm typů materiálu, přičemž jejich vlastnosti byly modifikovány přidáním komerčního aditiva, dvou typů experimentálních aditiv, a kyseliny olejové s přídavkem di-tert-butyl peroxidu Pro přípravu dvou materiálů byla modifikována vlákna pomocí kyseliny a zásady. Připravené biokompozity byly charakterizovány pomocí diferenciální skenovací kalorimetrie, gelové permeační chromatografie, termogravimetrické analýzy a skenovací elektronové mikroskopie. Pro stanovení mechanických vlastností byly provedeny zkoušky v tahu, ohybu a testy rázové houževnatosti. Získané výsledky byly hodnoceny vícekriteriální analýzou aby byla nalezena nejoptimálnější varianta kompatibilizace. Biokompozity modifikované přidáním komerčního a experimentálního aditiva 2 vykazovaly nejlepší výsledky, všemi metodami ale byly vlastnosti kompozitů výrazně vylepšeny.

Klíčová slova: biokompozit, přírodní vlákna, kompatibilizace

ABSTRACT

The presented master thesis is dedicated to polyester urethane based biocomposites with special focus on compatibilization techniques for improving of interfacial adhesion between polyester urethane matrix and flax fibers. To achieve the goals, seven types biocomposites were prepared whereas the properties were modified by adding commercial additive, two types of experimental additives and the oleic acid and di-tert-butyl peroxide or treating fibres with acid and alkaline. Prepared biocomposites were characterized by gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis, scanning electron microscopy. Mechanical properties were investigated by using tensile testing, flexural testing and impact strength Obtained results were evaluated with multicriteria analysis to find the best technique of compatibilization for material properties improvement. Biocomposites with commercial additive and experimental additive 2 was assessed as the best solution; nevertheless all modification significantly increased material performance.

Keywords: biocomposite, natural fibres, compatibilisation

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

CONTENTS

INTRODUCTION

In recent years, polymer composite industry gained great development and played the leading role in almost every field of industry, especially aircraft, automotive, navy or aerospace industries.

As composite we can call every heterogeneous system of two materials with significantly different chemical and physical properties. Material in continuous phase is called matrix – its main role is to give shape to final product; it surrounds the reinforcement, hence it works as the reinforcement's protection and serve for load transfer between single reinforcement components. The basic role of reinforcement is to provide strength, stiffness, and other mechanical or electrical properties to composite. With usage of reinforcement we can increase material characteristics of low performance polymers, for example polypropylene, and use it for engineering application. Another reason for usage of composite can be economical aspect. For applications with low mechanical demands (packaging industry, short term products….) we can significantly decrease the price of final product with cheap fillers. [1]

Polymer composite materials have many advantages, but they have disadvantages as well. Multicomponent system needs complex development; it is more difficult to predict processing parameters and also properties of final product. Some of them require special manufacturing procedures. With the increasing importance of environmental impact assessment, the main drawback of composite materials is their bad recyclability.

From this reason recent researches are focused on composites that are designed with the lowest environmental 'footprint' possible. This can be achieved by using reinforcements from natural resources or by replacement synthetic, petroleum based matrices to biodegradable one, preferably with natural origin.

In this field the most promising group of "green" composites are materials from biodegradable polymers, especially poly (lactic acid) reinforced by natural fibres.

This master thesis deals with biocomposites prepared from poly(lactic acid) filled with flax fibres. The research follows project carried out at Polymer Centre Tomas Bata University investigating poly(lactic acid) production from diary waste by-product, whey. The presented work deals with the problem of compatibility between polymer matrix and fibres, which can be improved by using different additives and fibre treatments. In the experi-

mental part, the effect of compatibilization on thermal and mechanical properties was investigated to find out optimal solution for PLA/flax composite production.

I. THEORY

1 BIOCOMPOSITES

Biocomposites are heterogeneous materials similar to classical polymer composites formed by a matrix and reinforcement. The difference is in the effort to promote natural origin or biodegradable components to the structure to decrease environmental impact of the composite.

This can be done by two major ways:

- Replacement traditional petroleum based, non-biodegradable matrices (polyethylene, polypropylene….) to biodegradable one (PLA, PCL…)
- Replacement non-biodegradable reinforcement (glass fibres, carbon fibres, talc…) to natural fillers (natural fibres, starch…)

1.1 Biodegradable reinforcement

Wood or natural fibres are in the interest of polymer industry for more reasons, especially it is low cost, low weight, non-abrasiveness while processing. Furthermore, they are biodegradable, not oil based and has very low carbon footprint (Figure 1). Introducing natural fibres to composite brings attractive acoustic and vibration insulation properties, and sufficient mechanical properties. [2]
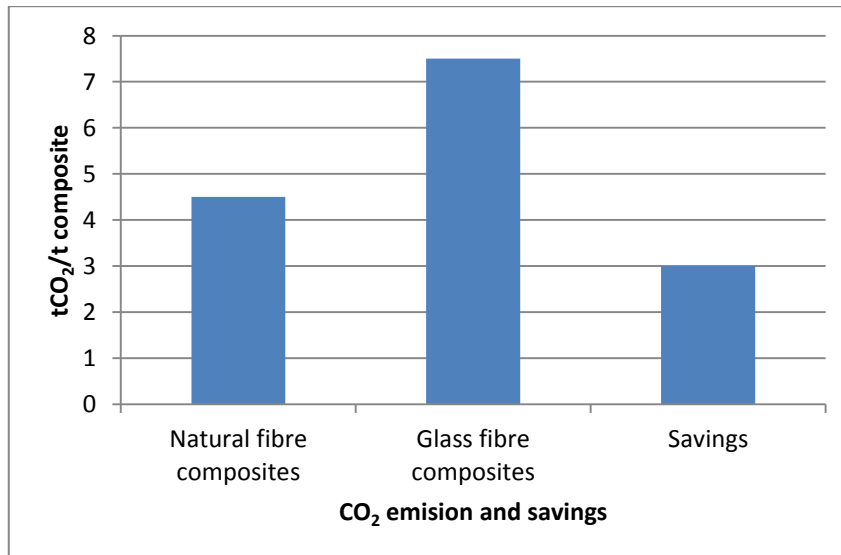

Figure 1 Comparison of composites reinforced with natural fibres and glass fibres (3]

Drawbacks of this reinforcement could be high water absorption, thus low dimensional stability, variation in source quality, and necessity of pretreatment for higher polymer – fibre compatibility. [4]

Wood

Wood is natural material in woody plants. From the chemical point of view, it consists of cellulose (40-50%), hemicellulose (15-25%) and lignin (13-30%). Furthermore fresh wood contains also water, natural oils and minerals. For wood plastic composite manufacturing, wood is prepared into wood flour, wood flakes or wood fibres. As the wood source, mostly pines, oaks, beeches and maples are used. [5]

Natural fibres

Fibre reinforced composites are the most important group of composites and natural fibre reinforced composites are also coming into interest. Natural fibres are vegetable, cellulose based (exact composition can be seen on Figure 2) fibres from various origins in plant bodies. We can classify them into six groups: bast fibres (jute, flax, hemp, ramie and kenaf), leaf fibres (abaca, sisal and pineapple), seed fibres (coir, cotton and kapok), core fibres (kenaf, hemp and jute), grass and reed fibres (wheat, corn and rice). [3] Comparing to the most common fibre reinforcement, E-glass, they perform sufficient mechanical properties and lower density, thus natural fibre reinforced composites could be 25-30% stronger than glass reinforced composites for the same weight. [6]
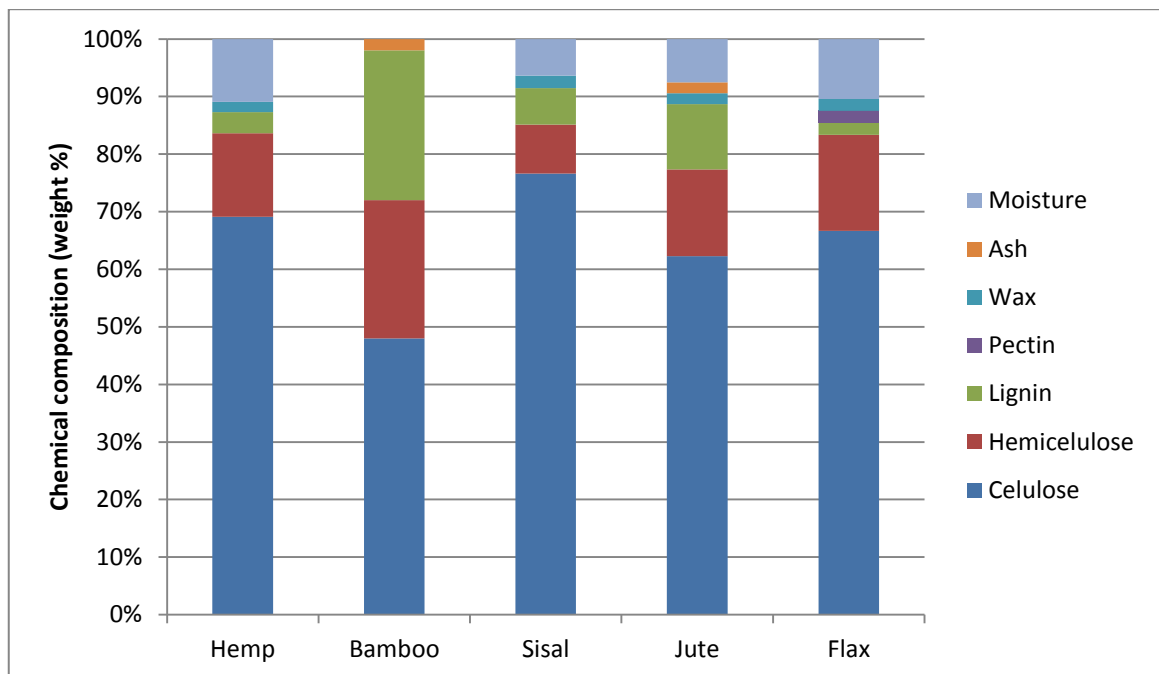

Figure 2 Chemical composition of natural fibres used in biocomposites [6]

1.2 Compatibilization of natural fibre/matrix

The main disadvantage of natural fibre reinforcement is its low compatibility to hydrophobic polymer resin. The higher interface adhesion between fibres and polymer is, the better mechanical properties the final composite shows. The strong interface layer provides good stress transfer and reduces crack propagation. This problem can be solved by two ways – natural fibre pretreatment, polymer modification or both.

Physical treatment

Physical treatment includes mainly corona discharge treatment, plasma treatment or laser. These methods change structural and surface properties of natural fibre and thereby influence mechanical bonding to polymer. Chemical composition of fibre surface is not changed extensively.

Corona discharge treatment

Corona treatment is promising approach for surface activation which leads to higher interface adhesion. Figure 3 shows changes in stress – strain curve of jute fibre/polypropylene composite while fibres are corona discharge treated. In the case of treated fibres, the strength at break is significantly increased (37,8 against 28,6 MPa) but the deformation has almost the same value. Conversely, with treated PP, the deformation is 30% greater but the increase in strength at break is very low. [7]
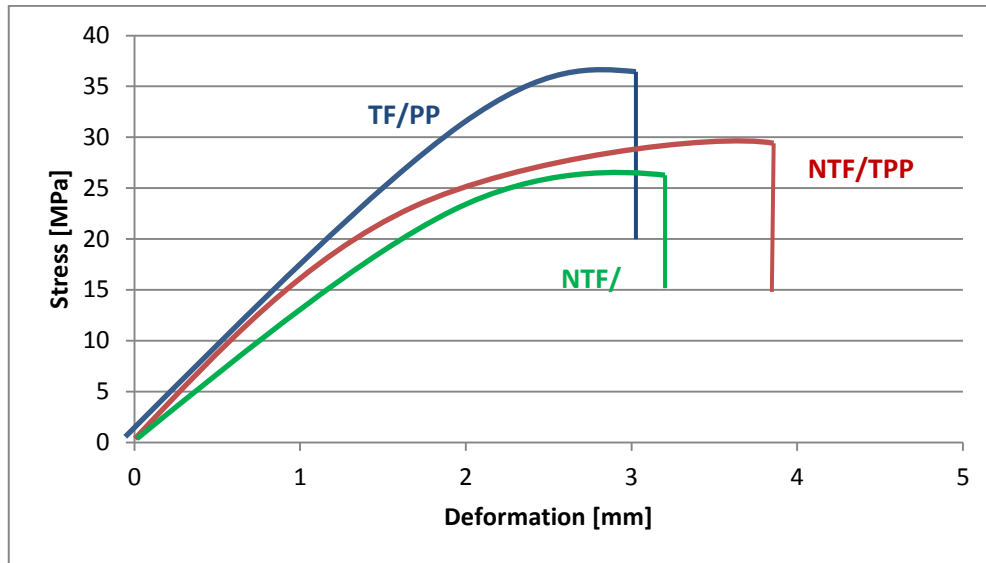
Figure 3 Effect of corona treatment on mechanical properties. Graphical result of tensile testing for composites made of treated fibres/non-treated polypropylene (TF/PP), non-treated fibres/treated polypropylene (NTF/TPP) and non-treated fibres/non-treated polypropylene (NTF/PP) [7]

On Figure 4, we can see SEM image of fracture surface of PLA/mischantous fibres. It is evident that corona treated fibres are more incorporated into PLA bulk and only small cavities can be observed on interface area. [8]
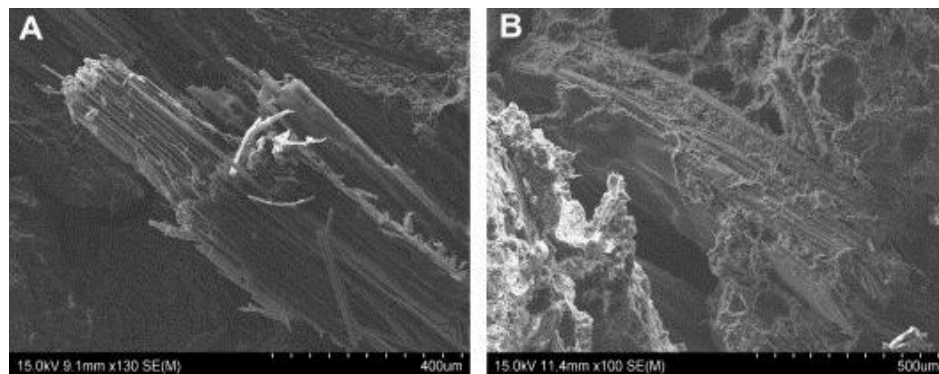

Figure 4 Fracture surface analysis of PLA composites based on 20 wt % (A) raw and (B) treated mischantous fibres. [8]

Plasma treatment

For natural fibre surface modification both, air pressure and low pressure, plasma can be used. Final properties and plasma effect differs a lot according to discharge power, exposure type and mainly the gas used for treating. When the non-polymerizing gas (helium, argon, oxygen, air and nitrogen) is used, plasma treatment leads only to cleaning and acti-

vation of surface. Plasma can serve also for plasma induced polymerization or grafting, if polymerizing gases (fluorocarbons, acetone, acrylic acid e.g.) is used. [9]

Chemical treatment

The mechanism of chemical treatment is to change chemical properties of fibre or polymer surface by grafting of specific group to maximize interface forces. Basically, we have two approaches for modification: decrease hydrophilic character of fibres or increase hydrophilic character of polymer. The chemical sources for surface treatment include alkali, silane, acetylation, benzoylation, acrylation and acrylonitrile grafting, maleated coupling agents, permanganate, peroxide, isocyanate, stearic acid, sodium chlorite, triazine or fatty acid derivate. [10]

Alkaline treatment

Principle of alkaline treatment is immersing fibres in NaOH solution (concentration 0,25% – 10% according type of fibre and matrix) This procedure cause chemical reaction (Reaction 1),changes in orientation of cellulose and its unpacking, cleaning fibre surface from wax and oil impurities. Final chemical character of fibres is more compatible with the hydrophilic matrix, which cause improving of mechanical properties of composite.[11],

$$\text{Fibre-cell-OH} + \text{NaOH} \longrightarrow \text{Fibre-cell-O}^-\text{Na}^+ + \text{H}_2\text{O} + \text{impurities} \tag{1}$$
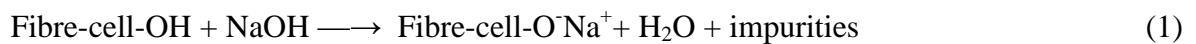
Acetylation

Acetylation is method of surface treatment based on esterific reaction between hydroxyl function groups (OH) on natural fibres and acetyl group (CH_3CO) of the treatment agent, acetylic anhydrides are mostly used. [3]

Coupling agents

A coupling agent is a chemical that functions at the interface to create a chemical bridge between the reinforcement and matrix. It can be substance with two ends, when one end reacts with the reinforcement and the other is linked to polymer matrix. [12]

Extensively used coupling agents for natural fibre reinforced composites are copolymers containing maleic anhydride such as maleated polypropylene (MAPP) or maleated polyethylene (MAPE).[13, 14] The mechanism of coupling reaction can be seen in Scheme 1
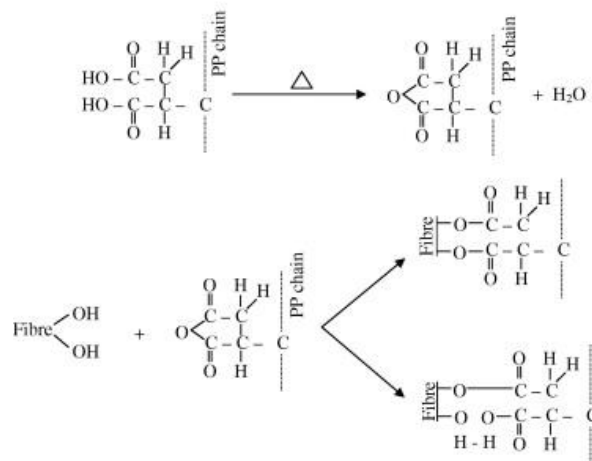
Scheme 1 Mechanism of the maleated polypropylene coupling agent activity for natural fibre - polypropylene compatibilization [12]

Other coupling agent used for natural fibre composites is silane coupling agent. Silane coupling agents have a generic chemical structure R(4−n)-Si - (R′X)n (n = 1,2) where R is alkoxy, X represents an organofunctionality, and R′ is an alkyl bridge (or alkyl spacer) connecting the silicon atom and the organofunctionality. The number of structures used for coupling natural fibres is limited, mostly trialkoxysilanes are used. [12]

1.3   Biocomposites with non-biodegradable matrices

Biocomposites with non-biodegradable matrices were the first steps of usage of natural reinforcement in industrial application. Since the matrix is not biodegradable, we cannot consider the whole composite to be biodegradable. While ageing composite in biologically active environment, as for example landfill, the natural reinforcement is yielded degradation process and the composite loses its consistent shape. Polymer matrix does not degrade as the filler, thus it only falls into the small fragments and stays without remarkable changes in substrate for a long time. This process is called desintegration.

Non-biodegradable matrices for biocomposites

As the resin thermoplastics and thermosets are both used. From the thermoplastic group, the biggest research is done on polypropylene or polyethylene based biocomposites reinforced with almost every type of natural fibres. [15–17] Lower number of studies was investigating by usage of polystyrene as matrix.[18, 19] Biocomposites with thermoset matrices are mostly based on epoxy resins [20, 21], polyester resins [22, 23] or phenolic resins [3]

Industrial application

Natural fibre reinforced composites coming in extensive use in automotive industry, partly thanks to EU legislation process. According to EU edict by 2006 80% of a vehicle must be reused or recycled and by 2015 it must be 85%, similar edicts are e.g. in Japan. (Holbery and Houston, 2006) From this reason, all car producers are focusing on the whole life cycle of the product, from sources to manufacturing, usage and disposal. Natural fibre reinforced composites meet their requirements, especially because of its low density and good vibration absorption. Current trends in vehicle design are to decrease weight of the car as much as possible to save fuel and this type of composite provides good specific mechanical properties for this application.

Daimler Chrysler company started with usage of abaca/PP in Mercedes Benz Class A in 2005 and continues with its usage in new car too. Almost all car companies (Mitsubishi, Volkswagen, Porsche, etc.) introduced natural fibre reinforced polymers to their interior. This material is used for door cladding, seatback linings, seat bottoms, back cushions, head rests or under floor body panels as can be seen on Figure 5. [24]

Another reason for usage biocomposites in car interior could be aesthetic. Luxury cars are equipped with parts made from epoxy resin/wood flour which looks like expensive exotic woods or amber material. Example of this application is gear shift of Jaguar or Audi car.

Figure 5 Indoor applications of natural fibre reinforced polymers in Mercedes Benz Class A [25]

In the field of building and civil engineering the most extensive usage received wood plastic composites. Thanks to their great properties they are used as alternative to classical wood for indoor (flooring, ceiling, doorframes, etc.) and outdoor application (terrace, facade, building panels, furniture, etc.)

2 BIOCOMPOSITES WITH BIODEGRADABLE MATRICES

Biocomposites with biodegradable matrices are the most important group of the biocomposites mostly because of their full biodegradability which can be used for wide variety of application, from goods for everyday use to high-tech medical application.

2.1 Biodegradable polymers

Biodegradable polymers have potential to be a solution for traditional synthetic polymers weaknesses, mainly in environmental aspects. Since half of twenty century, many researches on biodegradable polymers have been done. These studies have been leaded by two tendencies; firstly to solve increasing amount of solid waste produced by our society; secondly to find advanced materials for medicine and pharmaceutical applications, which are biodegradable and biocompatible in human body. According to these tendencies, we can describe two definitions of biodegradability

- simple biodegradability –biodegradable materials break down in environmental conditions, attacked by enzymes produced by microorganisms (bacteria, yeasts, molds…); these materials applications are mostly in packaging and products with short life cycle
- complex biodegradability – also called "in vivo" degradability, defined especially for medicine and pharmaceutical applications; these materials needs to by biodegradable inside human or animal body and fulfill high requirements on their quality, purity, biotoxicity….

Polymers for biomedical applications are out of scope of this work, form this reason we will define key parameters of biodegradable materials:

- material manufactured to be biodegradable must relate to a specific disposal pathway such as composting, sewage treatment, denitrification, or anaerobic sludge treatment,
- the rate of degradation needs to be consistent with the disposal method and other components of the pathway into which it is introduced, such that accumulation is controlled,
- end products of aerobic biodegradation of a material manufactured to be biodegradable are carbon dioxide, water and minerals in case of aerobic degradation or carbon dioxide, water and methane in case of anaerobic degradation

- Materials must biodegrade safely and not negatively impact on the disposal process or the use of the end product of the disposal.[26, 27]

The most common classification of biodegradable polymers is according to their origin – natural polymers or synthetic ones. Group of synthetic polymers can be consequently divided if the production comes from petroleum, gas or coal or from renewable resources.
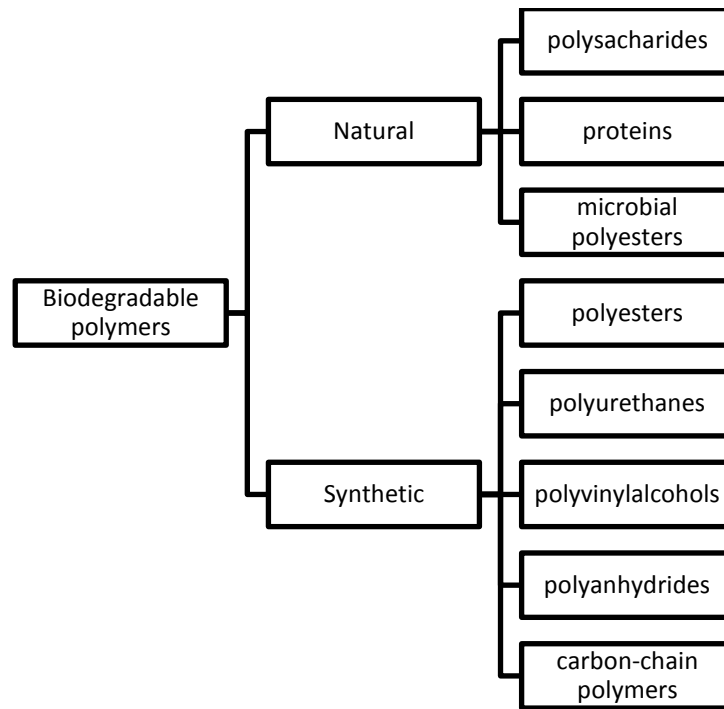

Figure 6 Classification of biodegradable polymers [27]

Natural polymers

Group of natural biodegradable polymers contain polymer materials derived from natural materials founded anywhere in the environment. The most important groups of natural polymers are polysaccharides and proteins, which were used for long time in history

The main advantage of natural polymers is their biodegradability, independence on fossil resources and usage of renewable resources, thus the very low environmental impact. However, they have also some disadvantages; their properties are sensitive to quality and purity of their sources and could be influenced especially by humidity [27] using agriculture feedstock as material source will significantly increase price of food and price of advanced natural polymers is really high and not competitive on market with traditional petroleum based polymers.

Natural polymers	Polysacharides	From plant: starch, cellulose, pectin, …
		From animal: hyluronic acid
		From fungal: pulluan, elsinan, …
		From bacteria: chitin, chitosan, xanthan…
	Proteins	Vegetable: soy, zein, wheat gluten…
		Animal: casein, collagen, elastin…
	Special polymers	lignin, natural rubber…

Table 1 List of natural polymers according to their chemical classification and origin [28]

Polysaccharides

Polysaccharides are group of natural polymers composed of a chain of monosaccharaides joined together by glycosidic bond. [29]Examples are storage polysaccharides such as starch and glycogen, and structural polysaccharides such as cellulose and chitin.

Starch is vegetable origin polysaccharide composed from two homopolymers of D-glucose – linear amylase and branched amylopectin. The ratio of these two components depends on the starch source. It is most widely used in food industry but it has promising future also in material application. Mechanical properties of virgin starch are not often sufficient for such usage and it is poor in processability and thermal stability. Therefore it is often blended (e.g. with poly(vinyl alcohol) or glycerol), grafted or chemically or physically modified [30]For decrease in price it is used as filler for polyolefine materials. [31]

Cellulose is structural polysaccharide which is contained in every primary cell of green plants and some algae. It is the most common organic compound on the Earth. From the chemical point of view, cellulose is long, linear chain of β 1,4 D-glucoses. For industrial usage, cellulose is mostly modified to cellulose acetate, cellulose diacetate or cellulose nitrate. Those materials are thermoplastic and can be processed with film casting, molding or injection molding.[32] While preparing biocomposite, natural fibres, based on cellulose, play significant role as reinforcement.

Proteins

Proteins are biopolymers mainly with animal origin, but there exist also proteins of vegetable origin as soya protein, maize zein, and other proteins from vegetable and legumes.

The chemical structure of proteins is long chain of amino acids connected with peptide (amide) bond -CONH- Those chains create in nature higher structures influencing their chemical and physical properties.

Proteins perform many functions in animal body, the most important are:

- Structural proteins: collagen, elastin, keratin
- Transport: haemoglobin
- Motor proteins: myosin, actin
- Preservative proteins: imunoglobin, fibrinogen
- Signal and control proteins: enzymes and hormones

In industry, the most promising proteins are collagen and keratin which found applications in medical and pharmaceutical industry for tissue engineering or drug release. In commercial sphere products based on collagen or keratin are used for skin and hair refreshing and nutrition. Their advantages are biodegradability and biocompatibility. The by-products of food industry could serve as their source.

Microbial polyesters

Microbial polyesters are new group of biodegradable materials, mostly hydroxyalkanoates (PHAs). They are synthesised by bacteria species, e.g. Clostridium, Syntrophomonas, Pseudomonas or Alcaligenes as a storage material for carbon and energy. According to conditions of bacteria life, polymers with more than 150 different monomer compositions can be produced. Nevertheless only few of them are produced on industrial scale, mainly-polyhydroxybutyrate (PHB), poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH).

The main areas for polyhydroxyalkanoates are biomedical (tissue engineering) and packaging industry, which is still limited with the high price of the material comparing traditional oil based polymers. Trademarks of some industrial polyhydroxyalkanoates are Mirel™,

Biocycle®, Biomer®, Enmat®, Nodax™, etc. [33]
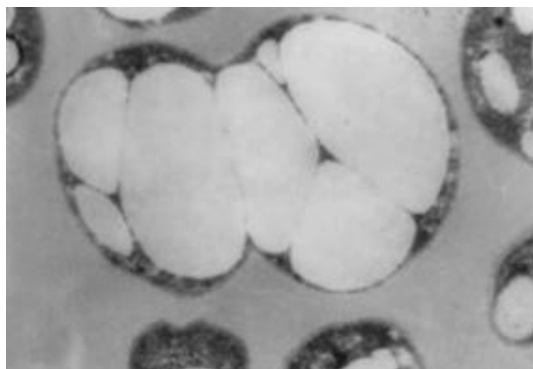
Figure 7 PHA granules in bacteria cells – optical microscopy image Synthetic biodegradable polymers [34]
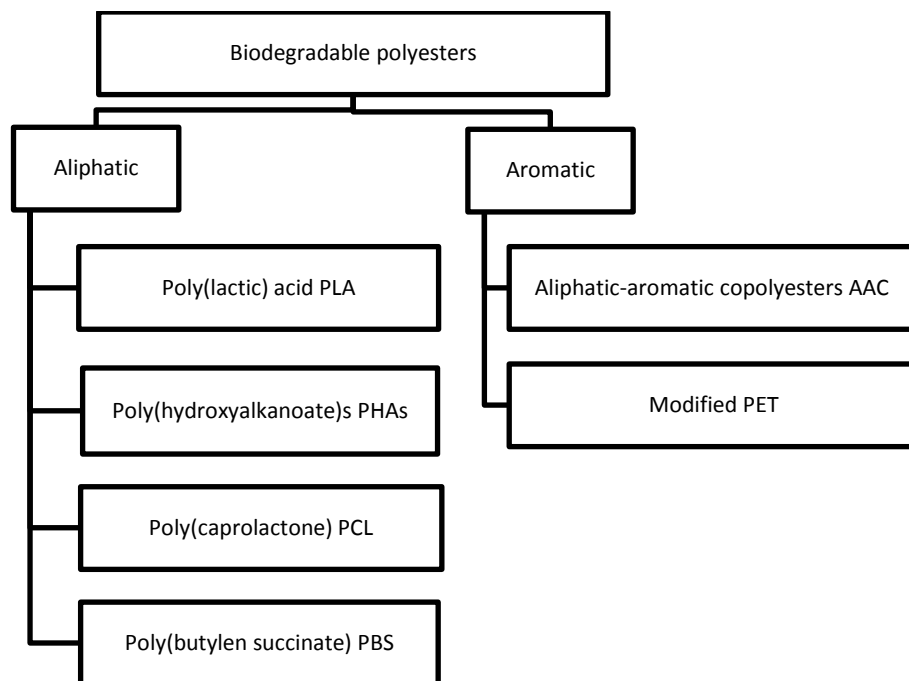
This group of biodegradable polymers is not produced by living organism but synthesised by mankind. However those polymers can come from both, petrochemical and renewable resources. Structural premise for polymers to be biodegradable is to have hydrolysable linkage. Therefore number of biodegradable polymers is limited and we can count only with some polyesters, polyurethanes, polyamides and carbon-chain polymers.

Biodegradable polyesters

Biodegradable polyesters are the most promising group of biodegradable polymers which come into the focus of extensive research and already met the market requirements. They found application in packaging industry and wide usage is in field of medicine.

Polyesters contain hydrolytically labile ester bond which can be scissioned with or without catalytic action of specific enzymes produced by organisms. The classification of biodegradable polymers can be according to their chemical structure into aliphatic and aromatic. Structural formulas of the most important aliphatic polyesters are summarised in Table 2

Scheme 2 Biodegradable polyesters classification

Polymer	Repeating Unit	Example (Acronym)
Poly(α-hydroxy acid)		R = H, poly(glycolic acid) PGA R = CH$_3$, poly(lactic acid) PLA
Poly(ω-hydroxy alkanoate)		x = 4, poly(δ-valerolactone) PVL x = 5, poly(ε-caprolactone) PCL
Poly(hydroxy alkanoate) microbial polyesters		R = CH$_3$, x = 1 poly(3-hydroxy butyrate) PHB
Poly(alkylene dicarboxylate)		x = 2, y = 2 poly(ethylene succinate) x = 2, y = 4 poly(butylene succinate) x = 4, y = 4 poly(butylene adipate)

Table 2 Chemical structure of the most important biodegradable polyesters [35]

Generally, polyesters can be synthetized by two principal ways, by direct polycondensation of hydroxyl acids and diols or by ring-opening polymerizations. First polyesters were prepared by direct polycondensation and did not reach desired properties. To obtain high quality product polycondensation reaction has to be driven under strictly defined conditions, high temperature, long reaction times and continuous removal of reaction by-products. If these requirements are not fulfilled, product with low molecular weight is received. The

second way, ring-opening polymerization of cyclic esters proceeds under milder conditions and can be easily controlled; polyesters produced by this way has higher molecular weights. Detailed information about polyesters synthesis is discussed in Chapter 3.4.[35]

The most promising biodegradable polyester is poly(lactic acid) PLA which is prepared from monomer lactic acid. According to optical activity of lactic acid we can obtain polymers with various properties. PLLA and PDLA are semi-crystalline while crystallization of racemic mixture leads to amorphous PDLLA. Similarly to crystallinity, the rest of mechanical and chemical properties is influenced also. [35]

Very similar properties to PLA has other polyester poly(glycolic acid) PGA, which is prepared from glycolic acid. For increasing properties, mainly solubility and biodegradability, copolymers of PLA and PGA are often used. Polycaprolacton is polymer prepared by ring opening of ε-caprolactone.

All of these materials and their blends and copolymers are used as scaffolds for tissue engineering and bioabsorbable materials, e.g. for chirurgical sewings and screws. Their possible application in packaging industry depends on competitiveness in price with petroleum based polymers [36, 37]

Biodegradable polyamides

Polyamides are polymers with the amidic (-NHCO-) linkage in their chain. It is one of the most extended polymer groups with many industrial applications. Development of biodegradable polyamides is still in the beginning. Previous work about biodegradable polyamide 6/PVA blends was presented by Ramaraj and Poomalai [38]This blend appears to be biodegradable in soil and provide sufficient properties for engineering application. Majó et al. [39]and Okamura et al.[40] based their research on α- and β- aminoacids and prepared biodegradable polyamides possible for medical applications such drug release or tissue engineering.

Biodegradable polyurethanes

Polyurethanes are prepared by coupling polyols (alkendiols, glycerol, poly(ε-caprolactone), etc.) with diisocyanate. As a result of this reaction, polyurethane chains content urethane linkages (-R-NH-COO-R´-). Generally, polyurethanes are resistant for biodegradation, but urethane bond in low molecular weight oligomers can be hydrolysed by some microorganisms. From this reason, short segments of polyurethanes are connected with biodegradable ether or ester chains forming biodegradable poly(ether urethanes)or poly(ester urethanes).

Promoting ester chains to polyurethanes, we can avoid usage diisocyanate, which is not ideal from ecological point of view. [41]

Oxo-biodegradable polymers

Synthetic, petroleum based plastics, such as polyethylene, polypropylene, poly(ethylene terephthalate) or polystyrene, degrade for years or decades in the natural environment. The term oxo-biodegradable plastics is commonly used for these plastics modified by special additives called pro-oxidantes. These substances, based mostly on salts of transition metals (cobalt (Co), iron (Fe), manganese (Mn) or nickel (Ni)), can accelerate degradation process to last only months, maximum couple of years. With help of temperature, UV radiation, and humidity polymer goes under peroxidation reaction which leads to decrease in molar mass of polymer. Consequently, products of abiotic reactions are transformed by microorganism into water, carbon dioxide and biomass. (42)

3 POLY(LACTIC ACID) AND ITS BIOCOMPOSITES

3.1 Lactic acid

Lactic acid is one of the most frequently occurring carboxylic acids in nature playing important role in many biochemical processes. Its systematical name is α-hydroxypropionic acid with formula $CH_3CHOHCOOH$. Because the structure contains chiral carbon atom, there exist two optically active isomeric forms. L(-) lactic acid and D(+) lactic acid and the mixture of isomers called racemic lactic acid. [43]
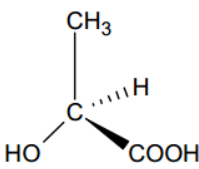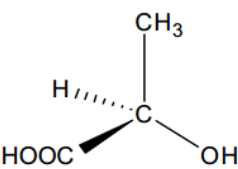
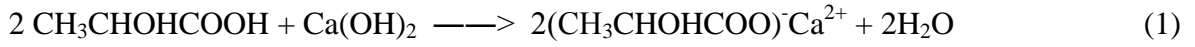| L – lactic acid	Property	Unit	D – lactic acid
	Molecular weight	90,08 g.mol-1	
	Melting point	16,8°C	
	Boiling point	122°C at 2 kPa	
	Dissociation const., Ka at	1,37.10-4	
	Heat of combustion, ΔH	1361 KJ/mole	
	Specific heat, Cp at 20°C	190 J/mole/°C	

Table 3 Physical properties of lactic acid [44]

Lactic acid achieves great importance especially in food industry as acid regulator, antimicrobial agent, or dough conditioner. Applications can be founded also in cosmetic, pharmaceutical or textile industry. For industrial application there exist two ways of lactic acid synthesis, chemical way or fermentation.
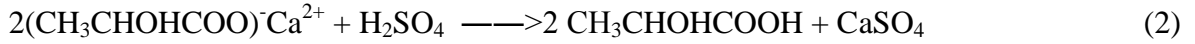
Lactic acid synthesis

Chemical synthesis of lactic acid was invented in early 1960s to produce heat stable lactic acid for baking industry. The principle of chemical synthesis is reaction of acetaldehyde and hydrogen cyanide producing lactonitrile, which is hydrolysed to lactic acid. [45] Since only racemic mixture of D,L – lactic acid can be obtain via chemical synthesis from petrochemical sources, current production is provided by fermentation from renewable sources. According to active microorganism only selected isomer can be synthesized. [46]Microbial fermentation is process when carbohydrate substrates are changed to lactic acid by activity of bacteria yeast or molds. Microbial process includes fermentation, product recovery and purification, as can be seen on Scheme 3.

Incoming raw material must be prepared to obtain pure sugar. Hence, sugar, water and bacteria are mixed and put into fermentor. During fermentation $CaCO_3$, $Ca(OH)_2$,

Mg(OH)$_2$, NaOH, or NH$_4$OH are added to neutralize the fermentation acid and to give soluble lactate solutions (Reaction 1).

$$2 \text{ CH}_3\text{CHOHCOOH} + \text{Ca(OH)}_2 \longrightarrow 2(\text{CH}_3\text{CHOHCOO})^-\text{Ca}^{2+} + 2\text{H}_2\text{O} \qquad (1)$$

In the first step, the solution is filtered to remove biomass. Secondly, sulfuric acid converts calcium lactate to lactic acid and gypsum (or other corresponding salt – Reaction 2).

$$2(\text{CH}_3\text{CHOHCOO})^-\text{Ca}^{2+} + \text{H}_2\text{SO}_4 \longrightarrow 2 \text{ CH}_3\text{CHOHCOOH} + \text{CaSO}_4 \qquad (2)$$

Salt is filtered out and the crude lactic acid is purified and concentrated according desirable quality and future use. For food and pharmaceutical industry, by-products of reaction need to be disposed. For following polymerization reaction, separation techniques like ultra-filtration, nano-filtration or electro-dialysis are used. [47]
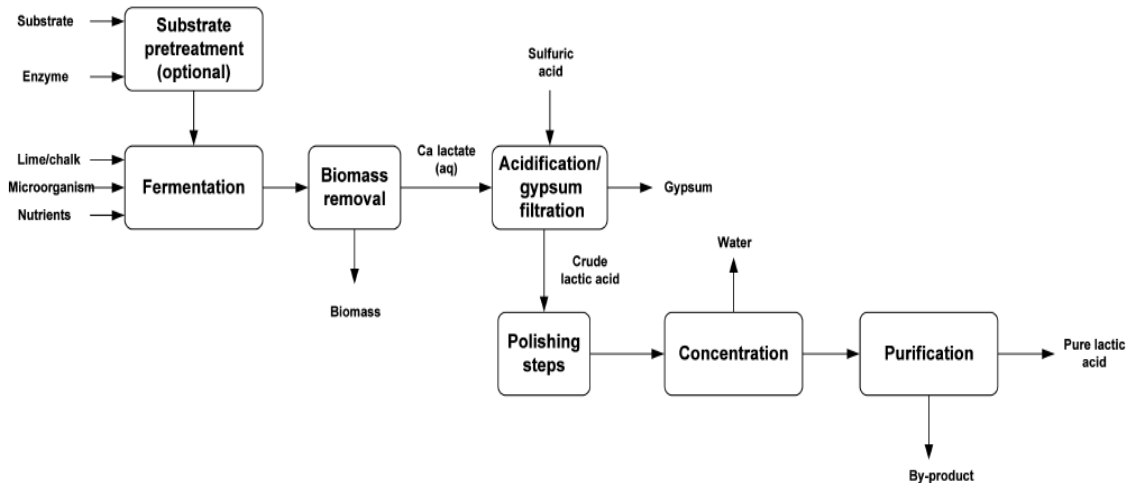
Scheme 3 Simplified block scheme of traditional lactic acid production process [45]

Generally, all carbohydrate sources containing pentose or hexose can serve for lactic acid production. Pure sucrose from sugarcane or sugar beet is preferable for fermentation reaction. However, polysaccharides as starch or cellulose based materials are mostly chosen thanks to their low cost, renewability and availability. The only disadvantage is that their structure is more complex and need pretreatment. As a source for fermentation reaction, industrial by-products as molasses or whey can serve also.

Microorganisms for fermentation are bacteria or molds and yeast. The greater industrial importance achieved bacteria, especially Lactobacillus species. We can divide bacteria into two groups – heterofermentative (produce lactic acid and other metabolic products) and homofermentative (produce lactic acid only). This classification needs to be taken into account as important parameter of fermentation process. Others are carbohydrate source

specification, desired isomer, yield, production rate or conditions as temperature, pH, or oxygen presence because most of the bacteria are anaerobic. Mold and yeast are mostly used because of its ability to convert polysaccharides into lactic acid directly without previous hydrolysis and better tolerance to acidic pH than bacteria. Their disadvantage is lower yields and forming co-products [44, 45]

3.2 Poly(lactic acid)

Poly(lactic acid) (PLA) is the most promising biodegradable polymer, thanks to its properties (high elasticity modulus, high stiffness, good processability…) comparable to petroleum based polymers. Current development and research about PLA production, modification and application possibilities makes this material able to compete on market in numerous fields. Global Poly Lactic Acid market is expected to reach US$2.6 billion by 2016 at a Compounded Annual Growth Rate (CAGR) of 28%, globally.[48]

PLA is ranked into group of biodegradable polyesters, with the main structural unit of lactic acid (Figure 8) According to optical activity of lactic acid molecule, properties of polymer are significantly influenced by its stereo isomeric form. Thus, poly(lactic acid) can exist in three forms, PLLA, PDLA, PLDLA.
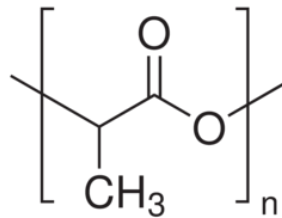

Figure 8 Chemical structure of PLA [49]

3.3 PLA properties

General properties

All properties of PLA polymer are strongly dependent on ratio and distribution of stereoisomers in molecular chain. Homopolymer containing only L-PLA is a semicrystalline material with high melting point while with increasing content of D-PLA ratio of crystallinity dramatically decreases. Material with content of D-PLA form higher than 12-15% is totally amorphous. Crystallinity also affects thermal, rheological and mechanical properties, with tailoring of D and L isomers ratio we can prepare materials with wide range of properties satisfying requirements of future application. [45]

Typical temperatures for PLA vary a lot. Melting point T_m is around 180°C for enantiomeric pure PLLA and decrease with introducing second enantiomer to 50°C and low. Glass transition temperature T_g of pure PLLA is between 55-60°C. [35]

A good solvent for PLA is chloroform and other chlorinated or fluorinated solvents. As solvent acetone, dioxane or furan can be used; non-solvents are water, alcohol, or hydrocarbons as hexane or heptanes. [47]

Because PLA is promising material for packaging industry, its barrier properties are in interest. The CO_2 permeability coefficient is lower than for polystyrene but higher than for PET. Almost the same behavior was described for oxygen. However, PLA shows excellent barrier properties for hydrophobic aroma compound, such as limonene, comparable to PET. [50]

Mechanical properties

The mechanical properties of PLA can vary to a large extent, ranging from soft elastic plastic to stiff and high strength plastic. Properties are mainly influenced by molecular weight (increase in molecular weight induce increase in mechanical properties) and ratio of crystallinity. [47]

According to application field of plastic, properties can be modified. In Table 4, properties of Ingeo Biopolymer 2003D (product of NatureWorks LLC) are summarized. This material is suitable for thermoforming of food packages and can be considered as biodegradable and compostable according ASTM standards. It is used for dairy containers, food service ware or cold drink cups. [51]

Physical	Nominal Value Unit	Test method
Specific Gravity	1,24 g.cm3	ASTM D792
Melt Mass-Flow Rate	5,0 – 7,0 g/10 min	ASTM D1238
Films		
Secant Modulus - MD	3450 MPa	ASTM D882
Tensile Strenght - MD		ASTM D882
Yield	60,0 MPa	
Break	53,1 MPa	
Tensile Elonbation – MD (Break)	6%	ASTM D882
Impact		
Notched Izod Impact	13 J/m	ASTM D256
Optical		
Clarity	transparent	

Table 4 Properties of PLA material - Ingeo Biopolymer 2003D by NatureWorks LLC [51]

Processing properties

PLA can be processed as normal thermoplastic material, by extrusion, film blowing, bottle blowing, thermoforming, injection molding…. The major drawback of the material is its low thermal stability and some weaknesses in mechanical properties. Thus it is often modified by various ways. [47]

The brittleness and stiffness are major drawbacks of PLA. This can be improved by promoting plasticizers into material. Recently citrates or polyethylene glycol [52] and fatty acids were used for the improvement of PLA flexibility.

There also exist a lot of PLA blends. Reasons for blending are reducing material cost and maintaining some material properties. A lot of papers were written about PLA/starch blends [53–55] Generally, increase in starch content decrease material cost; increasing content of PLA improve mechanical properties such as tensile modulus. PLA can be blended also with PET for crystalline behavior modification [56], PMMA for drug release [57] or with other biodegradable polymers such as PHBV, PCL or EVA[58–60]

Biodegradability

Degradation of PLA takes place in multiple steps. Firstly, after moisture exposure the mechanism is abiotic and PLA degrades by hydrolysis. Chain-scission of ester bond leads to decrease in molar mass and material becomes more brittle. This step is strongly influenced by pH of the environment, temperature and humidity or material crystallinity and

product size and shape. Secondly, oligomeric products are attacked by microorganisms which transform material into final products of biotic degradation, CO_2, water and humus. Average degradation time in real compost conditions is around 30 days. [47, 61, 62]

3.4 PLA synthesis

There are different routes of PLA synthesis. The main differences are in incoming sources, polymerization conditions, methods and properties of resulting polymer. Various ways of PLA preparation are shown in Scheme 4. It is direct melt polycondensation, ring opening polymerization, solution polycondensation and solid state polycondensation. For industrial use only ring opening polymerization and solution polycondensation is widely used. [44]
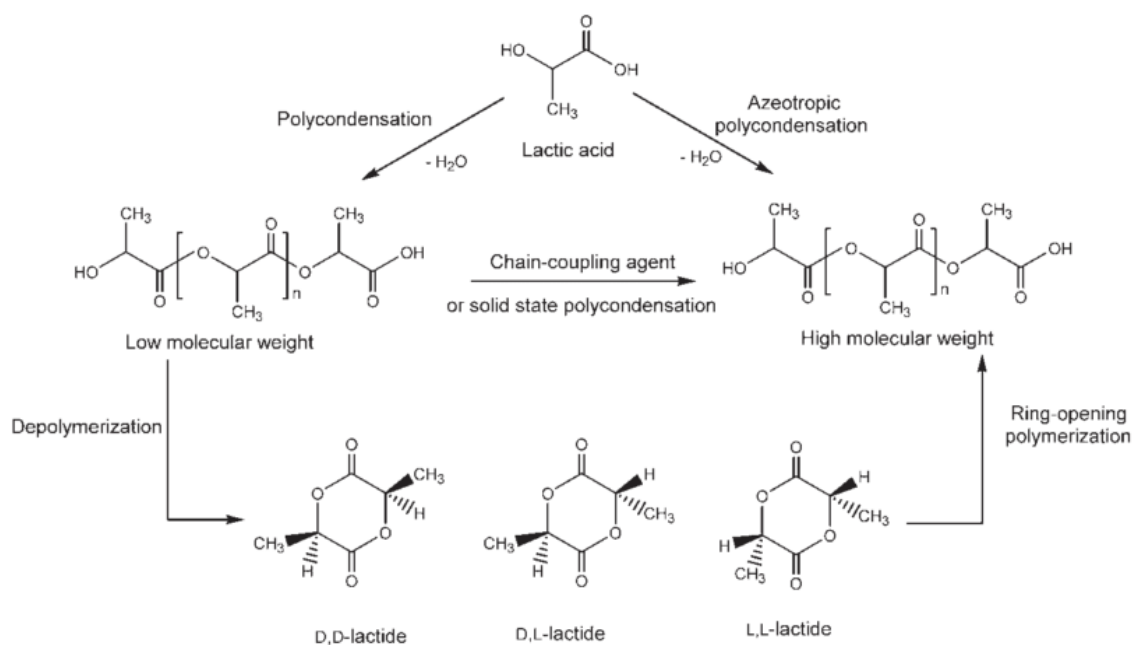

*Scheme 4 Different routes of preparation of high molecular weight PLA* [35]

Ring opening polymerization (ROP)

Ring opening polymerization is the most commonly route to achieve high molecular weight PLA. It includes polycondensation of lactic acid followed by a depolymerization into dehydrated cyclic dimer, lactide (3,6-dimethyl-1-1-dioxane-2,5-dion). Consequently, lactide can be ring-opening polymerized into high molar mass poly(lactic acid).
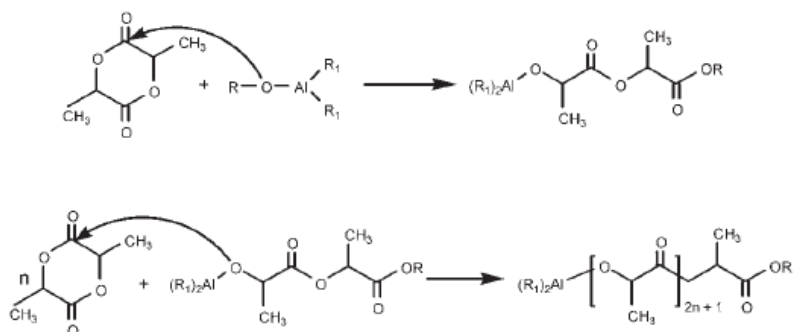
Cationic mechanism
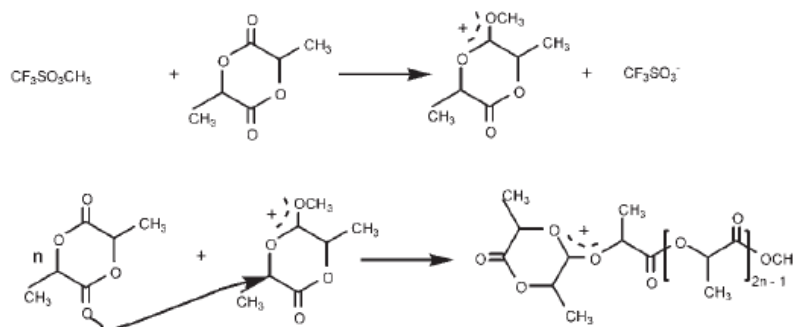
Anionic mechanism
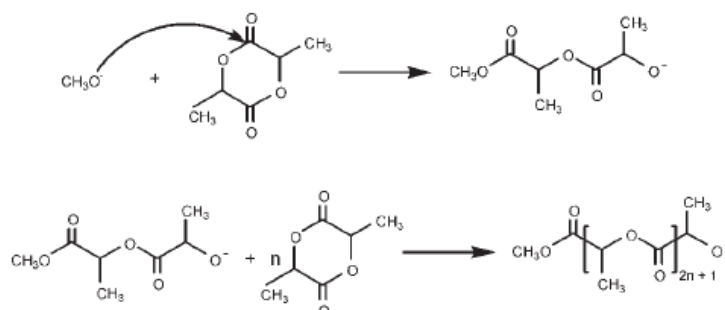
Coordination-insertion mechanism

Scheme 5 Mechanism of the cationic, anionic and coordination insertion ROP of lactide [35]

The reaction can be carried out in melt, bulk or in solution. Depending on used catalyst, mechanism of reaction is cationic, anionic or coordination-insertion mechanism (schematical description of reaction mechanism is shown in Scheme 5). Among various types of initiator stannous octoate is usually preferred because it provides high reaction rate, high conversion rate and high molecular weight even in milder conditions. The important properties of this catalyst are also low toxicity and food and drug contact approval. [47, 63]

Typical reaction conditions for lactide ROP are: temperature below 180°C, relatively short reaction time 2-5 hours, catalysts and presence of initiator. This technique is widely used and good for large scale production of high molecular weight poly(lactic acid) with good properties. The main weakness of this process is expensive lactide manufacturing and purification steps. [44]

Direct melt polycondensation

Direct melt polycondensation is the simplest way of PLA production. The principle of reaction is direct condensation of lactic acid molecules by reactions between hydroxyl and carboxyl groups in presence of catalysts with water as a by-product. Water and other impurities and its removing from reactor is the limiting factor of the process. Presence of water or catalysts impurities affects the equilibrium state of the reaction and leads to low molecular weight PLA (M_w~5000 kg.mol^{-1}).

Problem with low molecular weight of the products can be solved by followed-up reaction of chain extending. Final product could have satisfying properties comparable with PLA prepared by other ways, e.g. ROP. However the main benefits are simplicity and low cost of the process. [47, 64, 65]
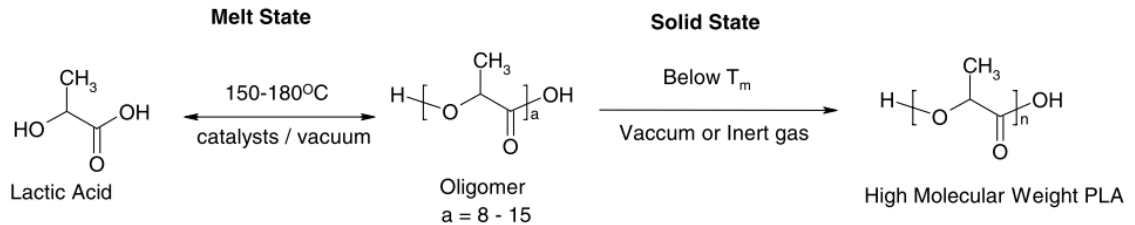
Solution polycondensation

The main problem of direct melt polycondensation – water removal – is sold in polycondensation in solution. In this process, purified lactic acid is dissolved in a suitable low-boiling solvent and a catalyst is added. The polymerization is promoted by removal of the by-products in a refluxing system with molecular sieves. The advantage of solution method is that it is one-step process, proceeding on relatively low temperatures, which prevents side reaction and degradation. Disadvantage is presence of small amount of solvent in final product. [35]

This type of process is used by the Japanese company Mitsui Tatsu chemical for the product called LACEA [44]
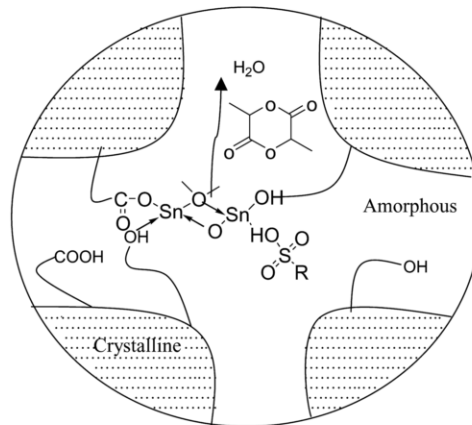
Solid state polymerization

Solid state polymerization seems to be effective alternative to ROP for high molecular weight PLA synthesis. It is based on catalyzed esterification reaction of hydroxyl and carboxyl end groups inside amorphous region of low molecular weight prepolymer.

Scheme 6 Reaction along solid state polycondensation [66]

The process starts with semi-crystalline prepolymer of relatively low molecular weight in powder, pellets or chips. Then the material is heated to temperature 5-15°C lower than melting point but higher than glass transition temperature in the presence of suitable catalyst. Simultaneous removal of by-products from surface is needed. This can be handled under pressure or by driving it away by carrier gas.


Figure 9 Schematic illustration of esterification of end groups in amorphous region of PLA [67]

The advantages of solid state polycondensation include low operating temperatures, which control the side reaction as well as degradation of the products. Although the reaction time is relatively long, polymer of high molecular weight (around 5.10^5 g.mol^{-1}) can be obtained. Finally there is practically no environmental pollution, because no solvent is required. [66, 67]

Chain extension

Chain extending method is a solution for increasing molar mass of oligomeric prepolymers with chain extenders. Chain extenders are usually bifunctional small chemical compounds reacting with one type of functional groups of oligomeric PLA. PLA contains equal number of hydroxyl and carboxyl groups, thus it has to be modified to contain only one type. For hydroxyl ended chains, the polycondensation reaction is lead in presence of small amount of 2-butane-1,4 – diol, glycerol or 1,4 – butanediol; for carboxyl ended chains succinyl, adipic or maleic acid needs to be present. [66]
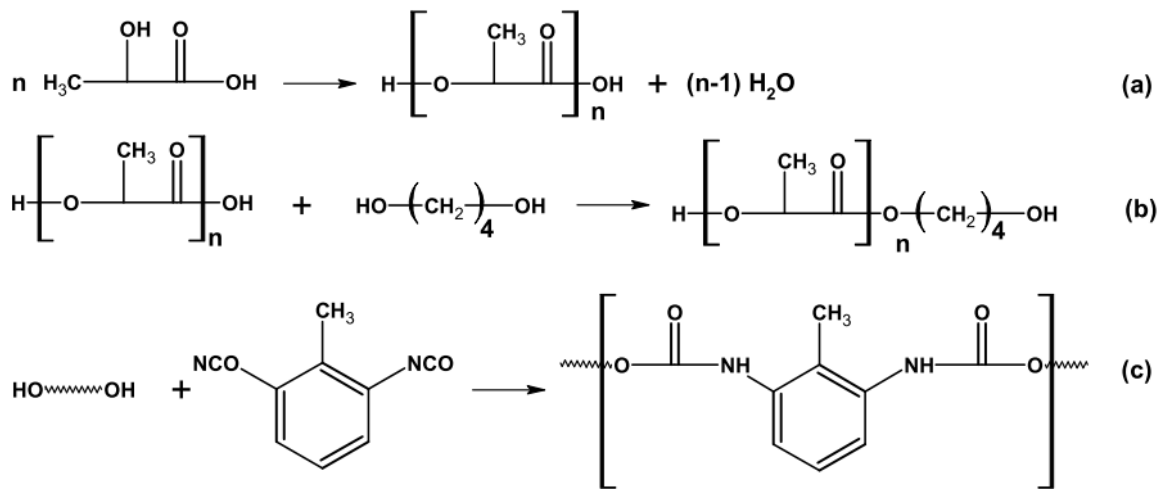
Scheme 7 Reaction of lactic acid polycondensation (a), hydroxyl termination (b) and chain extending (c) [44]

Chain linking proceeds typically in molten state e.g. in extruder where prepolymer is mixed with chain coupling agent and reaction of function groups performs. Suitable chain extenders are isocyanates or bisoxazolines. While using trifunctional coupling agent branched polymer can be prepared. [35]

This technique is promising way for high molecular weight PLA preparation. In relatively short reaction time (40 min) polymers with $M_W \sim 300\,000$ g.mol^{-1} can be achieved. The process is very fast and simple (can be done in extruder). However drawbacks as undesirable reactions (branching) or low thermal stability exist. Furthermore some chain extenders affect negatively biodegradability, for example isocyanates are toxic. [63]

3.5 PLA applications

PLA can be proceeding by traditional techniques such as extrusion, injection molding, film casting or spinning. Since the material properties are comparable to other commodity plastics like PS or PET the usage is almost the same. Thanks to its biodegradability, the biggest area of applications are disposable throwaway goods – plates and cups, composting bags, tea bags, diapers, etc. In agriculture, PLA is used for mulch foils, seeding belts, delivery systems for fertilizers or pesticides. Great potential has also PLA in textile industry. Mechanical properties are similar to PET (which is second most used in textiles) but garments made from PLA are more comfortable. It has better moisture spreading and drying, so that it can be used for sport clothes. Comparing to natural fibres like cotton, it appears better in after-care properties. After laundering, PLA textiles are not damaged, degraded, non-creased and very clean. [68]

High interest gets PLA in medical and pharmaceutical industry. PLA and its copolymers have been used for applications like drug delivery system or hydrogels. PLA is great material for manufacturing medical devices (screws, rods, plates) for fracture fixation. It gives support to damaged bones, but since it is absorbable the support is decreasing as the tissue is healing. It means that the loading to healing tissue is increasing continuously and second surgery is not needed. PLA/hydroxyapatite composites or pure PL are used for tissue engineering.

PLA composites can be reinforced with any type of natural fibres. Recent papers studied PLA composites reinforced with, kenaf fibres, abaca fibres or sisal. They have mechanical properties comparable to synthetic polymers reinforced with glass fibres, which gives them possible areas of application in building, civil engineering or automotive industry.

4 AIMS OF THE WORK

Literature review gives theoretical base of PLA production from dairy waste by-product, whey. According to previous research project of Polymer Centre Tomas Bata University in Zlín it is possible to produce high molecular polyester urethane from this sources by direct melt polycondensation and follow up chain-extension.

This material can be used for preparation of biocomposite filled with natural fibres. The main limitation of future application of this biocomposite is the low compatibility between polymer matrix and fibres. This problem can be solved by adding additives or fibre pre-treatment. [69]

The goals of this master thesis are mainly:

1) Preparation of biocomposite of PEU resin and flax fibres. For interfacial adhesion improvement commercial additive, and two types of experimental additives are mixed into biocomposite, or the flax fibres are alkali and acid treated.

2) Characterization of prepared biocomposites with gel permeation chromatography, differential scanning microscopy, thermogravimetric analysis, scanning electron microscopy, and mechanical testing.

3) Results discussion and suggestion of optimal way for interfacial adhesion improvement.

II. ANALYSIS

5 MATERIALS

L-lactic acid (LA), 80% water solution; PEG, (M_w= 380 – 420 g.mol^{-1}) were products of Merck, Hohensbrunn, Germany. Tin(II) 2-ethylhexanoate (Sn(Oct)$_2$), ~95%; hexamethylene diisocyanate (HMDI), 98%; were purchased from Sigma Aldrich, Steinheim, Germany. Solvents: chloroform, acetone, methanol, and ethanol (all analytical-grade) came from IPL Petr Lukes, Uhersky Brod, the Czech Republic. Chloroform (HPLC-grade) was sourced from Chromspec, Brno, the Czech Republic. All chemicals were used as obtained without further purification.

Synthesis of PLA-PEG polymer

100 mL of L-LA was added into 250 mL two-neck distillation flask equipped with a Teflon stirrer. The flask was then connected to a condenser and placed in an oil bath. Firstly, dehydration of L-LA solution at 160°C took place, under a reduced pressure of 20 kPa for 4 hours. Then, 0.5 wt. % Sn(Oct)$_2$ and 7.5 wt. % PEG were added and reaction continued for 6 hours at 10 kPa. After that, pressure was reduced to 3 kPa for another 10 hours. The resultant hot melt was poured out on an aluminium foil and cooled. The whole procedure was repeated till sufficient amount of material was collected. Finally, all batches were cut and mixed in cutting mill (Retsch SM 100) to particles having diameter about 3 mm. Product was stored in desiccator.

For the PLA-PEG chain linking 30 g of PLA-PEG prepolymer was added into 250 mL two-neck flask equipped with mechanical stirrer. Material was slowly heated to predetermined temperature (160 °C), under N$_2$ atmosphere. Once the mixture was completely melted HMDI was added and value of torque was recorded (mixer Heidolph RZR2052). Reaction was stopped when the torque remained constant or after 30 minutes; in order to prevent thermal degradation. Resultant product was cooled down, dissolved in chloroform, precipitated into water/methanol mixture (1:1), filtered and dried in vacuum at 30 °C for 24 hours.

PLA-PEG/flax fibre composite preparation

The flax fibres were provided by Havivank Bv (Netherland) company. The properties guaranteed by supplier were density around 1,45 g.cm^{-3} and tensile strength around 600 MPa.

For samples C and D the flax was treated for 30 min in 10% acetic acid and 10% NaOH dissolution, respectively. The modified fibres were than dried in hot air (80°C) for 4 hours.

To improve interfacial adhesion of sample B, commercial additive 3-(aminopropyl) tri-methoxy silane was added. Properties of samples E and F were modified with usage of experimental additives developed at University of Pannonia, Veszpren, Hungary. Their chemical composition and characteristic properties are given in Table 4. The sample G was modified adding 0,2% of oleic acid and 0,1% of di-tert-butyl peroxide (DTBP). All information about sample composition is summarized in Table 5.

Table 5 Experimental additives characterization

	Experimental additive-1	Experimental additive-2
Type	polyalkenyl-poly-maleic-anhydride	polyalkenyl-poly-maleic-anhydride-ester
Olefin component	styrene	C15-C25
Alcohol component	-	dodecanol
Appearance	white yellow	white yellow
Acid number, mg KOH/g	125,2	14,8
Mw	1620	3435
Mn	1355	2420
α	1,2	1,42
ASTM colour	0,5	0,5

Table 6 PLA-PEG/flax fibre composite compositions

	A	B	C	D	E	F	G
Natural fibre	20%	20%	20%	20%	20%	20%	20%
PLA-PEG-TDI	80%	79,90%	80%	80%	79%	79%	79,70%
Commercial additive		0,50%					
Acid treating			Yes				
Alkali treating				Yes			
Experimental additive-1					1%		
Experimental additive-2						1%	
Oleic acid+DTBP							0,2%+0,1%

A two-roll mill (Laboratory two-roll mill, Lab Tech LRM-S-110/T3E) was used for composite manufacturing. Temperatures were 95°C (first roll, n=8rpm) and 125°C (second roll, n=19rpm). The mixing time was 10 min. Before mixing modified PLA was dried at 80°C

during 3 hours. Treating materials and additives were added into the molten polymer during the mixing procedure.

There occurred some problems during preparation of composite with alkaline treated fibres (D) thus this material was not used in experimental part for analysis.

6 METHODS

For aims of this work some experimental techniques were used to analyze effect of compatibilization methods on thermal and mechanical properties of final composite. In this chapter, a short theoretical background and detailed experimental settings of each method are given.

Gel permeation chromatography (GPC)

GPC analysis was conducted using Agilent chromatographic system (PL – GPC 220). Samples were dissolved in THF (~2mg/mL) overnight. Separation and detection took place on two PL gel-mixed-D bed column (300 × 7.8 mm, 5 μm particles) connected in series with a RI and viscosity detectors. Analyses were carried out at 40°C with a THF flow rate of 1.0 ml/min and a 100 μL injection loop. The universal calibration was made from narrow polystyrene standards (580 - 353 700 000 g.mol^{-1}, Polymer Laboratories Ltd., United Kingdom). The weight average molar mass M_w, number average molar mass M_n, and molar-mass dispersity ($Đ_M = M_w/M_n$) of the tested samples were determined from their peaks corresponding to polymer fraction, and expressed as "true" molecular weights. All data processing was carried out using Cirrus software.

Differential scanning calorimetry (DSC)

The thermal properties of the samples were investigated using a Mettler Toledo DSC1 STAR testing machine, over a temperature range of 0°C to 190°C at a heating/cooling rate of 10°C.min^{-1} and nitrogen flow 30 cm^3.min^{-1}. The melting point temperature (T_m) with enthalpy of fusion ΔH_m was obtained from the first heating cycle, whereas the value of glass-transition temperature (T_g) was determined from the second heating scan, at the midpoint stepwise increase of the specific heat which is associated with glass transition.

Thermogravimetric analysis (TGA)

The thermal stability of the PLA samples thus prepared was analyzed using a thermogravimeter (TA INSTRUMENTS Q500), in adherence to the samples possessing masses from 15 to 22 mg. The heating rate was set at 10∘C/min over a temperature range from 25∘C to 500∘C; furthermore, a helium atmosphere (flow 30 cm^3/min)was employed. Decomposition temperature was taken as onset of TGA curve.

Mechanical properties testing

To determine the tensile and three point flexural properties (mainly stress and extension) (ČSN EN ISO 527-1-4:1999, ČSN EN ISO 14125:1999) an M350-5 CT Materials Testing Machine was used. Tensile and flexural tests were carried out at 50mm/min and at 10mm/min crosshead speed.

Charpy impact strength measurements of the produced composites were provided by ZWICK 5113 to measure according to CSN EN ISO 179-2:2000 standard.

Scanning electron microscopy

For the purpose of this thesis, fracture surface of prepared biocomposites were scanned by SEM technique, using instrument. The main focus was on the topography of the fracture surface and the visible confirmation of fibres and polymer adhesion.

Multicriteria evaluation

To select the best compatibilization technique, the multicriterial analysis was applied using experimental data as input for final evaluation. The TGA and mechanical testing results were chosen, because the data obtained from these techniques were complete and explicit. Normative scale method was used for ranking the techniques importance. 100% points were divided among the techniques according to its importance for future application and accuracy of the method.

Evaluation of sample performance was counted with point method. Every sample was scored with points from 1-10 on the basis of true experimental data, not only the order. The advantage of this method is saving information about the results´ value.

As the result of the scale and point definition, the three dimensional matrix was prepared. Value of every property of every sample was counted using Equation 1:

$$V_{s,t} = P_s \cdot S_t \qquad\qquad (1)$$

Where V is value of sample property, P are points for sample performance, S is scale of technique importance, and index $_s$ is variable of sample, and index $_t$ is variable of technique.

The final evaluation of samples is sum of its values. The higher the sum is, the better performance the material has.

7 RESULTS AND DISCUSSION

The aim of the work is to find the best solution for biocomposite preparation according to its thermal and mechanical properties. Because final properties of the biocomposite are significantly affected by the additives and ways of fibre pretreatment, six samples with different compatibilization method and pure polymer were measured. In this chapter, results from GPC, DSC, TGA, SEM and mechanical testing are summarized and discussed to find the optimal way of biocomposite preparation

Effect of compatibilization on molar mass distribution

The effect of compatibilization on molar mass distribution was evaluated by gel permeation chromatography. It is one of the separation methods that separate analytes on the basis of particle size, respectively hydrodynamic volume of macromolecule. Characterized polymer in solution (mobile phase) moves through column filled with porous material (stationary phase). Smaller molecules are able to enter pores of the gel and spend some time there. Therefore their elution is delayed. Larger molecules pass the column very fast and elute directly. On the basis of retention time, molar mass of the polymer and its distribution can be determined.

GPC tests confirm theoretical premise that by influence of thermoplastic processing the molar mass of polyester materials is dramatically decreasing. The main cause of observed phenomenon is the fact that PLA used in biocomposites was prepared only in experimental scale without adding any stabilizators, which is common industrial practice. Temperature and shear stress cause chain scission of weak polyester linkage. Due to this fact, the difference in weight average molar mass between pure PLA and biocomposites can be up to about 50% (for sample B). Significant changes are apparent also in number average molar mass, thus the polydispersity index stayed almost without any relevant changes.

		$\bar{\mathbf{M}}_\mathbf{n}$	$\bar{\mathbf{M}}_\mathbf{w}$	PDI
pure	PLA-PEG	18400	85500	4,65
A	No additive	18900	57600	3,05
B	Commercial additive	12000	39600	3,31
C	Acid treating	12500	44500	3,55
E	Experimental additive-1	12000	45200	3,77
F	Experimental additive-2	9900	44100	4,47
G	Oleic acid+DTBP	11900	42600	3,58

Table 7 GPC results - number average molar mass $\bar{M}_n$, weight average molar mass $\bar{M}_w$ and polydispersity PDI

Thermal properties of biocomposites

Thermal behavior was measured using differential scanning calorimetry technique. Differential scanning calorimetry is analytical technique measuring heat flow and heat capacity connected with material transitions as a function of time and temperature. Sample of material and comparative standard are heated and the heat necessary to decrease temperature of both materials is measured. The result of DSC measurement is graphical dependence of differential rate of heating (in $J.s^{-1}$) on temperature.

With DSC measurement, values of characteristic temperatures of thermal behavior of polymers were obtained (T_g – glass transition temperature, T_c – crystallization temperature and T_m – melting temperature, ΔH_c – specific enthalpy of crystallization, ΔH_m – specific melting enthalpy). All DSC results are summarized in Table 8.

As the DSC curve did not show any crystallization or melting peak for samples E and F we can consider that polymer matrix in this composites stayed amorphous. Usage of experimental additives based on the polyalkenyl-poly-maleic-anhydride strongly influence ability of the polymer to crystallize. For the rest of the samples, degree of crystallinity was calculated with the Equation 2, where $\Delta H_{m,100\%}$ is theoretical specific enthalpy of melting of theoretical material with 100% ratio of crystallinity.

$$X_c = \frac{|\Delta H_m - \Delta H_c|}{\Delta H_{m,100\%}} \cdot 100\% \tag{2}$$

Results of the calculation shows that ratio of crystallinity of PLA in composite is very low (between 2 and 9 %) whereas the highest ratio has the composite with commercial additive.

The significant difference was observed between glass transition temperature of pure PLA (T_g = 23°C) and composite without any additives – sample A. Incorporating fibres in polymer matrix, the mobility of macromolecules decreases and thus the glass transition temperature is higher. This fact can be connected also with decrease in molar mass of composites. According to Flory – Flox equation, the higher the molar mass is, the lower the glass transition temperature of material is [70]. However presence of additives or treating can affect this equation.

While comparing the biocomposites with or without compatibilization improvement, the values of melting temperature are almost the same for samples A, B and G, but acid treated sample (C) has almost about 10% higher melting point than the rest, which gives this biocomposite wider area of possible application.

Table 8 DSC results – effect of compatibilization on thermal properties of biocomposite. T_g – glass transition temperature, T_c – crystallization temperature, T_m – melting temperature, ΔH_c – specific enthalpy of crystallization, ΔH_m – specific melting enthalpy, X_c – degree of crystallinity

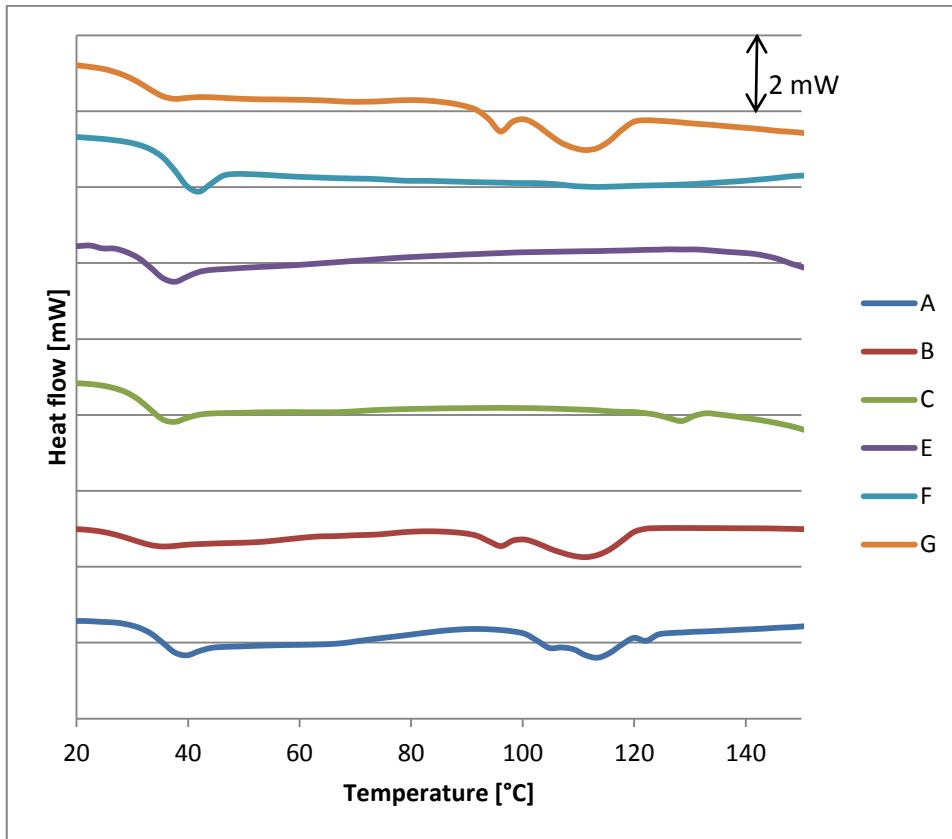|	T_g [°C]	T_c [°C]	ΔH_c [J.g^{-1}]	T_m [°C]	ΔH_m [J.g^{-1}]	X_c [%]
A	30,2	89,8	3,54	112,9	-3,74	7,82
B	20,7	82,7	3,82	111,6	-4,86	9,32
C	21,3	96,6	2,09	128,8	-0,45	2,73
E	21,7					
F	33,2					
G	21,1	84,24	1,69	111,2	-6,51	8,81

Figure 10 DSC curves, comparison of modified and unmodified samples

Thermal stability evaluation

Principle of thermogravimetric analysis is measuring of the weight loss as a function of temperature. The technique is used primarily to determine composition and thermal stability of materials. Result of TGA measurement is graphical dependence of weight loss on temperature.[71, 72] Graphical output of TGA shows curve with one inflex point for pure polymer, but two for composites which means that PLA and fibre decomposition happen at different temperatures. Sample A displayed one onset temperature as well, this can be caused by gradual decomposition of both, polymer and fibres.

Table 9 Summary of thermogravimetric analysis result – T_{O1} – onset temperature 1, T_{O2} – onset temperature 2 and weight percentage of residues.

	T_{o1}	Weight loss 1	T_{o2}	Weight loss 2	Residues wt %
A	259,8	96,95			3,1
B	267,8	78,9	325,5	17,2	3,9
C	271,3	83,2	340,5	12,5	4,3
E	269,6	77,9	323,0	17,6	4,5
F	266,3	78,9	325,5	17,1	4,0
G	270,0	72,3	324,0	21,7	6,0

Pure PLA onset temperature was measured to be 249,6°C which is lower in comparison with biocomposites. Adding fibres into polymer, the thermal stability was improved. Among compatibilized PLA/flax samples, the thermal stability was almost the same for all samples (onset temperature around 270°C) and during the first phase the sample loss around 80% of its weight. This fact corresponds with the sample composition (approximately 80% PLA, 20% flax). After decomposition, about 4% of residues stayed in the aparature, it was ash consisting of mineral substances. The only difference is sample G, which performed high thermal stability, small weight loss in first phase and the highest weight percentage of residues.
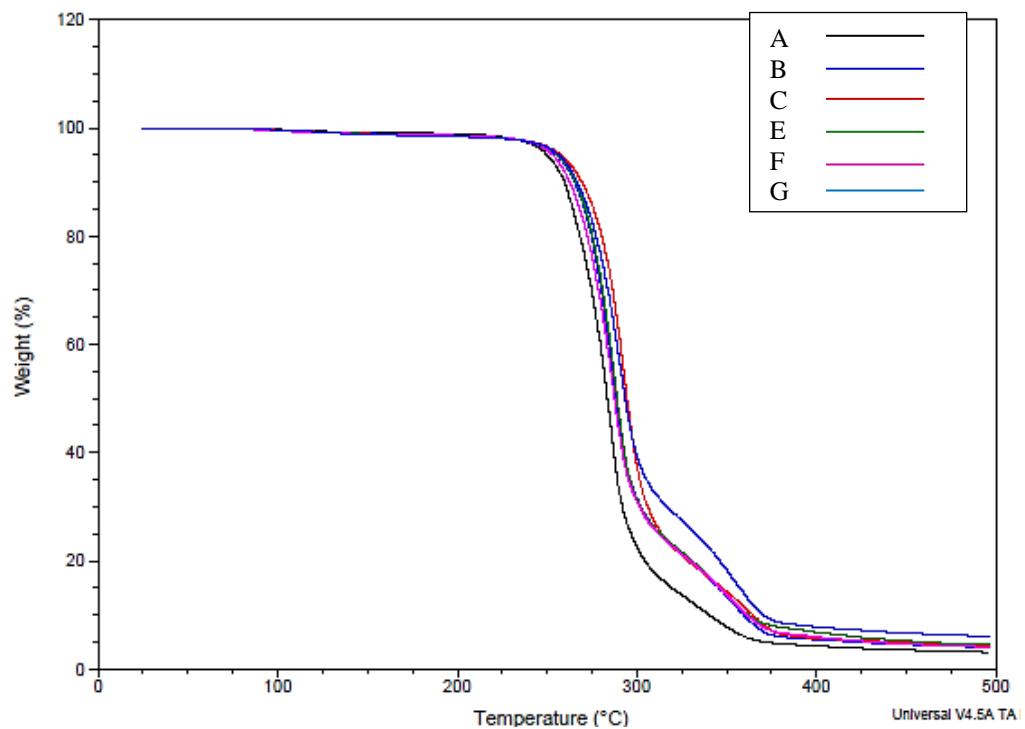

Figure 11 Thermal stability evaluation- TGA results

Mechanical properties

To measure tensile properties, blade-like specimens are prepared and clamped in a tensile testing machine in vertical position. The tensile stress is applied on specimen and the deformation as a response is measured. From the stress-strain curve the characteristic points and properties can be red. It is tensile strength (the limiting stress applied on material leading on failure), elongation at break and E – modulus (slope of the linear area of stress-strain curve). Table 10 shows that with usage of every way of compatibilization the tensile properties were improved. The biocomposite without any additives or fibre treatment performed the lowest tensile strength and E-modulus in tensile tests. All the techniques of compatibilization improved interfacial adhesion which causes better stress transition between fibres and polymer, thus better tensile properties. While comparing the samples according to tensile strength the samples with commercial and both experimental additives (B, E, F) has the highest values. Material prepared with experimental additive 2 (E) has also significantly enhanced tensile E-modulus.

Table 10 Results of mechanical testing for prepared biocomposites

	A	**B**	**C**	**D**	**E**	**F**
Tensile strength, MPa	11,3	15,3	13,3	15,1	14,9	13,4
Elongation, %	3,3	2,2	2,6	2,8	2,2	2,1
E-modulus (tensile), MPa	746	776	877	853	940	987
Flexural strength, MPa	26,9	26,9	24,9	18	27	29,3
E-modulus (flexural), MPa	2405	2844	2661	2523	2455	1974
Charpy impact strength, kJ/mm^2	2,472	3,802	2,706	3,585	4,193	3,36

Measuring flexural properties is very similar; the only difference is the specimen position. For this type of measurement, it is clamped in a machine in horizontal position on the ends of rod-like specimen and the stress is applied in the middle. The results of our flexural tests are not so definite. Some techniques of compatibilization does not affect flexural strength (commercial and 2. experimental additive), and some decrease its value significantly (acid treatment and experimental additive 1). The only technique for flexural strength improvement is usage of Oleic acid+DTBP.

Other important mechanical property is impact resistance. It gives information how the material is able to absorb the impact. The measurement is provided by machine with arm, which is falling and hitting the sample. The Charpy impact strength of biocomposites was

improved by using every compatibilization technique. The highest value was performed again by sample E.

SEM results

Scanning electron microscopy is a display technique producing image of a sample by scanning it with focused electron beam. Electrons from the beam interact with electrons of sample surface emitting signal which contain information about surface topography and composition. Figure 12 shows fracture surface of composite without any modification, sample A. It is evident that fibers are not in full contact with polymer matrix. The low interface adhesion cause slipping of fibers out from polymeric bulk and thus the low tensile properties. The high number of holes as the residues of the fibers is visible on the fracture surface.

a)   b)
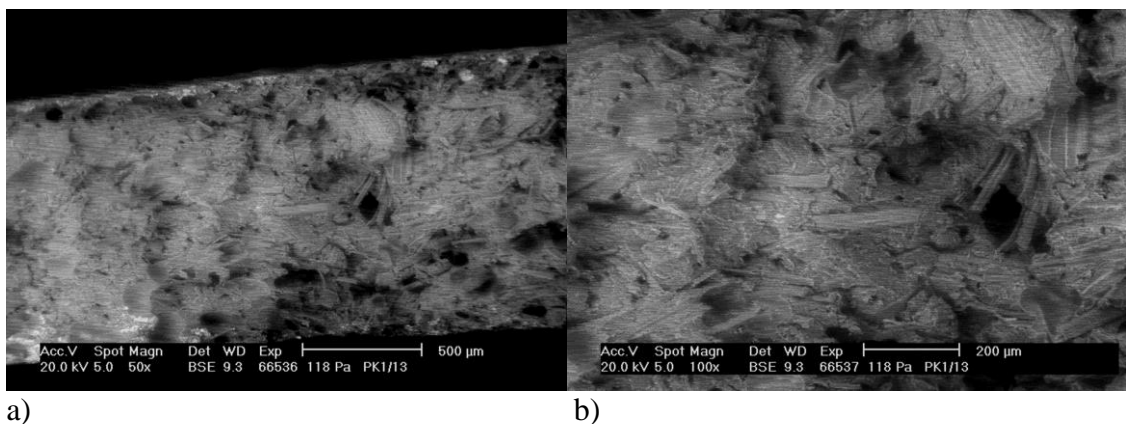
Figure 12 SEM micrographs of PLA/flax fibre composite without using any compatibilization technique – sample A. Magnification a)50x, b)100x

In comparison, fibres in sample PK 6_13 are much incorporated in the matrix. In the Figure 13 the fracture surface looks more homogenous without sharp visible borders between fibres and polymer. The interfacial adhesion is higher thanks to experimental additive 2 which affect also the tensile properties. It is apparent from the figure that there are not so many holes after slipped fibres on the surface (big holes in fibre structure are bubbles produced during mixing).
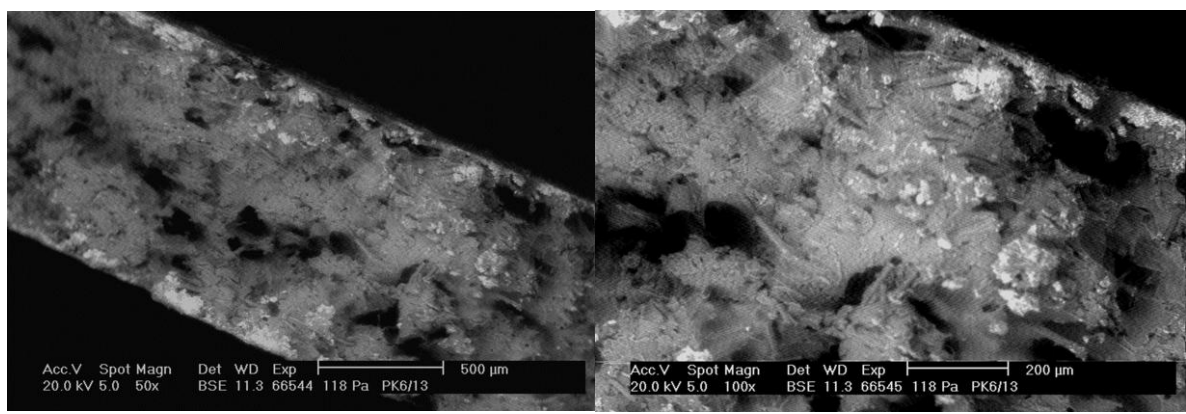
Figure 13 SEM micrographs of PLA/flax fibre composite with experimental additive 2 – sample F. Magnification a)50x, b)100x

Multicriteria evaluation

		Thermal stability	Tensile properties	Flexural properties	Impact Strength	
	Scale [%]	30	24	24	24	∑
A	Points	1	1	8	1	
	Value	**30**	**24**	**192**	**24**	**270**
B	Points	6	10	8	8	
	Value	**180**	**240**	**192**	**192**	**804**
C	Points	10	6	6	3	
	Value	**300**	**144**	**144**	**72**	**660**
E	Points	7	10	1	7	
	Value	**210**	**240**	**24**	**168**	**642**
F	Points	5	9	8	10	
	Value	**150**	**216**	**192**	**240**	**798**
G	Points	3	6	10	6	
	Value	**90**	**144**	**240**	**144**	**618**

Table 11 3-dimensional matrix for multicriteria evaluation

In multicriteria analysis calculation, samples B and F obtained the highest evaluation. We can consider acid treatment and usage of Experimental additive F the best compatibilization method. These samples received 2,5x higher amount of points than the biocomposite without any compatibilization.

CONCLUSION

In recent years, poly(lactic acid) and other biodegradable polymers came into great interest. The reasons are efforts of decreasing of mankind impact on the environment. These polymers provide solution of waste disposal problems, thanks to its biodegradability. Since they are often from natural sources, it can assure the independence on petroleum resources. Next to these advantages, there also exist some weaknesses, mainly in low stability and mechanical properties. It can be solved by preparing biocomposites reinforced with fibres, and natural fibres are great option.

In theoretical part, this thesis is dealing with biodegradable polymers, natural fibres and its biocomposites. In later chapters, the focus is on poly(lactic acid), its properties and methods of production. Direct melt polycondensation and follow-up chain linking reactions are described more detailed. These reactions were used later in experimental part for tested sample preparation.

The aim of experimental part is to find optimal compatibilization technique between fibres and polymer matrix to increase interfacial adhesion. The experiment follows the project carried out at Polymer Centre Tomas Bata University in Zlín. Seven materials were prepared mixing polyester urethane and natural fibres. Commercial additives, two types of experimental additives or Oleic acid+DTBP were added into some mixtures, or the fibres were alkaline or acid treated. The materials were then tested on differential scanning calorimetry, gel permeation chromatography, thermogravimetric analysis, and scanning electron microscopy. Mechanical properties were measured in tensile tests, flexural test and impact resistance tests.

The measurement shows that during biocomposites preparation the molar mass is dramatically decreasing because the polyester bond is not stable in conditions of thermoplastic processing conditions. DSC analysis gives values of glass transition temperature, temperature of crystallization and melting temperature. On the basis of the specific enthalpy of melting and crystallization, the ratio of crystallinity was calculated. Polyester urethane in biocomposites is not very crystalline. The ratio of crystallinity is between 2 and 9% materials with experimental additives stayed even amorphous. Thermal stability of biocomposites was evaluated by thermogravimetric analysis which shows the increase in thermal stability with fibre presence. Also the mechanical properties were improved. All methods of compatibilization improved interfacial adhesion, thus the stress transfer in bulk is better.

Results from experiments were than evaluated by multicriteria analysis. As the best method of compatibilization, the alkaline treatment was assigned. Nevertheless, all methods improved significantly properties of biocomposites comparing to unmodified materials.

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LIST OF ABBREVIATIONS

ASTM American Society for Testing and Materials

CSN Czech national norm

DTBP Di-tert-butyl peroxide

DSC Differential scanning calorimetry

EU European union

EVA Ethylene vinyl acetate

GPC Gel permeation chromatography

LLC Limited liability company

ISO International Organization for Standardization

MAPP Maleted polypropylene

MAPE Maleated polyethylene

PCL Polycaprolactone

PET Polyethylene terephthalate

PEU Polyester urethane

PGA Polyglycolic acid

PHA Polyhydroxy alkanoate

PLA Polylactic acid

PMMA Polymethyl metacrylate

ROP Ring opening polymerization

SEM Scanning electon microscopy

TGA Thermogravimetric analysis

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